GHENT UNIVERSITY

FACULTY OF BIOSCIENCE ENGINEERING

Physical-chemical treatment of landfill leachate: technological performance, spectral characterization and cost estimations

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Thesis submitted in fulfillment of the requirements to obtain the degree of Doctor (PhD) in Applied Biological Sciences: Environmental Technology

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Dutch translation of the title: Fysico-chemische behandeling van stortplaatspercolaat: technische performantie, spectrale analyse en kostenschattingen

Citing this PhD

Oloibiri V. 2018. Physical-chemical treatment of landfill leachate: technological performance, spectral characterization and cost estimations. PhD dissertation, faculty of bioscience Engineering, Ghent University, Belgium.

ISBN: 978-94-6357-115-9

Stay hungry, stay foolish

whole earth catalogue

Acknowledgements

The person who said that it takes a village to raise a child must have been a PhD student. I know this because so many people have encouraged, motivated and supported not only me but also my family through this PhD.

First and foremest I would like to express my deepest gratitude to Prof. Stijn Van Hulle and Prof. Kristof Demeestere for the opportunity to work under your tutelage. I must say you two make the best team!. Thank you for the critical ideas and discussions; am certainly a better researcher than I first started. Thank you for the times I was lost in the PhD chaos and you took time to help me find myself.

My masters students Innocent Ufomba, Sam Deconinck and Robbin Vandewalle, day and night you laboured in the lab so that we could get results to write home about. This thesis is a representation of your work too. Robbin thanks again for answering a last minute call to help me with my summary.

My current and former collegues at UGent campus Kortrijk; Junling Gao, Ze Liu, Michael Chys, Bernado, Coraddo Amodeo thank you for taking time to teach me how to use a machine, software or just talk about PhD life. Seyedahmad Hosseinzadeh, I remember struggling to fix my GAC columns in the lab and you came and fixed them in no time. You saved me a lot of time and for that and many more thank you. Molly Gabaza, I always looked forward to your coming back to Belgium, the stories we had and discussions always made the train ride wonderfull ☺. Am still trying to figure out how we came up with solutions for my EEMs ☺. Mona Bhkeet, in the short period I have known you, I found a mama PhD that I could relate with in so many ways, I wish you had come sooner. Nevertheless, am grateful and wish you nothing but the best in your PhD journey. My greatest fan Isabel Lappere, I don't know what I would have done without you. Thank you for always being there whenever I needed assistance.

My friend Lucy Evers am grateful to have met you during this PhD journey. The discussions we had were so profound and uplifting. You always challenged me to get out of my cormfort zone and embrace unfamiliarity. Bernadette Onyango and Lenet Kibugi, thank you for allowing me to exercise my Swahili and Dholuo and for the many *mandazi* sessions ☺. Gizeshwork Tadesse, through you I have come to learn what true friendship really means. Though we are separated by thousands of miles, it always felt like you were close by. Thank you mama for cheering me on ☺.

The Van Lancker family *Awuoro u!* from moemoe Lancker to Zawadi, am really gratefull to be part of you. Moemoe Lancker, for always asking about my thesis and progress. Daphne, Sophie, Stephanie and your families, I appreciate your support. I thank God for those days when you dropped by our home and took care of Lucas so that I could just squeeze a sentence or two in my work. Meme Lieve Turf and pepe Walter Van Lancker, when I think about you am lost for words. My deepest gratitude for not only taking me and my family in your home, but also for creating for me my own Bellagio centre where I could concentrate on my articles and thesis. *Hartelijk bedankt*

My dearest mama Margaret Akinyi and baba Tobias Okech, my greatest mentors, *adendu nade?* a*wer u nade*? its been a long walk, from Tumaini to Ghent University. Do you remember what you told me about my tin box when you took me to St Georges? I still live by it until today. So let me celebrate you, *Viva mama and baba!.* The Okech family, thank you for always bringing a piece of home to Belgium, for your prayers, encouragement and laughter to sooth my soul.

Osiepa Mathieu Van Lancker, *Erokamano!* for believing in and cheering me on every step of the way. During this marathon and final sprint, you held our family together. I know it was not easy on you but you did it with so much love and commitment. My dear Lucas Van Lancker and Zawadi Van Lancker, thank you for teaching me grace and reminding me everyday that life still happens. Because of you my lovlies I know that there are flowers which bloom in winter.

To God almighty who is still manifesting Jeremiah 29:11 in my life, I give you all the glory!

Viva to you all!

Violet Atieno Oloibiri

9th April 2018

Melle Belgium

Appreciation

I would like to thank IMOG Moen and Vanheede Roeselare for allowing me to sample leachate from their landfilling facilities. Special thanks go to Steven Deryckere who made sure my students and I got samples and information that we needed.

I appreciate the financial support that Kenya Industrial Research and Development Institute has given me through out this PhD study.

This PhD thesis was part of the IWT-Tetra project FYBAR [140218] and the LED H2O project supported by Vlakwa.

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List of abbreviations

AC	activated carbon
ANR	autotrophic nitrogen removal
AOP	advanced oxidation processes
BOD_5	5 days biological oxygen demand at 20 °c
BV	bed volumes
BW	brackish water
C_e	effluent concentration
CF	coagulation-flocculation
C_o	influent concentration
COD	chemical oxygen demand
COD_o	initial chemical oxygen demand concentration
DOM	dissolved organic matter
EBCT	empty bed contact time
EEM	excitation emission matrix
Em	Emission
Ex	Excitation
$FeCl_3$	ferric chloride
F_{max}	maximum fluorescence intensity
GAC	granular activated carbon
HMW	high molecular weight
$HO^{\bullet}$	hydroxyl radical
IMOG	intergemeentelijke maatschappij voor openbare gezondheid
LMW	low molecular weight
LRU	leachate recycling unit
MF	Microfiltration
Min	Minutes
MPB	methane phase bed
N	Nitrogen
N-dN	nitrification denitrification
NF	Nanofiltration
NH_4^+-N	ammonium
Ni	Nickel

NO_2^--N	nitrite
NO_3^--N	nitrate
O_3	Ozone
PAC	powdered activated carbon
PACl	polyaluminium chloride
PARAFAC	parallel factor analysis
q_{ex}	experimental adsorption capacity
RAS	returned activated sludge
RO	reverse osmosis
RU	raman units
SBBGR	sequencing batch biofilter granular reactor;
SBR	sequencing batch reactor
SOM	self-organizing maps
SVI	sludge volume index
SW	sea water
TOD	transferred ozone dose
UBAF	up-flow biological aerated filters
UF	ultra filtration
UV-VIS	ultra violet visible
α_{254}	absorbance coefficient at 254 nm
α_{436}	absorbance coefficient at 436 nm

Summary

The generation of landfill leachate is one of the key consequences of landfilling. Landfill leachate is characterized by high concentrations of COD, ammonium, heavy metals and xenobiotic organic compounds. If not properly collected, treated and disposed safely, landfill leachate can cause harm to the environment. To prevent this, proper treatment is imperative.

Several methods are available for the reduction of the aforementioned water quality parameters to the required environmental discharge limits (**chapter 2**). In view of their economy, biological techniques including nitrification-denitrification (N-dN) are preferred in the treatment of landfill leachate with high biodegradability. However, their performance is impeded by the presence of recalcitrant organic matter and various factors such as temperature. Moreover, an external source of carbon is often required. Therefore, to attain the required discharge standards, post treatment of biologically treated leachate is required. On the other hand, for old raw landfill leachate (from landfills older than 5 years) often characterised with high concentration of recalcitrant compounds and ammonium, physical chemical techniques are preferred. Therefore, this thesis focused on treatment of raw and post-treatment of biologically treated landfill leachate to reduce their harmful effects upon discharge into the environment.

The efficiency of a combination of four physical chemical techniques to treat raw and biologically treated landfill leachate was studied. This was done with the aim of (i) investigating the factors affecting the performance of the different techniques in a bid to obtain an optimised landfill leachate treatment train, (ii) evaluating the costs involved in treatment of raw and biologically treated landfill leachate and (iii) Identifying the type of DOM present in raw and biologically treated landfill leachate

and monitoring their behaviour during treatment with a combination of physical-chemical techniques. The physical-chemical techniques chosen included ozonation, coagulation-flocculation, granular activated carbon (GAC) and ion exchange. Ozonation is a chemical technique that was chosen because of its high potential to oxidize compounds which are recalcitrant to biological processes. Coagulation-flocculation was chosen as an alternative to ozonation. This was spurred by its simplicity in operation and ability to remove high molecular weight compounds from landfill leachate. GAC was chosen for its ability to unselectively remove organic pollutants from landfill leachate as a result of its large, porous surface area. Ion exchange is a physical technique chosen for its high efficiency in removing ions such as ammonium from landfill leachate (Primo et al., 2009).

To achieve sufficient treatment of biologically treated leachate (sampled from IMOG, Moen Belgium), ozonation, coagulation-flocculation and GAC were examined. Results from **chapter 4** shows that application of higher transferred ozone doses for example 820 mgO_3/L lead to higher reductions in organic matter as indicated by COD and UV absorbance at 254 nm (α_{254}). On the other hand, a high ozone dose implies higher operating costs which can discourage ozonation use. Following this, ozonation of landfill leachate at different initial COD concentrations (COD_o) and pH was done. Higher percentage COD removal efficiencies were achieved at lower COD_o compared to higher COD_o (**chapters 4 - 6**). A high COD_o is characterized by high amounts of organic matter. During ozonation, this organic matter is partially oxidised into intermediates which still contribute to the overall COD hence low ozonation performance in terms of COD. Whereas at lower COD_o there is tendency for complete mineralization of organic compounds to water and carbon dioxide. Better organic matter removal was observed at more alkaline leachate pH (**chapter 4**). For instance, at pH 10, the ozonation efficiency is 0.79 mg COD removed/mg O_3 compared to 0.32 mg COD removed/mg O_3 at pH 7. The alkaline pH promotes the production of hydroxyl radicals which are more reactive and unselective than ozone at oxidizing organic material. Given the minimal removal of organic matter from landfill leachate (especially at higher leachate COD_o) by ozonation, coupling of ozonation to GAC was explored **(chapter 5 and 6).** Combining ozonation with GAC proved that higher pollutant removals can be obtained when these techniques are combined in the treatment of landfill leachate. For instance, 6 bed volumes (BV) GAC adsorption of biologically treated leachate after ozonation with 0.48 mg O_3 /mg COD_o resulted in 77% COD removal compared to 31% COD removal with ozonation or 8% COD removal with GAC only.

In **chapter 6**, coagulation-flocculation was introduced as an alternative technique to ozonation. The performance of coagulation-flocculation depended on coagulant type and dose. The metal salt ferric chloride ($FeCl_3$) performed better than polyaluminium chloride (PACl) whereas better organic matter removals were obtained at higher coagulant dosages. The efficiency of coagulation-flocculation as a single technique at a dose of 1.96 mg $FeCl_3$/mg COD_o was comparable (30% COD removal) to ozonation (31% COD removal) – in the post-treatment of biologically treated landfill leachate. In the coupling of coagulation-flocculation with GAC, $FeCl_3$ was the coagulant of choice. Overall COD removal efficiency of 53% was achieved with coagulation-flocculation + GAC with the effluent COD concentration (287 mg/L) having potential to meet the Flemish discharge limit (450 mg/L). In comparison, ozonation + GAC reduced the initial leachate COD concentration by 77% with effluent concentration (133 mg/L) way below the allowed discharge standards. This difference is related to the mechanism of action of the two techniques. Ozonation oxidised the high molecular weight components into simpler components which could penetrate easily into the GAC meso and micropores. Whereas coagulation-flocculation removes only the high molecular weight components such as humic-like compounds leaving the low molecular weight fulvics which can easily block the GAC pores compared to the ozonation by-products. Nevertheless, experimental and modelled data showed that a GAC column receiving biologically treated leachate after coagulation-flocculation or ozonation could adsorb more compounds than when no intermediate treatment is done.

Assessment of the operating costs incurred during post treatment of biologically treated leachate with various techniques showed that coagulation-flocculation + GAC is the cheapest option **(chapter 7).** This is because coagulation-flocculation of biologically treated leachate prior to GAC adsorption greatly improved the capacity of GAC to adsorb more organic pollutants, hence the GAC column could be used longer which eventually lowers the GAC operating costs. Therefore, further leachate studies on post-treatment of biologically treated landfill leachate used coagulation-flocculation and GAC.

In follow-up (**chapter 8**) experiments involving post-treatment of biologically treated landfill leachate, combined optimization of coagulation-flocculation and GAC was done. The results show that 0.8 mg $FeCl_3$/mg COD_o is coagulant dose that would offer technical and economic benefits during treatment of biologically treated leachate with coagulation-flocculation and GAC adsorption. This dose (0.8 mg $FeCl_3$/mg COD_o) is contrary to the higher doses which are normally chosen.

Studies on treatment of raw leachate (sampled from Vanheede landfill facility in Roeselare) with coagulation–flocculation and GAC further concurs with the observation in **Chapter 8**. Here an optimum coagulant concentration of 1 mg $FeCl_3$/mg COD_o followed by 10.6 BV GAC adsorption gave comparable removals (80% COD, 81% α_{254}, 89% nickel) as those with double the dose - 2.2 mg $FeCl_3$/mg COD_o – and 10.6 BV GAC (79% COD, 91% α_{254}, 91% nickel). In comparison, lower removals -

COD 42%, α_{254} 23%, nickel 54% - were obtained with only 10.6 BV GAC treatment. To remove the high concentration of ammonium which was still prominent in the GAC effluent, ion exchange was used. Up to 100% of ammonium was removed from GAC effluent with and without previous coagulation-flocculation treatment. This high removal efficiency was as a result of the high driving force created by the high concentration of ammonium in leachate. Therefore from **chapter 8 and 9** it can be said that the optimum dose (economically and technically) for use of the coagulation-flocculation step of a leachate treatment train lies between 0.8 – 1 mg $FeCl_3$/mg COD_o.

Assessment of the operating costs incurred in the treatment of raw leachate with coagulation-flocculation + GAC + ion exchange resulted in an operating cost of 27.9 €/m^3 which is more expensive than (post)-treatment of biologically treated leachate with coagulation-floccuation + GAC (0.9 €/m^3). Though the coagulation-flocculation + GAC treatment of raw leachate is already more expensive (4.6 €/m^3) than treatment of biologically treated leachate, the ion exchange step is the one that drives the price up (23.3 €/m^3).

In previous Chapters that is 4-6 and 9 the performance of the four physical-chemical techniques was monitored using water quality parameters such as COD, ammonium and heavy metals. To gain a better understanding of how these techniques removed organic matter from leachate in-depth studies (**chapter 8 and 10**) on the type of dissolved organic matter (DOM) present in raw and biologically treated landfill leachate were carried out. Using fluorescence excitation emission matrices coupled with parallel factor analysis, qualitative and quantitative data on the identity of DOM components was obtained. Results showed that the biologically treated leachate is dominated with humic/fulvic- like components with maximum fluorescence intensity (F_{max}) at

Excitation/Emission (Ex/Em)250, 320/425 nm and humic- like DOM components with F_{max} at Ex/Em 250/460. These two DOM components were also identified in raw landfill leachate together with a third component identified as tryptophan- like with F_{max} at Ex/Em 270/340 nm. The difference between the biologically treated leachate and the raw leachate was also evident in the F_{max} values of the DOM components. The F_{max} of the humic/fulvic- like and humic- like DOM components in biologically treated leachate were 85 RU and 140 RU respectively compared to 2.13 RU and 2.16 RU respectively in raw leachate. The F_{max} of the tryptophan- like component was 1.14 RU.

During treatment, for both raw and biologically treated landfill leachate, coagulation-flocculation proved effective in reducing the F_{max} of humic/fulvic- like compounds while GAC and ion exchange unselectively reduced the F_{max} of three DOM components. Whereas humic- like components could only be removed by the GAC step until 4 BV (leachate without prior coagulation-flocculation treatment) and 6.4 BV (leachate with prior coagulation-flocculation) during treatment of raw landfill leachate, it was efficiently removed from biologically treated leachate post-treated with coagulation-flocculation with higher efficiencies. This shows that in leachate with a low organic load, humic- like components can be easily removed by GAC adsorption since there are fewer pollutants that might block or compete for the GAC adsorption sites. Similar to the reductions in COD, α_{254}, Ni; the combination of coagulation-flocculation + GAC (+ ion exchange) gave better reductions in F_{max} of raw and biologically treated leachate in comparison to treatment with GAC only or GAC + ion exchange. This is because initial steps such as biological techniques and coagulation-flocculation reduce the bulk of pollutants giving the activated carbon adsorption and ion exchange steps a higher chance of removing more pollutants. Therefore, the benefits of combining various techniques for treatment of landfill leachate can be clearly seen when monitoring the removal of DOM components

Samenvatting

Een van de belangrijkste consequenties van het gebruik van stortplaatsen is het ontstaan van stortplaatspercolaat. Indien stortplaatspercolaat niet opgevangen, behandeld en geloosd wordt, kan dit leiden tot milieuschade. Om dit te vermijden is behandeling van stortplaatspercolaat van het grootste belang. Er zijn verschillende mogelijke methoden om het onbehandelde stortplaatspercolaat te behandelen tot die aan de toegestane lozingsnormen voldoen (Hoofdstuk 2).

Economische motieven in acht genomen, zijn biologische technieken met nitrificatie/denitrificatie (N-dN) aangewezen in het behandelen van stortplaatspercolaat met hoge biologische afbreekbaarheid. Hun prestaties worden echter gehinderd door recalcitrante componenten. Bovendien is vaak een externe koolstofbron vereist. Om deze reden is nabehandeling van het biologisch behandeld percolaat vereist.

Anderzijds hebben fysisch-chemische technieken de voorkeur voor het behandelen van oud onbehandeld stortplaatspercolaat (afkomstig van stortplaatsen ouder dan 5 jaar) die vaak worden gekenmerkt door een hoge concentratie recalcitrante componenten en ammonium. Daarom focust dit proefschrift zich op de behandeling van onbehandelde en nabehandeling van biologisch behandeld stortplaatspercolaat om hun schadelijke effecten na lozing in het milieu te verminderen.

De efficiëntie van een combinatie van vier fysisch-chemische technieken voor de behandeling van onbehandeld en biologisch behandeld stortplaatspercolaat werd bestudeerd. Dit gebeurde met het doel (i) de factoren te onderzoeken die invloed hebben op de prestaties van de verschillende technieken in een poging om een geoptimaliseerde storplaatspercolaat behandelingsreeks te verkrijgen, (ii) de kosten te evalueren die gemoeid zijn met de behandeling van onbehandeld en

biologisch behandeld stortplaatspercolaat en (iii) Identificatie van het type DOM dat aanwezig is in onbehandeld en biologisch behandeld stortplaatspercolaat en het monitoren van hun gedrag tijdens de behandeling met een combinatie van fysisch-chemische technieken.

De gekozen fysisch-chemische technieken omvatten ozonisatie, coagulatie, granulaire actieve kool (GAC) en ionenuitwisseling. Ozonisatie is een chemische techniek die werd gekozen vanwege zijn hoge vermogen om verbindingen te oxideren die recalcitrant zijn voor biologische processen. Coagulatie werd gekozen als een alternatief voor ozonisatie. Dit omwille van de eenvoudige werking en het vermogen om verbindingen met een hoog molecuulgewicht te verwijderen uit het stortplaatspercolaat.

GAC werd gekozen vanwege zijn vermogen om niet-selectief organische verontreinigende stoffen uit het stortplaatspercolaat te verwijderen als gevolg van zijn grote, poreuze oppervlak. Ionenuitwisseling is een fysische techniek die wordt gekozen vanwege zijn hoge efficiëntie in het verwijderen van ionen zoals ammonium uit het stortplaatspercolaat.

Voor het bereiken van een voldoende grote behandeling van biologisch behandeld percolaat (bemonsterd bij IMOG, Moen België), werden ozonisatie, coagulatie en GAC gebruikt.

Resultaten uit hoofdstuk 4 laten zien dat een langere ozonatie tijd, b.v. 240 minuten, resulteert in een hogere dosis ozon die wordt overgebracht naar het percolaat, waardoor hogere reducties in organisch materiaal optreden, zoals aangegeven door CZV en UV-absorptie bij 254 nm (α_{254}). Anderzijds impliceren hoge ozondoseringen hogere oxidatiekosten die het gebruik van ozonatie kunnen ontmoedigen. Hierna werd ozonisatie van het stortplaatspercolaat bij verschillende initiële CZV-concentraties (CZV_o) en pH uitgevoerd. Hogere CZV verwijderingsrendementen werden bereikt bij een lagere CZV$_o$ in vergelijking met hogere CZV$_o$ (hoofdstukken 4 - 6). Een hoge CZV$_o$ wordt gekenmerkt door grote hoeveelheden organisch materiaal.

Tijdens ozonisatie worden deze gedeeltelijk geoxideerd tot intermediairen die nog steeds bijdragen aan de totale CZV en daardoor leiden tot lage ozonisatie prestaties. Terwijl bij lagere CZV$_o$ de neiging aanwezig is om de organische verbindingen volledig te mineraliseren tot water en koolstofdioxide. Betere verwijdering van organische stoffen werd waargenomen bij meer alkalisch percolaat (hoofdstuk 4). Bijvoorbeeld, bij pH 10, is de ozonisatie-efficiëntie 0,79 mg CZV verwijderd / mg O_3 vergeleken met 0,32 mg CZV verwijderd / mg O_3 bij pH 7. De alkalische pH bevordert de productie van hydroxylradicalen die reactiever en selectiever zijn dan ozon bij oxidatie van organisch materiaal.

Gezien de minimale verwijdering van organisch materiaal uit het stortplaatspercolaat (met name bij hogere CZV$_o$ van het percolaat) door ozonisatie, werd de koppeling van ozonisatie aan GAC onderzocht (hoofdstuk 5 en 6). Het combineren van ozonisatie met GAC bewees dat betere verwijderingen van poluenten kunnen worden verkregen wanneer verschillende technieken worden gecombineerd bij de behandeling van van stortplaatspercolaat.

Betere organische verwijdering werden waargenomen wanneer ozonisatie werd gecombineerd met GAC. Bijvoorbeeld, 6 bed volumes (BV) GAC-adsorptie van biologisch behandeld percolaat na ozonisatie met 0,48 mg O_3/mg COD$_o$ resulteerde in 77% CZV -verwijdering in vergelijking met 31% of 8% COD-verwijdering met respectievelijk ozonisatie of GAC.

In hoofdstuk 6 werd coagulatie-flocculatie geïntroduceerd als een alternatieve techniek voor ozonisatie. De prestaties van coagulatie waren afhankelijk van het type en dosis van het coagulant.

Het metaalzout ijzerchloride ($FeCl_3$) presteerde beter dan polyaluminiumchloride (PACl), terwijl betere verwijdering van organisch materiaal werd verkregen bij hogere doses coagulant.

De efficiëntie van coagulatie-flocculatie als enige techniek in een dosis van 1,96 mg $FeCl_3$ / mg CZV_o was vergelijkbaar (30% CZV -verwijdering) met ozonisatie (31% CZV -verwijdering) - bij de nabehandeling van biologisch behandeld stortplaatspercolaat.

Bij de koppeling van coagulatie-flocculatie met GAC was $FeCl_3$ het gekozen coagulatiemiddel. Totale COD-verwijderingsrendement van 53% werd bereikt met coagulatie-flocculatie + GAC met de effluent- CZV -concentratie (287 mg/L) met potentieel om te voldoen aan de specifieke lozingsnormen voor IMOG (250 mg/L). Ter vergelijking, ozonisatie + GAC reduceerde de aanvankelijke CZV -concentratie van het percolaat met 77% met de effluentconcentratie (133 mg/L) ver onder de toegestane lozingsnormen.

Dit verschil is te wijten aan het werkingsmechanisme van de twee technieken. Ozonatie oxideerde de componenten met hoog molecuulgewicht tot eenvoudiger componenten die gemakkelijk in de GAC meso- en microporiën konden doordringen. Terwijl coagulatie-flocculatie alleen de componenten met hoog moleculair gewicht verwijdert, zoals humusachtige componenten die de fulvines met laag molecuulgewicht achterlaten, die de GAC-poriën gemakkelijk kunnen blokkeren in vergelijking met de ozonatiebijproducten. Desalniettemin toonden experimentele en gemodelleerde gegevens aan dat een GAC-kolom die biologisch behandeld percolaat na coagulatie-flocculatie of ozonisatie ontving, meer verbindingen zou kunnen adsorberen dan wanneer geen tussenbehandeling werd uitgevoerd.

Beoordeling van de kosten gemaakt tijdens nabehandeling van biologisch behandeld percolaat met verschillende technieken toonde aan dat coagulatie + GAC de goedkoopste optie is (hoofdstuk 7). Dit komt omdat coagulatie-flocculatie van biologisch behandeld percolaat voorafgaand aan GAC-adsorptie het vermogen van GAC om meer organische poluenten te adsorberen aanzienlijk heeft verbeterd, vandaar dat de GAC-kolom langer zou kunnen worden gebruikt hetgeen uiteindelijk de GAC-behandelingskosten verlaagt. Daarom hebben verdere percolaatstudies met betrekking tot nabehandeling van biologisch behandeld stortplaatspercolaat gebruik gemaakt van coagulatie-flocculatie en GAC.

In opvolgexperimenten (hoofdstuk 8) met betrekking tot nabehandeling van biologisch behandeld stortplaatspercolaat, werd gecombineerde optimalisatie van coagulatie-flocculatie en GAC uitgevoerd. De resultaten tonen aan dat 0,8 mg $FeCl_3$/mg CZV_o een coagulantdosis is die technische en economische voordelen zou bieden tijdens de behandeling van biologisch behandeld percolaat met coagulatie-flocculatie en GAC-adsorptie. Deze dosis (0,8 mg $FeCl_3$/mg CZV_o) is afwijkend van de hogere doses die normaal worden gekozen.

Studies over de behandeling van onbehandeld percolaat (bemonsterd uit de stortplaats van Vanheede te Roeselare) met coagulatie-flocculatie en GAC komen verder overeen met de waarneming in hoofdstuk 8.

Hierbij gaf een optimale concentratie van 1 mg $FeCl_3$/mg CZV_o gevolgd door 10,6 bedvolumes (BV) GAC adsorptie vergelijkbare verwijderingen (80% CZV, 81% α_{254}, 89% nickel) als die met dubbele dosis - 2,2 mg $FeCl_3$/mg CZV_o - en 10,6 BV GAC (79% CZV, 91% α_{254}, 91% nickel). Daarom gebruikten verdere studies de combinatie van 1 mg $FeCl_3$/mg CZV_o + GAC. Ter vergelijking: lagere verwijderingen - CZV 42%, α_{254} 23%, nickel 54% - werden verkregen met slechts 10.6 BV GAC-behandeling.

Om de hoge concentratie ammoniumstikstof die nog steeds prominent aanwezig was in het GAC-effluent te verwijderen, werd ionenuitwisseling gebruikt. Tot 100% ammoniumstikstof werd verwijderd uit GAC-effluent ongeacht eerdere coagulatie-flocculatiebehandeling. Dit hoge verwijderingsrendement was het resultaat van de hoge drijvende kracht die werd gecreëerd door de hoge concentratie ammoniumstikstof in percolaat. Daarom kan uit hoofdstuk 8 en 9 worden gesteld dat de optimale dosis (economisch en technisch) voor gebruik bij de coagulatiestap van een percolaatbehandelingsreeks ligt tussen 0,8 - 1 mg $FeCl_3$/mg CZV_o.

Beoordeling van de kosten voor de behandeling van ruw percolaat met coagulatie-flocculatie + GAC + ionenwisselkosten 27,9 € / m^3 is duurder dan (na) behandeling van biologisch behandeld percolaat met coagulatie-flocculatie + GAC (0,9 €/m^3) . Hoewel de coagulatie-flocculatie + GAC-behandeling van onbewerkt percolaat al duurder is (4,6 €/m^3) dan de behandeling van biologisch behandeld percolaat, is de ionenwisselingsstap diegene die de prijs opdrijft (23,3 €/m^3).

Diepgaande studies (hoofdstuk 8 en 10) over het type opgeloste organische stof (DOM) aanwezig in onbehandeld en biologisch behandeld stortplaatspercolaat met behulp van fluorescentie-excitatie-emissiematrices in combinatie met parallelle factor analyse, leverden kwalitatieve en kwantitatieve gegevens over de identiteit van DOM-componenten .

De resultaten toonden aan dat het biologisch behandelde percolaat wordt gedomineerd door humus/fulvine-achtige componenten met maximale fluorescentie-intensiteit (F_{max}) bij excitatie / emissie (Ex / Em) 250, 320/425 nm en humus-achtige DOM-componenten met F_{max} bij Ex / Em

250/460. Deze twee DOM-componenten werden ook geïdentificeerd in onbehandeld stortplaatspercolaat, samen met een derde component geïdentificeerd als tryptofaan-achtig met F_{max} op Ex / Em 270/340 nm.

Het verschil tussen het biologisch behandelde percolaat en het onbehandelde percolaat was ook duidelijk in de F_{max}-waarden van de DOM-componenten. De F_{max} van de humus/fulvine-achtige en humus-achtige DOM-componenten in biologisch behandeld percolaat was respectievelijk 85 RU en 140 RU vergeleken met 2.13 RU en 2.16 RU in onbehandeld percolaat. De F_{max} van de tryptofaan-achtige component was 1,14 RU. Tijdens de behandeling bleken coagulatie-flocculatie voor zowel onbehandeld als biologisch behandeld stortwaterpercolaat effectief in het verminderen van de F_{max} van humus/fulvine-achtige componenten, terwijl GAC en ionenuitwisseling de F_{max} van drie DOM-componenten niet-selectief verminderden. Terwijl humus-achtige componenten alleen konden worden verwijderd door de GAC-stap tot 4 BV (percolaat zonder eerdere coagulatie-flocculatiebehandeling) en 6.4 BV (percolaat met eerdere coagulatie-flocculatiebehandeling) tijdens de behandeling van onbehandeld stortplaatspercolaat , werd het efficiënt verwijderd uit biologisch behandeld percolaat dat nabehandeld is met coagulatie-flocculatie met hogere efficiëntie.

Dit toont aan dat in percolaat met een lage organische belasting, humus-achtige componenten gemakkelijk kunnen worden verwijderd door GAC-adsorptie, omdat er minder verontreinigende stoffen zijn die de GAC-adsorptieplaatsen zouden kunnen blokkeren of ermee concurreren.

Vergelijkbaar met de reducties in COD, α_{254}, Ni; gaf de combinatie van coagulatie-flocculatie + GAC (+ ionenwisseling) betere reducties in F_{max} van ruw en biologisch behandeld percolaat in vergelijking met behandeling met alleen GAC of GAC + ionenuitwisseling. Dit komt omdat de eerste stappen, zoals biologische technieken en coagulatie, het overgrote deel van de poluenten verminderen , waardoor de adsorptiestappen van actieve kool een grotere kans hebben om meer verontreinigende stoffen te verwijderen. Daarom zijn de voordelen van het combineren van verschillende technieken voor de behandeling van percolaat van stortplaatsen duidelijk te zien bij het observeren van de verwijdering van DOM-componenten.

PART I: General introduction

Chapter 1

Introduction

1.1 Introduction

Urbanization and rapid population growth have led to an increase in the amount and heterogeneity of waste produced (Mukhtar et al., 2016). The complexity of waste produced poses challenges for waste management and recycling techniques. For this reason, a big percentage of waste produced worldwide ends up in landfills. According to El-Fadel et al. (1997), up to 95% of the total municipal solid waste (MSW) collected worldwide is disposed off in landfills. In developed countries such as the EU28 area and the USA, respectively 34% and over 50% of MSW is landfilled annually (Brennan et al., 2016; Deng, 2009), although specifically for Belgium, only 3% of MSW was landfilled in 2014 as a result of stringent regulations implemented over the years (Eurostat 2017). In rapidly developing economies such as China, as of 2006, there were 324 active landfills for the disposal of the MSW generated, and about 43% of the MSW was landfilled (Xu, 2008). The preference of landfilling in many countries over other waste disposal methods is often because of economic reasons. Moreover, methods such as incineration produce 10-20% residues which must be landfilled (Abbas et al., 2009). In recent decades, landfills are further overused because of the disposal of municipal biosolids including a variety of chemicals among them fluorochemicals, pharmaceuticals, personal care products and pesticides (Huset et al., 2011).

One important environmental impact of landfills is the generation of the leachate, produced in different volumes (Alkalay et al., 1998). According to Abdoli et al. (2012), landfill leachate is high-strength wastewater generated when waste moisture and rain water percolate through the landfill. Upon closure, landfills continue to produce contaminated leachate and this process could last for 30-50 years (Ngo et al., 2008). Landfill leachate contains several (classes of) organic compounds with concentrations ranging from less than one µg/L to several g/L. Some compounds may be toxic to life, or simply alter the ecology of receiving streams. According to the survey of the United States Environmental Protection Agency (USEPA), approximately 75 percent of landfills in the USA are polluting groundwater (USEPA, 2004). Water polluted by landfill leachate has also been found globally, especially in European countries, Australia and China (Ngo et al., 2008). In Europe, the Landfill Directive 99/31/EC and the Waste Framework Directive 2008/98/EC demand the proper management of leachate from landfills to avoid harm to human and ecosystem health (Council of the European Union, 1999; The European Parliament and the Council of the European Union, 2008).

The best method of controlling environmental pollution and health risks by leachate is treating the leachate to remove the hazardous substances before it is discharged into the water system (Ngo et al., 2008). However, leachate treatment experiences major challenges, such as the variability of the leachate characteristics, composition and quantity (Kulikowska and Klimiuk, 2008; Tatsi and Zouboulis, 2002), which are in turn influenced by factors like age of landfill, waste type and composition, precipitation (Li et al., 2010b), site hydrology, landfill design and operation, landfill cover, waste compaction (Abbas et al., 2009). In particular, landfill age plays an important role in the type of components present in landfill leachate at a particular time. Young landfills contain large amounts of biodegradable organic matter which is easily fermented into volatile fatty acids (Renou et al., 2008). These fatty acids contribute to the characteristic low pH of young leachate. Additionally, during this phase, the highest BOD_5 and COD are measured in the leachate (Kjeldsen et al., 2002). As the landfill matures, it enters the methanogenic stage. Here, acids accumulated during the anaerobic phase are converted to carbon dioxide and methane by methanogenic bacteria (Renou et al., 2008). This phase is characterized by old leachate with low COD values and high ammonium and methane concentrations. The BOD_5/COD ratio also decreases as the amount of carboxylic acids reduces and as the amount of recalcitrant organic molecules increases (Kjeldsen et al., 2002).

Generally, three types of leachate can basically be distinguished, depending on the landfill age (Table 1.1).

Table 1.1: Classification of landfill leachate according to age (Abbas et al., 2009; Deng, 2009; Li et al., 2010b).

	Young	**Medium**	**Old**
Landfilling phase	aerobic and acidic		methanogenic
Age (year)	<1	1-5	>5
pH	<6.5	6.5-7.5	>7.5
COD (g/L)	>15	3-15	<3
BOD_5 /COD	0.5-1.0	0.1-0.5	<0.1
TOC/COD	<0.3	0.3-0.5	>0.5
NH_4^+-N (mg/L)	<400	NA	>400
Kjeldahl nitrogen (g/L)	0.1-0.2	NA	NA
Heavy metals (mg/L)	>2	<2	<2
Organic compound (dominant species)	80% VFA	5-30% VFA+ HA+FA	HA+FA
Molecular size distribution	over a broad range - high fraction of low MW organics	NA	over a narrow range - high fraction of high MW organics
Biodegradability	important	medium	low

NA: not available; VFA: volatile fatty acids; HA: humic acids; FA: fulvic acids; MW: molecular weight; TOC: total organic carbon

Climatic conditions are critical factors that determine leachate quantity and quality, and thus must be taken into account to allow efficient operation of leachate treatment installations. Increase in precipitation (e.g. rainfall) has been observed to increase the amount of leachate generated (Warith, 2002) whereas reduced rainfall and increased evaporation leads to lower volumes of highly concentrated leachate. For instance, Kawai et al. (2012) report average COD concentrations of 4539 mg/L during the rainy season and 9004 mg/L during the dry season. Kim and Lee (2009) also report a decrease in BOD_5 values as a result of leachate dilution by infiltrating leachate. For a successful operation of an anaerobic digester, the COD concentration of landfill leachate should be at least 1000 mg/L (Kawai et al., 2012). Therefore, reduction in rainfall infiltrating into the landfill is important in maintaining proper nutrient levels for efficient biological operation.

Landfill leachate treatment, especially in municipal areas, has received significant attention. Additionally, in the last 10 years, as a consequence of the special attention paid to the environment by social, political and legislative international authorities, severe regulations have been implemented in some countries (Table 1.2) (Dai et al., 2011). For instance, in the European union, the Water Framework Directive and the urban wastewater treatment regulations have imposed stringent environmental standards for discharge of treated wastewaters into surface water bodies. To abide by these legislations hence avoid harming the ecosystem because of the discharge of untreated landfill leachate, landfilling operators have introduced on-site treatment facilities and, where not possible, off-site options are used.

Table 1.2 Revised discharge limits from landfill leachate in several countries (Dai et al., 2011; Dewandel et al., 2016).

Parameter	**Discharge limits (mg/L)**					
	China	**USA**	**Germany**	**France**	**Korea**	**Belgium***
COD	100	NA	200	120	50	450
BOD_5	30	NA	20	30	NA	150
NH_4^+-N	25	NA	2	NA	150	78
Total Nitrogen	40	NA	70	30	NA	NA
Total Phosphorus	3	NA	3	NA	NA	NA
Cd (II)	0.01	0.01	0.1	NA	NA	0.6
Cr (III)	NA	NA	0.5	NA	NA	NA
Cr (VI)	0.05	0.05	0.1	NA	NA	NA
Ni (II)	NA	0.013	1	NA	NA	NA
Pb (II)	0.1	0.03	0.5	NA	NA	NA
Cu (II)	NA	0.07	0.5	NA	NA	NA
Zn (II)	NA	0.3	2	NA	NA	NA
Ag (I)	NA	0.05	NA	NA	NA	NA

NA: not available

*Values are for the Flemish region of Belgium

Several wastewater treatment techniques - physical-chemical and biological - have been used to treat landfill leachate. Whilst these techniques have been optimized for the treatment of municipal wastewater, satisfactory treatment of leachate using these methods is not an easy task (Lin and Chang, 2000).

Biological treatment - the most popular technique for treatment of landfill leachate - is quite effective for relatively young leachate containing high BOD concentrations (2500 – 24000 mg/L), but it is less efficient for the treatment of older landfill leachate (Alvarez-Vazquez et al., 2004; Ehrig and Stegmann, 1992). A low BOD_5/COD ratio, the presence of recalcitrant organic matter and toxic substances such as heavy metal ions and other factors e.g. temperature and flow variations cause unique difficulties in biological treatment of older landfill leachate (Amokrane et al., 1997; Deng and Englehardt, 2006; Park et al., 2001). Moreover, landfill leachate has been identified as a significant source of new and emerging pollutants (Eggen et al., 2010), that might show significant adverse effects on ecosystems and on the food web (Stuart et al., 2012). Therefore, biological treatment alone is most often not sufficiently efficient in improving the quality of leachate to the required discharge standards. For these reasons, physical-chemical post-treatment of biologically treated leachate to reduce the environmental impact has to be considered.

Physical-chemical methods such as coagulation-flocculation and granular activated carbon (GAC) adsorption can be used to compliment the biological treatment process, as exemplified in Chapter 2, Sections 2.1.5.2 and 2.1.5.3. Physical-chemical techniques are also important in the treatment of raw old leachate, either through a single step treatment (Section 2.1.4) or through a combination of various techniques (Section 2.1.5.1). Because of the complex nature of landfill leachate, a combination of techniques – either biological and physical-chemical or only physical-chemical – is preferred. Such arrangements are known to take advantage of the merits of each technique while reducing the disadvantages. However, care should be taken not to overload a single technique. For instance, in landfilling facilities, activated carbon adsorption is often used as a final step after the biological process or, in the case of old raw landfill leachate, activated carbon adsorption is used after prior treatment with a physical or chemical technique. In the event that the initial treatment step doesn’t perform optimally, there will be undue pressure to the activated carbon step since the activated carbon bears the biggest load; hence the treatment is becoming expensive in the long run as a lot of activated carbon is required. To avoid such scenarios, this thesis puts forward several solutions which can allow landfill leachate to be treated to the required environmental discharge standards in a more economical way.

1.2 Scope and objectives of the thesis

To reduce the negative impacts that untreated or insufficiently treated landfill leachate can cause to the environment, appropriate treatment is required. **Therefore, the overall scope of this PhD research was to develop an optimized and cost-effective physical-chemical post-treatment train for both biologically treated and raw landfill leachate in order to meet the required environmental discharge limits**. With this in mind, landfill leachate from two different landfilling facilities were considered. Biologically treated leachate was obtained from the landfilling facilities of the Intergemeentelijke Maatschappij voor Openbare Gezondheid (IMOG) at Moen, Belgium. IMOG was chosen as a representation of facilities with on-site leachate treatment and would like to improve or find other ways of treating their leachate while meeting the environmental discharge limits. It is also a facility which manages old clay pits which are in the aftercare phase and are still producing landfill leachate, hence providing a good case study for other similar facilities around the world. Raw landfill leachate was obtained from the Vanheede landfilling facility at Roeselare, Belgium. Vanheede was chosen as a representation of landfilling facilities without provision for on-site leachate treatment and potentially considering to invest in an on-site treatment plant in the future. The specific characteristics of leachate from these two landfills will be provided in Chapter 3.

Additionally, the overall goal included the technical and economical evaluation of (combinations of) four different treatment techniques: ozonation, coagulation-flocculation, GAC adsorption, and ion exchange. **Ozonation** is an advanced oxidation process which is commonly used in post-treatment of biologically treated landfill leachate due to its ability to remove refractory organic matter. This is because ozone is a powerful oxidant (E_0 = 2.08V), which can alter the molecular structure of dissolved organics like humic acids and also bio-recalcitrant micropollutants. Moreover, ozonation offers benefits such as no sludge production, and – importantly – the ability to oxidize at slightly alkaline pH which is the typical pH of most leachates. Operating ozonation at these higher pH values favors the production of hydroxyl radicals (E_0 = 2.80V) which can accelerate the removal of recalcitrant organic matter from complex wastewater like landfill leachate. **Coagulation-flocculation** is a physical-chemical technique which has been chosen due to its simplicity of application and cost effectiveness. It is also effective in removing high molecular weight compounds such as humic compounds which are recalcitrant to biological degradation. **GAC adsorption** is one of the most frequently used physical techniques in post treatment of biologically treated landfill leachate; hence including it in this PhD study was important. It is favored due to its large porous surface area and ability to unselectively remove pollutants from landfill leachate. **Ion exchange** is also a physical technique used in the removal of charged substances such as ammonium and metals from landfill leachate. The operation of ion exchange is not affected by variations in leachate characteristics, and it is a compact technique thus not requiring a lot of space.

Following this selection of treatment techniques, **three specific research objectives** were defined in order to reach the overall scope of this PhD:

(i) To investigate the factors (leachate characteristics and operational parameters) affecting the **technical performance** of the different techniques in a bid to obtain an optimized and integrated treatment train for both raw and biologically treated landfill leachate.

(ii) To **evaluate the operating costs** related to the (post-)treatment of raw and biologically treated landfill leachate. Since costs have a large influence on the choice of techniques to be implemented in real practice, the goal was to come-up with a cost-effective treatment strategy for landfill operators.

(iii) To **characterize the dissolved organic matter** (DOM) present in the raw and biologically treated landfill leachate using rather simple and fast (e.g. UV-absorbance) as well as innovative **techniques** like fluorescence excitation emission matrix. By use of advanced chemometric techniques such as parallel factor analysis (PARAFAC) and self-organizing maps (SOM), the goal was to identify and obtain quantitative and/or visual data on the different types of DOM components present in landfill leachate, and to monitor their behavior during physical-chemical post-treatment.

1.3 Thesis outline

The content of this thesis are organized in four parts (Figure 1.1).

Following this introductory chapter, **Part I, Chapter 2** gives an in-depth literature review of the techniques currently available for the treatment of landfill leachate. Main principles, applications and their effectiveness for reducing the amount of pollutants in landfill leachate are comprehensively discussed. **Chapter 3** describes the two different types of leachate samples that have been considered in this PhD, as well as some basic information on the studied landfill facilities and on the sampling/sample treatment procedures. Next, this chapter provides the general information regarding the experimental set-ups and conditions that have been used during physical-chemical treatment of raw and biologically treated leachate.

Part II consists of **Chapter 4 – 8** and deals with the post-treatment of biologically treated landfill leachate sampled from the IMOG landfilling facility in Moen, Belgium. **Chapter 4** introduces ozonation as a promising post-treatment technique for biologically treated leachate. Using water quality parameters such as COD and UV-VIS absorbance, this chapter brings to light how the efficiency of ozonation is impacted by the organic matter content, initial leachate pH and other operational factors such as treatment time and ozone dosage. Given that ozonation as a single post-treatment is not sufficient in the reduction of COD from landfill leachate at economically feasible doses, **Chapter 5** investigates the possibility of coupling ozonation with granular activated carbon. This chapter also highlights the advantage of ozonation in increasing the biodegradability of leachate and demonstrates how the ozonated effluent can be utilized in the biological step. Finally, both the technical performance and cost effectiveness of a coupled ozonation-GAC treatment train is compared with that of ozonation and GAC as single techniques for the post-treatment of biologically treated leachate. In **Chapter 6**, coagulation-flocculation is investigated as an alternative to ozonation to be used in the post-treatment of biological effluent. A sequence consisting of coagulation-flocculation + GAC is compared to ozonation + GAC. Attention is paid to (i) the effect of the coagulant type and dosage in removal of recalcitrant organic matter, represented by COD as well as by UV-VIS absorbance at 254 nm as a potential surrogate, from landfill leachate, (ii) the settling characteristics of the sludge, and (iii) experimental and modeled data to assess the effect of both coagulation-flocculation and ozonation on the adsorptive properties of granular activated carbon. In addition to the technological performance, operating costs are focused on in **Chapter 7**. Using a sequence involving biological and GAC treatment as the base model, Chapter 7 takes into account the results of Chapters 5 and 6 – together with other leachate studies – and presents an economic assessment of three scenarios of leachate treatment by a combination of both biological and physical-chemical techniques. A more in depth study and further optimization of the coagulation-flocculation + GAC treatment train is performed in **Chapter 8** using emerging techniques such as excitation emission fluorescence coupled with parallel factor analysis (PARAFAC) and self-organizing maps (SOM) as chemometric techniques. A distinct fingerprint of the dissolved organic matter components present in biologically treated leachate is unraveled, and the removal of identified DOM components is studied using quantitative data obtained from PARAFAC.

Part III of this PhD thesis deals with the technical performance and operating costs for raw landfill leachate sampled from the Vanheede landfilling facility in Roeselare, Belgium**. Chapter 9** discusses the efficiency of coagulation-flocculation, granular activated carbon and ion exchange in reduction of COD, α_{254}, ammonium and nickel, with also particular attention to the effect of the coagulant type and dose on the downstream treatment by granular activated carbon and ion exchange. The latter technique is investigated to remove ammonium with potential for regeneration. This chapter also compares the operating costs of treating raw landfill leachate with that of biologically treated leachate (Chapter 7). Using the same fluorescence and chemometric techniques as in Chapter 8, **Chapter 10** addresses the main components of dissolved organic matter in raw landfill leachate and their behavior during treatment with coagulation-flocculation, granular activated carbon and ion exchange. Lessons learnt in this chapter offer more insights on the effectiveness of the studied coagulants for raw leachate treatment.

Finally, **part IV – Chapter 11** – presents an integrated discussion of the lessons learnt in the different experiments and proposes interesting research points to be considered in near future.

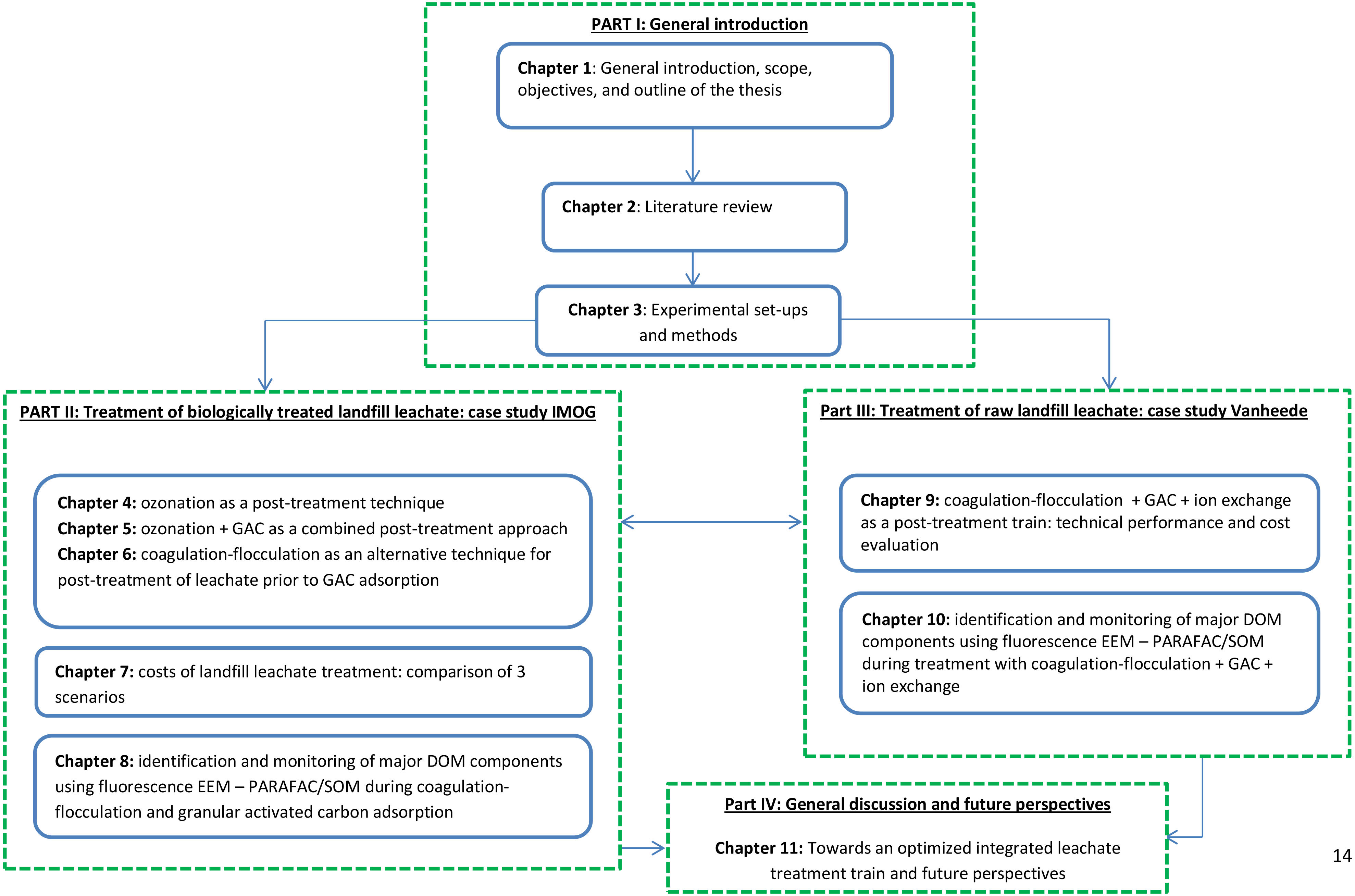


Figure 1.1: Schematic overview of the different chapters in this PhD thesis and their relationship to one another.

Chapter 2

Literature Review

Redrafted after:

Junling Gao, Violet Oloibiri, Michael Chys, Wim Audenaert, Bjorge Decostere, Yanling He, Herman Van Langenhove, Kristof Demeestere, Stijn WH Van Hulle (2015). The present status of landfill leachate treatment and its development trend from a technological point of view. Reviews in Environmental Science and Bio/Technology, 14(1), 93 – 122.

Contribution of Violet Oloibiri: writing a substantial part of the manuscript

2.1 Landfill leachate treatment

This literature review presents a critical comparison of various landfill leachate treatment processes which can be classified as (1) biological methods (2) physical and chemical methods, and (3) combination of physical-chemical and biological processes. It discusses and summarizes the state-of-the-art of these technologies for landfill leachate treatment with a focus on technological performance. Future work focusing on the study of different promising treatment techniques, especially combination of chemical techniques such as ozonation, coagulation-flocculation with biological processes was put forward. The use of physical techniques such as activated carbon adsorption and ion exchange as polishing steps was also highlighted.

Current strict environmental legislations (e.g. the European Water Framework Directive in Europe) especially on ground and surface water coupled with the need for water reuse have necessitated the treatment of landfill leachate. Complete or partial treatment can be done on-site where the leachate is produced or at an off-site facility. Many processes have been used for treatment of leachate, either alone or in combinations.

They are specifically discussed in this chapter, and the different roles which specific processes can play have been described under each individual process heading. This technical overview presents a summary and comparison of the types of leachate treatment activities in use, and the broad categories of leachate for which they are appropriate.

2.1.1 Recycling

Leachate recycling is one of the least expensive treatment techniques since a treatment plant is not required. It involves controlling and promoting of landfill biological, chemical and physical processes by the addition of leachate into the landfill leading to waste and leachate stabilization (Figure 2.1) (Warith et al., 2005). Such a set-up is often referred to as bioreactor landfill.

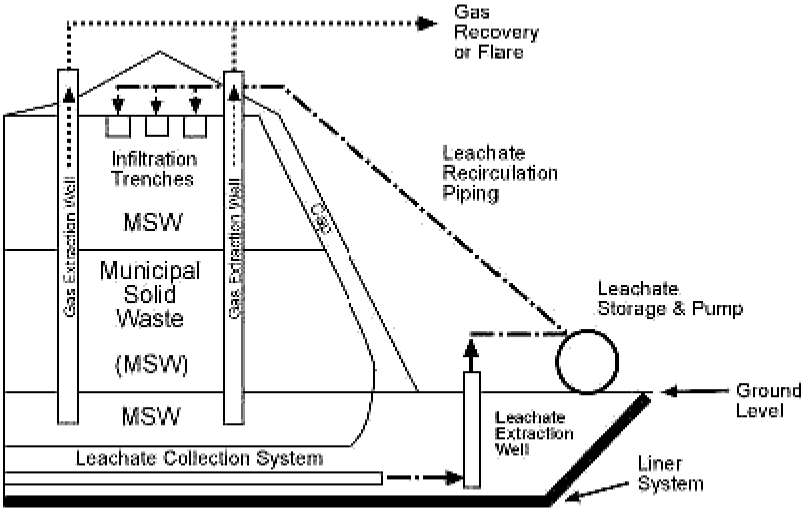


Figure 2.1: Recycling of a fraction of landfill leachate into the landfill (Bendere et al., 2012)

A study by Benson et al. (2007) provides a perspective on how leachate quality progresses with leachate recycling. In their study, the BOD_5/COD of leachate varied between 0.5 and 0.7 at the onset of recycling but declined to 0.1 after 4 years. Leachate recycling also lead to a decrease in COD of leachate from 9910 mg/L to less than 200mg/L and decrease in BOD_5 from 2055 mg/L to less than 200 mg/L (Warith, 2002). In a lab scale aerobic landfill bioreactor, up to 90.6% COD and 99% BOD_5 removal efficiency was obtained however, this resulted into a low BOD_5/COD ratio of 0.017 (Giannis et al., 2008).

Renou et al. (2008) reported that recycling increased the moisture content in the landfill. Additionally, recirculation of leachate at 30% initial waste bed volume led to a significant reduction in methane production and measured COD. According to Diamadopoulos, (1994), irrigation of leachate over wastes in the landfill contributed to a significant reduction in COD and BOD by 90% and 98%, respectively. However, the nitrogen concentration increased by 30% probably due to the continuous degradation of nitrogen containing matter. Promotion of short leachate stabilization periods is also one of the benefits of recycling.

Frequent introduction of leachate into the landfill leads to an increase in the moisture content of waste above their field capacity. This results into ponding, saturation and acidic conditions in the landfill. High acidic conditions ($pH < 5$) will further impair methanogens; hence poor anaerobic degradation of wastes (Renou et al., 2008). However, these setbacks can be managed by reducing the frequency of recirculation or volume of recirculated leachate (Warith et al., 2005). For instance, in a pilot scale bioreactor landfill, Huang et al. (2016) showed that the concentration of leachate COD can be reduced by half after 10 weeks when a recirculation rate of less than 0.3% total waste volume/day is used. On the other hand, Jiang et al. (2007) recommended adjustment of leachate recirculation to take into account the waste stabilization phases. E.g. the recirculation rate adopted during acidogenesis should not be high enough to allow wash out of organic matter before methanogenesis takes place as this will adversely impede methane production.

2.1.2 Combined treatment with municipal waste water

Treatment of landfill leachate together with municipal waste water has been reported to be an economical and feasible solution because leachate contributes to the nitrogenous fraction whereas the sewage contributes the phosphorus needed (Abbas et al., 2009; Borghi et al., 2003). Majority of the European countries carry out co-treatment of diluted leachate with the municipal wastewater

(Gierlich and Kollbach, 1998). Borghi et al. (2003) also reported that a concentration decrease of organic pollutants would be realized through dilution and adaptability of the activated sludge. However, this is refuted by studies which reported that the organic pollutants and heavy metals from leachate reduced treatment efficiency and increased effluent concentrations (Renou et al., 2008). Borghi et al. (2003) showed that COD and ammonium from a mixture of landfill leachate and municipal waste (in a ratio of 1/10) can be removed at a rate of 126 mg/L.hr and 51 mg/L.hr, respectively, using the activated sludge method with previously acclimated sludge at a hydraulic residence time of 4 hours. Up to 92% COD and 75% ammonium removal could be achieved in a sequencing batch reactor (SBR) when landfill leachate is sonicated before mixing with municipal waste waters (Neczaj et al., 2007). Co treatment of landfill leachate with domestic wastewater has also gained traction in developing countries if the infrastructure for municipal wastewater treatment is available. For instance, in Egypt, combining leachate from a local landfill with domestic wastewater at a ratio of 1:1 and treatment of the mixture with an aerobic reactor (HRT = 24h) resulted in 30% COD removal (El-Gohary and Kamel, 2016). Such low removals could be due to the increased ammonium levels which impede biological processes.

2.1.3 Biological Leachate Treatment

Many biological techniques currently in use in treatment of landfill leachate are adaptations of waste water treatment methods. Biological treatment processes are very effective methods to reduce high strength biodegradable organics present in the leachate. Also from younger leachate containing relatively high BOD and COD concentrations, the COD may be removed by biological treatment up to 50%. However, for other aged landfill leachate with rich nitrogen concentrations and poor BOD_5/COD ratios (<0.2), such systems are less suitable except for nitrification/denitrification/anammox process, which could be an alternative to remove ammonium and degrade some organic matter from leachate.

Based on the presence or absence of oxygen, biological techniques can be classified as aerobic, anaerobic or anoxic. According to Alkalay et al. (1998), the decision to select aerobic or anaerobic treatment can be done using the decision model of Forgies (1998) for leachate treatment train selection. Biological treatment methods such as anaerobic techniques are preferred compared to physical-chemical techniques because they are not only economical but also energy recovery can be achieved (Kheradmand et al., 2010). However, it is important to note that sole treatment of landfill leachate by biological methods will not yield satisfactory results (Kargi and Pamukoglu, 2003a; Oller et al., 2011). This is because frequent nutrient imbalances such as high ammonium, low phosphorus and carbon content in landfill leachate make it difficult to maintain proper biological treatment (Zhao et al., 2012). Furthermore, recalcitrant substances such as humic acids, fulvic acids and xenobiotic organic substances (XOC's) are not degraded during biological treatment. Therefore, these bio-refractory compounds and XOC's pass through the biological treatment process consequently increasing the organic level in the effluent (Zhao et al., 2012). For this reason, it is important that biological methods are used in combination with physical and/or chemical techniques.

2.1.3.1 Aerobic biological treatment with nitrification-denitrification: suspended and/or granular growth systems

Technological assessment

Suspended growth systems are biological treatment processes which are based on the growth and maintenance of a suspension of micro-organisms. Suspended growth technologies which have been employed to treat landfill leachate include aerated lagoons, activated sludge, and sequence batch reactors.

Aerated lagoons are also known as stabilization ponds. Their low operation, and low maintenance costs make them the most popular method of waste water treatment (Renou et al., 2008). Essentially, an aerated lagoon is a 1-2 m deep basin dug in the ground and designed to look like a natural lake. The upper part of a lagoon is aerobic and oxidizes reduced compounds from the lower anaerobic part.

Activated sludge systems consist of a completely mixed aeration reactor where biodegradation takes place and clarifiers where sludge is settled. Part of the sludge is recycled whereas excess sludge together with clarified water is discharged appropriately. These systems offer more intensive treatment than aerated lagoons because they operate with intensive aeration and large populations of acclimatized bacteria (IPPC, 2007). Inadequate sludge settling, the need for longer aeration times, high energy requirements and inhibition of microorganisms by high ammonium concentrations are some of the disadvantages that have shifted the focus on activated sludge to other more robust technologies (Renou et al., 2008).

Sequencing batch reactors (SBR's) are systems which allow aerobic biological treatment, equalization, sludge settling and clarification to take place in the same tank over a time sequence. This kind of operation creates a treatment process which is robust and less affected by frequent variation of organic load or ammonium (Laitinen et al., 2006). This characteristic is important in landfill leachate treatment as leachate properties are known to change over time. Despite the good performance, and flexible nature, the use of SBR's is marred by problems such as sludge bulking and poor clarification (IPPC, 2007).

Application to landfill leachate

Aerated lagoons have been successfully used to treat landfill leachate. (Mehmood et al. (2009) reported overall COD and ammonium removal of 75% and 99%, respectively, at a hydraulic retention time (HRT) of 50 days. Fernandes et al. (2013) observed a chemical oxygen demand (COD) and ammonium removal of 56% and 82% when three sequential ponds were used. The low removal of COD was attributed to the inhibition by algae in one of the ponds. The COD removal efficiency of 97% at a HRT of 10 days was reported by Robinson and Grantham (1988). The removal of 93% ammonium was obtained due to adequate desludging. Though aerated lagoons exhibit high COD and ammonium removal efficiencies in the treatment of landfill leachate, the COD and N effluent levels do not meet the required discharge limits in some countries such as China (NH_4^+-N<25 mg/l; COD<200 mg/l). Hence, recirculation is required (Fernandes et al., 2013; Mehmood et al., 2009).

In experiments involving aerobic post treatment of anaerobically treated landfill leachate, Kettunen et al. (1996) reported 75% removal of the remaining COD in an activated sludge system. This contributed to 15-30% of the overall COD removal in the whole process.

The performance of SBR's was illustrated by Neczaj et al. (2005) who reported 85% COD removal when influent consisted of 10% leachate and 90% synthetic water (v/v). The average quality of municipal landfill leachate was reduced from about 2200 to 500 mg COD/L after treatment by a SBR in the study of Laitinen et al. (2006).(Uygur and Kargi, 2004) showed that SBR treatment of leachate resulted in 62% COD and 31% ammonium removal when a five step operation was used. Further COD removals were achieved when powdered activated carbon was added. In order to improve the performance of aerobic systems, other configurations have been adopted. Treatment of landfill leachate in a multi-stage biological contact oxidation set-up at HRT of 24 hours resulted in the influent COD being reduced by 91% (Yuan et al., 2017). Aerobic granular activated sludge SBR has also been promoted for leachate treatment due to the high settling velocity of the granules, compact nature and simultaneous nutrient removals. According to Ren et al. (2017), treatment of landfill leachate with an aerobic granular sludge SBR could achieve 99% total ammonium and 67-87% COD removal compared to 76-99% total ammonium and 52-83% COD removal with an activated sludge SBR.

2.1.3.2 Aerobic biological treatment with nitrification-denitrification: attached growth systems

Technological assessment

Attached growth systems, also known as fixed film systems, are biological treatment technologies where bacteria attach themselves on supporting material such as plastic, gravel, rotor blades. These technologies include trickling filters, rotating biological contactors and moving bed biofilm reactors. Attached growth systems offer special advantage such as immobilization of active biomass, nitrification at low temperatures (Renou et al., 2008) and high nutrient removal (Table 2.1). Nitrification-denitrification processes can occur at the same time on both the outside and inside parts of a biofilm.

Constructed wetlands are also referred to as reed bed systems due to the extensive use of macrophytes. The treatment mechanisms in wetlands are complex (IPPC, 2007). Nevertheless, wetlands can reduce organic load of leachate, oxidize ammonium, and remove suspended solids. Often, these systems are used in the polishing of previously treated waste waters (EPA, 1999).

Wetlands can be vegetated or free flow systems with free floating macrophytes such as duckweed; emergent aquatic plants such as bulrush or submerged aquatic plants such as pondweed.

Application to landfill leachate

Table 2.1shows a summary of the performance of some attached growth systems for landfill leachate treatment. From this Table 2.1, it can be seen that is possible to reach 68-90% ammonia reduction and 52-96% COD reduction by attached growth systems. Trickling filters are not generally used for treatment when the leachate contains high concentrations of organic matter because of large volume sludge production causing clogging of the filters. Biofilters remain an interesting and attractive option for nitrification due to low-cost filter media and above 90% nitrification of leachate was achieved in biofilters and laboratory scale in situ denitrification (Jokela et al., 2002). Renou et al. (2008) showed that depending on the HRT a COD removal between 20 % and 75% can be achieved with the Moving-Bed Biofilm Reactor process (MBBR). Removal of other components such as heavy metals can also be accomplished in constructed wetlands. Up to 91.5 – 99.2% Fe and 94.7 – 99.8% Mn removal was achieved during treatment of landfill leachate using horizontal (HRT = 24.1 days) and vertical (HRT = 19.7%) subsurface flow constructed wetland (Kamarudzaman et al., 2011). It is important while treating landfill leachate to reduce biomass susceptibility to toxicity and variations in the environmental conditions because that means no inhibition of nitrification is encountered. In fact, with high nitrogen content there might be a risk of substrate as well as product inhibition during nitrification (Visvanathan et al., 2004).

Table 2.1: Typical performance of attached growth biological treatment systems

Reactor type	Operating conditions			Leachate characteristic (mg/L)	Performance (% removal)	Reference
	Temp (°C)	HRT[a] (days)	Loading Rate			
Trickling filters	20		NA	1930 COD	69 COD	Gourdon et al. (1989)
Upflow biofilter	25	1.4-3.8	2300 mg $N/m^3.d$	60-170 NH_4^+-N	>68% NH_4^+-N	Jokela et al. (2002)
Downflow biofilter	25	5.1-7.3	$1.0\text{-}1.3*10^5$ mg $NH_4^+/m^3.d$	60-170 NH_4^+-N	>90 NH_4^+-N	Jokela et al. (2002)
Suspended carrier film biofilter	25	1.6	$1*10^5$ mg $NH_4^+/L.d$	60-170 NH_4^+-N	>90 NH_4^+-N	Jokela et al. (2002)
Rotating biological contactors	NA	1	24.7g $COD/m^2.d$	3950-14000 COD	52 COD	Castillo et al. (2007)
Moving bed biofilm reactor	21	1	NA	2000-3000 COD	75 COD	Renou et al. (2008)
	5-22	2-5	NA	800-1300 COD	20-30 COD	Renou et al. (2008)
Aged refuse biofilter	5	NA	NA	5478-10842 COD	87.8-96.2 COD	Li et al. (2009)
	5	NA	NA	955-1821 BOD	94.7-97.3 BOD	Li et al. (2009)
Sub surface flow constructed wetland	NA	21		923 COD	91.8 COD	Akinbile et al. (2012)
Vertical sub surface flow constructed wetland	NA	2.5	15.6 g COD/ $m^2.d$	NA	47.8 COD	Wojciechowska (2017)

HRT: Hydraulic residence time

NA: not available

2.1.3.3 Partial nitritation/anammox processes

Technological assessment

Anammox (anaerobic ammonium oxidation), an autotrophic nitrogen removal method, uses ammonium as electron donor and nitrite as electron acceptor to accomplish nitrogen removal (Van Hulle et al., 2010). As such it should be referred to as anoxic ammonium oxidation. The anammox process should always be combined with a partial nitritation process, where half of the ammonium is oxidized to nitrite (aerobic ammonium oxidation). These two processes can be combined in 1 reactor (1 step process) or in 2 separate reactors (2 step process). Both autotrophic processes will increase the sustainability of wastewater treatment as the need for carbon addition (and concomitant increased sludge production) is omitted and oxygen consumption is largely reduced. By allowing operating conditions which favor anaerobic instead of aerobic ammonium oxidation, the N_2O emission from biological plants using partial nitrification and anammox can be minimised (Domingo-Félez et al., 2014). Partial nitritation/anammox technology has been developed to mainly treat ammonium rich wastewaters, such as landfill leachate (Beylier, 2012; Xu et al., 2010).

Application to landfill leachate

The application of the anammox process for treating landfill leachate seems promising and is currently at full-scale operation (Denecke et al., 2007; Hippen et al., 2001). In a landfill leachate treatment plant in Germany, modification of the activated step allowed the growth of anammox bacteria (Azari et al., 2017). At an average nitrogen loading rate of 0.71 Kg N/m^3.d, the anammox process achieved 83% nitrogen removal efficiency. Combination of the activated sludge process with a GAC reactor improved the nitrogen removal efficiency to 94% since the GAC acted as an external surface where by granular anammox biofilms could develop (Azari et al., 2017). Table 2.2 summarizes the main studies about the leachate treatment in combined partial nitritation-anammox either in one and two step processes.

As it can be seen in Table 2.2, nitrogen removal by anammox in nitrogen rich landfill leachate is the current challenge. Important nitrogen losses could be detected, in spite of the absence of available organic matter for denitrification and further analysis revealed the presence of anammox bacteria. According to Table 2.2, RBC is the main reactor configuration used in landfill facilities for autotrophic nitrogen removal. For certain studies e.g. (Hippen et al., 1997) treatment were carried out in reactors designed for nitrification-denitrification purposes and the performance of anammox process in treating leachate would not only depend on anammox bacteria but also on the co-existence of other important bacteria. Partial nitritation, anammox and denitrification processes were carried out in an SBR to treat mature landfill leachate. A total nitrogen removal efficiency of 99% was achieved with the anammox process contributing 77% removal (Zhang et al., 2017). In comparison to nitrification-denitrification systems, anammox reactors require longer start up times. This is related to the slow growth rate of the anammox bacteria and sensitivity to high concentrations of nitrite and ammonium (Lackner et al., 2014; Van Hulle et al., 2010). However, these start up periods can be reduced by using inoculum with high abundance of anammox bacteria and accustomed to landfill leachate. Moreover, knowledge on the conditions that favour growth of anamox bacteria has increased hence shorter start up times.

Table 2. 2: Main studies reporting anammox process for treatment of landfill leachate, according to (Beylier, 2012)

Reactor Type	**Volume m^3**	**Ammonium g NH_4^+-N/m^3**	**Nitrite g NO_2^- - N/m^3**	**NLR gN/m^3.d**
BC	-	1650	5.12	1600⁽¹⁾
RBC	33	0.1-0.4	-	1500-4000⁽¹⁾
RBC	40	349	-	5800⁽¹⁾
RBC	0.014	1500⁽²⁾	-	930
FBBR	0.036	885	1011	110
SBR	0.003	1442	-	960
SBR	384	634	-	500

BC: Biological Contactor

RBC: Rotating Biological Contactor

FBBR: Fixed-bed Biofilm Reactor

SBR: Sequencing Batch Reactor

(1) NLR: nitrogen loading rate, expressed as g N/m^3.d^1

(2) Total nitrogen (ammonium plus nitrite)

2.1.3.4 Anaerobic biological treatment

Technological assessment

Anaerobic treatment is a biochemical process which takes place in the absence of oxygen; it involves two phases: the acid phase where facultative microorganisms convert complex organic matter into organic acids. In the second phase, obligate anaerobic organisms change volatile organic acids to carbon dioxide and methane. The methane formed can be harvested and used as a source of energy in reactor heating (Kheradmand et al., 2010). The benefits of anaerobic treatment include its ability to treat high-strength organic effluents (COD > 10,000 mg/L) and reduced sludge production (Abbas et al., 2009) Furthermore, hydrogen sulphide produced by the reduction of sulphates is a good precipitant for the toxic metals in landfill leachate. The metal sulphides formed accumulate in sludge as inert solids and sludge disposal leads to their overall removal from landfill leachate (IPPC, 2007).

Configurations can be either fixed film or suspended growth systems. Though anaerobic systems offer several benefits in leachate treatment, they also have disadvantages. Anaerobic treatment offers low removal or even increase in ammonium content (Liang and Liu, 2008). For this reason, novel techniques such as coupling of partial nitritation with anammox have been developed to economically reduce ammonium in landfill leachate. After anaerobic treatment, effluent is in a reduced state containing high levels of dissolved amines, sulphides and methane. Discharge of such an effluent to surface waters will lead to severe loss of aquatic life. Therefore, aerobic post treatment is required (IPPC, 2007).

Application to landfill leachate

Several scientific reports have shown that anaerobic systems can be used in landfill leachate treatment (Table 2.3). These systems include Upflow anaerobic sludge blanket (UASB) (Kawai et al., 2012), anaerobic sequencing batch reactor (AnSBR) (Kennedy and Lentz, 2000; Timur and Ozturk, 1999), Upflow anaerobic filter, anaerobic hybrid bed (Calli et al., 2006), CSTR (completely stirred tank reactor), and anaerobic digesters (Lin et al., 1999). Anaerobic lagooning of landfill leachate has also been reported in warmer climates (IPPC, 2007). Up-flow Anaerobic Sludge Blanket (UASB) process is a modern anaerobic treatment that can have high treatment efficiency and a short hydraulic retention time (Lin et al., 2000). At 24°C, a COD removal of up to 75% was achieved with a 10 h HRT by Kettunen et al. (1996). Further, a pilot-scale reactor was used to study municipal landfill leachate treatment (COD 1.5-3.2 g/L) at 13-23°C by Kettunen and Rintala (1998). The results showed that leachate can be treated on-site UASB reactor at low temperature. COD (65-75%) and BOD (up to 95%) removals were achieved at organic loading rates of 2-4 kg /m^3 .d of COD. Some studies revealed good performances of anaerobic sequencing batch reactors. For instance, COD reduction from sanitary landfill leachate was carried out using lab-scale anaerobic sequencing batch reactors (ASBR) at 35°C by Kennedy and Lentz (2000) and the COD removal efficiencies of 64–85% was reached, at varying hydraulic retention times (HRT) (10-1.5 days) and influent wastewater COD's (3800-15900 mg/L). Calli et al. (2006) found that the anaerobic filter and hybrid bed reactor were generally slightly more efficient and stable than the UASB reactor. Henry et al. (1987) demonstrated that anaerobic filter could reduce the COD by 90%, at loading rates varying from 1.26 to 1.45 kg/m^3.d of COD and this for different ages of landfill. Nedwell and Reynolds (1996) reported steady state COD removal efficiencies of 81-97% can be gained under by hybrid bed reactor methanogenic digestion. The drawback of a hybrid reactor, as well as anaerobic filter, is the added cost of the support media. Though these reactors have exhibited relatively superior and stable performance for COD removal compared to the other processes (Table 2.3), anaerobic processes are difficult in management to control longer SRT or HRT requiring larger volume reactors (Visvanathan et al., 2004).

Table 2.3: Typical performance of anaerobic biological leachate treatment systems

Reactor type	**HRT**	**Influent COD (mg/L)**	**% COD removal**	**Reference**
Upflow anaerobic sludge blanket	10 hrs	1300±120	71±3	Kettunen et al. (1996)
	34 hrs	1600±110	45±5	Kettunen et al. (1996)
	1.3±0.7 days	1900±52	52±3	Kettunen and Rintala (1998)
	2-7 days	1770	40	Kawai et al. (2012)
Hybrid anaerobic reactor	35 hrs	780±60	56±3	Kettunen et al. (1996)
CSTR anaerobic digester*	20 days	670-1223 SCOD	81-86(SCOD)	Lin et al. (1999)
	10 days	992-1555 SCOD	75-83(SCOD)	Lin et al. (1999)
	5.3 days	1722-2526 SCOD	68-76(SCOD)	Lin et al. (1999)
Continuous stirred anaerobic digester	NA	15000	60	Imen et al. (2009)
2 stage anaerobic digester	15 days	55351	92	Kheradmand et al. (2010)

CSTR: Completely stirred tank reactor, SCOD: Soluble COD, NA: not available, *Sample used is mixed with septage at different ratios

2.1.4 Individual physical-chemical treatment techniques

Physical and chemical methods include air stripping, precipitation/coagulation-flocculation, chemical oxidation processes, activated carbon adsorption, membrane processes (microfiltration, ultrafiltration, nanofiltration and reverse osmosis), ion exchange, electrochemical treatment and floatation. These techniques are often applied for removing non-biodegradable and undesirable compounds from the landfill leachate. These pretreatment step are useful, especially for fresh leachate, prior to biological treatment, or a post-treatment (purification) step for partially stabilized leachate and when the biological oxidation process is hampered by the presence of bio-refractory materials. These methods are used along with the biological methods to improve treatment efficiency or make them possible, or to treat a specific pollutant (e.g. stripping-ammonium removal) (Renou et al., 2008; Wiszniowski et al., 2006).

2.1.4.1 Flotation

This is a physical method which is used to reduce floting matter such as colloids, oil and greasy substances, and fibres. Using configurations such as dissolved air flotation units, flotation can be used in the harvesting of dissolved metals or micro-organisms acclimatized to landfill leachate (Rubio et al., 2002). Despite its potential in lowering the pollutants in landfill leachate, few studies have been devoted to it. Zouboulis et al. (2003) investigated the use of flotation in column, as a post-treatment step for removing residual humic acids (non-biodegradable compounds) from synthetic landfill leachates. Under optimized conditions, almost 60% humic acids removal has been reached. This flotation technique was used for removing the humic acids from leachate based on the theory of Froth flotation. Froth flotation is a highly versatile method for physically separating particles based on differences in the ability of air bubbles to selectively adhere to specific mineral surfaces in water slurry. The particles with attached air bubbles are then carried to the surface and removed, while the particles that remain completely wetted stay in the liquid phase. Humic acids are the substances, which is soluble in alkaline solutions, but precipitates in acid solution. Therefore, in the study of Zouboulis et al. (2003), flotation of humic acids was performed with N-cetyl-N,N,N-trimethylammonium-bromide (CTAB) and ethanol as a frother to remove high concentration of humic acids from landfill leachates.

2.1.4.2 Air stripping

Technological assessment

Air stripping, involves passing a large volume of air through the leachate, so to promote mass transfer of some undesirable substances from the liquid passed to the gas phase. Air stripping is used to remove methane, ammonium and volatile organic compounds (VOCs) in leachate (Figure 2.2).

Figure 2.2: Full scale plant for treatment of landfill leachate by ammonia stripping (Organics, 2018)

Ammonium can be removed from leachate as a gas by using air stripping, as an alternative to biological nitrification. The efficiency of the process is increased significantly by increasing values of pH or temperature. Typically, either pH values in excess of 10.0, or temperatures in the order of 60-70°C, are needed for efficient ammonium removal (IPPC, 2007). Although ambient air is used and generally cause a significant temperature drop (5-6°C) in the stripping tower, this can be solved by using part of the incinerating heat which results from flaring the landfill biogas. Due to its effectiveness, ammonium stripping is often employed for the removal of ammonium from landfill leachate (Calli et al., 2005; Diamadopoulos, 1994; Marttinen et al., 2002; Ozturk et al., 2003). Further, also significant removal of volatile organic components (VOC), often present in landfill leachate, can be achieved during air stripping as almost all VOCs have low boiling points (Lamarre and Shearouse, 1994).

However, this treatment presents some disadvantages and limitations. A major concern about air stripping is the control and destruction of exhaust air (such as ammonia gas) from the stripping processes. The off-gases released into the atmosphere cause severe air pollution and may require treatment. To avoid pollution, the released ammonia gas is captured using an acid solution such as sulphuric acid (Demeestere et al., 2001). Another concern is calcium carbonate scaling of the stripping tower, when lime is used for pH adjustment and the foaming trouble which might require a large stripping tower (Li et al., 1999).

Additionally, as illustrated by the studies cited in Kurniawan et al. (2006a) the COD removal efficiency of air stripping is limited. Therefore, further treatment of effluent from this step is required to reduce the COD load.

Application to landfill leachate

To review the efficiency of air stripping for landfill leachate, Cheung et al. (1997) studied ammonium removal for two different flow rates (1 L/min, 5 L/min) at 20 °C and at pH 11. Results revealed that after 24 hour-aeration, 81% and 90% removal efficiencies could be obtained for flow rates of 1 L/min and 5 L/min, respectively. (Collivignarelli et al., 1998) studied ammonium removal from landfill leachate having 2100 mg/L ammonium. Experiments were carried out at 70°C and at pH 11 and the removal efficiency was 90%. A full-scale study on the treatment of leachate from the Shanghai Laogang Solid Waste Disposal Facility, Ltd. (China) using ammonium stripping was recently carried out for the lowering of ammonium and total nitrogen (Blauvelt, 2009). The results showed the air stripping reduced ammonium by 8 – 15%, total nitrogen by 8 – 29%, and COD by 42%. By increasing the treatment time and treatment volume, it was found that 70 – 80% of ammonium could be removed with a daily treatment requirement of 1000 m^3/day of leachate.

In Hong Kong, an air stripping system was installed and applied as a pre-treatment option for landfill leachate. The leachate flows ranged from 720-1800 m^3/d and the initial concentration of ammonium was about 6700 mg NH_4^+-N/L. Using landfill gas to raise leachate temperatures to 70°C before passage over the stripping tower, the air stripping resulted in an effective removal of ammonium gas (>99.99 percent). As such the ammonium concentration could be reduced below 100 mg/L before subsequent biological treatment in an SBR system (IPPC, 2007).

2.1.4.3 Coagulation-flocculation

Technological assessment

Coagulation- flocculation is a relatively simple and cost-effective method to treat landfill leachate, e.g. for the removal of heavy metals (Amokrane et al., 1997; Marañón et al., 2008; Silva et al., 2004). It may be employed successfully for the treatment of older landfill leachate (Amokrane et al., 1997). However, only moderate (50-65%) removal of COD (or TOC) is reported. Further, excessive sludge production, high cost of chemical dosing and sludge disposal, dependence on pH and in certain cases, increased aluminium and iron concentrations in the resulting effluent hamper the individual use of coagulation-flocculation in leachate treatment (Trebouet et al., 2001). Coagulation-flocculation has thus been investigated mainly as a pretreatment method for young leachate or as a post-treatment technique for the stabilized leachate (Tatsi et al., 2003). Several studies have been reported on the examination of the coagulation – flocculation process for the treatment of landfill leachate, aiming at performance optimization, i.e. selection of the most appropriate coagulant, assessment of pH effect and investigation of flocculant dose (Amokrane et al., 1997; Sletten et al., 1995; Tatsi et al., 2003). Aluminium sulphate (alum), ferrous sulphate, ferric chloride and ferric chlorosulphate are commonly used as coagulants. Iron salts seem more efficient than aluminium ones, resulting in sufficient COD reductions (up to 56%) (Amokrane et al., 1997), whereas the corresponding values in case of alum or lime addition were lower (39 or 18%), respectively (Diamadopoulos, 1994). Furthermore, the addition of flocculants together with the coagulants may enhance the floc-settling rate hence better pollutant removals (Amokrane et al., 1997).

Application to landfill leachate

Kargi and Pamukoglu (2003b) observed 60% COD removal when ferric chloride was used at an optimum dose of 6.1 mmol/L and pH 6.0. coagulation-flocculation with $FeCl_3$ was also studied for removal of heavy metals from stabilized leachate containing high concentrations of organic and inorganic matter (Kurniawan et al., 2006a). The results reveal that heavy metal removal occurs best at alkaline pH. Further, with an optimum aluminium sulphate dose of 15 g/L and a pH value of 7.0, a maximum COD and colour removal of 34% and 66%, respectively were observed by Mahmud et al. (2012). Recalcitrant compounds such as humic acids can also be removed by coagulation-flocculation. Humic acid removal efficiencies of 80%, 53%, 70% were reported by Liu et al. (2012) when ferric chloride 6-hydrate, ferric sulphate 7-hydrate, and polyferric sulphate were used, respectively. Since xenobiotic organic substances (XOC's) such as phthalic acid esters can be sorbed to dissolved organic matter (DOM), removal of DOM from leachate results into overall removal of phthalic acid esters (Zhang and Wang, 2009).

The effect of a coagulation-flocculation process with ferrous sulfate as a coagulant on COD, apparent color and turbidity was evaluated using a jar test method and a response surface methodology (RSM) by Amir et al. (2009) for the pre-treatment of mature landfill leachate of the Pulau Burung Sanitary Landfill, Malaysia. Amir et al. (2009) reported that ferrous sulfate was most efficient under alkaline conditions (pH = 11.7) with a coagulant dosage of 10 g/L. This resulted in a maximum of 22% COD removal, 42% apparent color removal and 31% turbidity removal. It was observed that the COD, apparent color and turbidity reductions decreased with pH and $FeSO_4$ concentration beyond the optimum conditions. Ghafari et al. (2009) showed that at optimum conditions of poly-aluminum chloride (PACl) dosage of 2 g/L at pH 7.5 and alum dosage of 9.5 g/L at pH 7; the COD, turbidity, color and TSS removal efficiencies of 43, 94, 90, and 92% for PACl, and 63, 88, 86, and 90% for alum were reached. The results indicated the COD removal was high using alum than PACl. In contrast, higher removal efficiencies for turbidity, color and TSS were achieved using PACl than those using alum.

Amokrane et al. (1997) demonstrated that 40% COD and 90% heavy metal removal can be achieved when lime is used as a coagulant. Kurniawan et al. (2006a) reports a study on the removal of heavy metals from landfill leachate. It was shown that 8 g/L of lime could reduce the concentration of manganese and iron by 77% and 78%, respectively. Coagulation-flocculation of leachate at a dose of 2000 mg $FeCl_3$/L (0.35 mg $FeCl_3$/mg COD_o) and pH 5 led to a reduction of the initial COD by 63% (Amor et al., 2014). In a bid to reduce the dose of PACl required to treat leachate, Yusoff et al. (2018) partially replaced PACl with cross linked *Durio zibethinus* seed starch (CDSS). At a dose of 2000 mg PACl/L (0.53 mg PACl/mg COD_o) and 40 mg CDSS/L,(0.01 mg CDSS/mg COD_o) removal efficiencies for COD and color were 61 and 96% respectively. In comparison, PACl at a dose of 2700 mg/L (0.72 mg PACl/mg COD_o) managed removals of 40.3% COD and 94% color.

2.1.4.4 Chemical precipitation

Technological assessment

Chemical precipitation has been used for the removal of non-biodegradable organic compounds, ammonium and heavy metals from landfill leachate because of its capability, the simplicity of the process and inexpensive equipment employed (Calli et al., 2005; Li et al., 1999). During chemical precipitation, dissolved ions in the solution are converted to the insoluble solid phase via chemical reactions (Kurniawan et al., 2006a). There are different optimum pH-values for precipitation of different components (Kurniawan et al., 2006a). Chemical precipitation is a good technical alternative to air stripping of ammonia which suffers operational problems such as carbonate scaling.

Struvite (magnesium ammonium phosphate, MAP) - precipitation is one of the methods used in the removal of ammonium from landfill leachate. The efficiency of struvite precipitation is controlled by pH, the molar ratio of magnesium, ammonium and phosphate and the sequence with which the precipitation is carried out (Kim et al., 2007). Though struvite precipitation is an excellent method for ammonium removal, the need for external sources of magnesium and phosphate is its major limitation. This is because landfill leachate is highly deficient in magnesium and phosphorus. Furthermore, since the stochiometric molar ratio of magnesium, ammonium and phosphate i.e. 1:1:1 gives low removal efficiencies, optimization of these three components is necessary to achieve better removal efficiencies (Di Iaconi et al., 2010).

Difficulties may also arise from specific need of the removal of heavy metals in landfill leachate, reducing the cost-effectiveness of the process (IPPC, 2007).

Application to landfill leachate

Precipitation of heavy metals in leachate using sulphides has been proposed by Enzminger et al. (1987). The usage of sulphides was seen to be advantageous due to their ability to work over a broad pH range and their extremely low solubility. However, the probability that sulphide might end up in the effluent and generation of hydrogen sulphide were major drawbacks in sulphide use as a precipitant.

Recent developments have seen the use of struvite, chemically known as magnesium ammonium phosphate (MAP), in chemical precipitation of ammonium from landfill leachate. Li et al. (1999) proved that as a pre-treatment process, the MAP precipitation can be effective to remove the high ammonium strength of over 5,000 mg/L from the raw leachate collected at the local landfill in Hong Kong. The removal efficiency of ammonium was more than 90%. In their review, Abbas et al. (2009) report the use of MAP at a pH of 8.5 to 9.0 to reduce ammonium concentration from 5600 mg/L to 110 mg/L. Results from Di Iaconi et al. (2010) indicate that 95% ammonium removal was achieved when the Mg^{2+}:NH_4^+:PO_4^{3-} ratio was set at 2:1:1, at a pH of 9. Similar studies by Kim et al. (2007) corroborated with this and demonstrated that ammonium precipitation efficiencies greater than 90% were achieved when struvite was used in a sequence that involves addition of magnesium and phosphorus sources before control in pH. In other studies, the elimination of other ions e.g. Ca^{2+} by at least 90%, enhanced the recovery of magnessium from leachate (from 65% - 98%) through struvite precipitation (Wu et al., 2018). In a bid to lower struvite precipitation costs, the use of waste phosphoric obtained during production of phosphoric acid and low cost magnesium oxide was proposed. Observing a molar ratio of 3:1:1 for Mg:N:P, led to 82% and 9% reduction of leachate ammonia and COD respectively and the treatment costs by 68% (Huang et al., 2014).

2.1.4.5 Chemical oxidation and advanced oxidation processes (AOPs)

Technological assessment

Chemical oxidation is required for the treatment of landfill leachate to remove specific organic and inorganic pollutants such as soluble organic, non-biodegradable and/or toxic substance, but is unlikely to provide full treatment of the wide range of contaminants present in typical leachate samples (IPPC, 2007). According to Amokrane et al. (1997) commonly used oxidation agents as chlorine, ozone, potassium permanganate and calcium hydrochloride for landfill leachate treatment resulted in COD removal of around 20-50%. Advanced Oxidation Processes (AOPs) is a special class of oxidation techniques which are all characterized by the same chemical feature: production of OH radicals. OH radicals are extraordinarily reactive species with an oxidation potential of 2.8V, and destroy or detoxify halogenated organics, while enhancing the biodegrability of the effluent by rupturing aromatic structures, and dissociating the carbon-halogen (C-X), carbon-carbon single and carbon-carbon double (C=C) bonds (Ince, 1998). A list of the different possibilities offered by AOPs is given in Table 2.4. Different oxidation techniques such as photocatalytic oxidation，catalytic wet air oxidation, fenton oxidation, electrochemical oxidation, catalytic oxidation, chemical oxidation, plasma technique and ultrasonic technology have been reviewed by Gui and Yang (2007).

Many researchers using AOPs have demonstrated the effectiveness in eliminating COD but most of them only used this process as a tertiary treatment prior to discharge in the environment and it is not always in an efficient way. 48% COD removal was only attained when the highest ozone dose of 3.0 g O_3/L was employed, and rather than being removed, there was actually an increase in the TOC content of the ozonated sample (Silva et al., 2004). Other draw backs of AOPs is the high demand of electrical energy for devices such as ozone generators, UV lamps, ultrasound systems, which results in rather high treatment costs. Also, for complete degradation (mineralization) of the pollutants to occur, high oxidant doses would be required rendering the process economically expensive (IPPC, 2007). Tizaoui et al. (2007) estimated the operating cost of an O_3/H_2O_2 system to be about 2.3 euro/kg COD. While Chys et al. (2015) estimated the operational cost for fenton treatment of leachate was 2.5 €/kg COD of leachate, while the cost for ozonoation was 3.1 €/kg COD. The relative high treatment costs are the main restriction for successful application of AOPs next to its treatment efficiency. Therefore, this PhD thesis and future studies on AOPs should focus on combination of advanced oxidation process and biological treatment. Also, efficient control of such systems will be necessary as the currently applied control strategies are mainly flow rate based. During rainy periods, when the flow rate is high, but the pollution load is low, these control systems are dosing too much.

Table 2.4: List of typical AOP systems, according to Lopez et al. (2004)

With irradiation	**Without irradiation**
Homogeneous System	
O_3/ultraviolet (UV) H_2O_2/UV Electron beam Ultrasound (US) H_2O_2/US UV/US H_2O_2/Fe^{2+}/UV (Photo- fenton's)	O_3/H_2O_2 O_3/OH^- H_2O_2/ Fe^{2+} (fenton's)
Heterogeneous Systems	
TiO_2/O_2/UV TiO_2/O_3/UV TiO_2/H_2O_2/UV	Electro- fenton

Application to landfill leachate

AOPs, adapted to old or well-stabilized leachate, are applied to enhance the biodegradability of contaminants through converting recalcitrant contaminants into smaller and consequently more biodegradable intermediates and oxidize organics substances to their highest stable oxidation states being carbon dioxide and water (i.e., to reach complete mineralization).

Ozone oxidation finds wide scale application in the treatment of landfill leachate as illustrated by various lab scale and industrial scale applications. For instance, over 30 leachate treatment facilities in Germany apply ozonation to reduce the concentration of pollutants in leachate before discharge into surface waters (Gottschalk et al., 2000). Ozonation is highly valued because it can transform recalcitrant organic compounds into lower molecular weight compounds thus increasing biodegradability. However, its efficiency depends on various factors. To illustrate the effect of pH on ozonation efficiency, Cortez et al. (2010) reported an increase in the percentage of COD removal and BOD_5 content from 23% to 40% and 30-65 mg/L, respectively, when the pH changed from 3.5 to 11. In other studies, the decrease in UV absorbance at 254 nm improved from 42% (pH 5.5) to 57% (pH 11) (Cortez et al., 2011). This is because alkaline pH favors the formation of the highly reactive hydroxyl radicals which react unselectively and rapidly with organic matter hence reducing COD and colour (Kurniawan et al., 2006d). However, at alkaline pH, bicarbonate ions converted to carbonate ions which readily scavenge the hydroxyl radicals, hence slowing down the oxidation kinetics (Li et al., 2010b). Other known scavengers include chlorides and sulphates (Tizaoui et al., 2007). Several studies (Cortez et al., 2010, 2011; Tizaoui et al., 2007) reported an overall increase in COD removal as the treatment time of oxidation increased. This is because of higher ozone doses. For instance, COD removal increased from 4% at 5 min reaction time to 10% at 60 minutes at an inlet ozone concentration of 63 mg/L (Cortez et al., 2010). A 50% difference in COD removal was observed when leachate was treated for 60 instead of 20 minutes (Tizaoui et al., 2007). At initial reaction time of 30 minutes, (Ntampou et al., 2006) reported 30% COD removal at 0.75 g/h.L ozone dosage. The percentage of COD removal increased to 57% upon extended reaction time (3 hours). An additional benefit of ozonation is that it increases the BOD/COD ratio from zero up to a maximum value of 0.21 (Derco et al., 2002).

Ozonation can be improved by coupling it with other oxidants such as UV or H_2O_2. (Li et al., 2010b). In their review, Li et al. (2010b) reported up to 97% COD reduction in an O_3/H_2O_2 system and 54% COD reduction in the photolytic ozonation system. A study to compare the efficiency of O_3, O_3/UV, O_3/H_2O_2 at an ozone dosage of 1.2 g/L reported that O_3/UV had better oxidation ability than O_3 and O_3/H_2O_2 systems. Photolytic ozonation systems further offer advantages such as no production of trihalomethanes (THM) which are found in other oxidation systems (Kurniawan et al., 2006a).

Fenton oxidation involves the use of hydrogen peroxide in the presence of ferrous salts leading to the generation of hydroxyl radicals which oxidise the organic matter (Deng and Englehardt, 2006). It involves four steps: (i) a pH adjustment step where the leachate pH is lowered to 2 – 3 which is the optimum range for fenton oxidation; (ii) the oxidation step where Fe^{2+} and H_2O_2 are added to the leachate; (iii) the neutralization step where the leachate pH is raised to stop the fenton process. During this step, ferric precipitates form which further assist in the reduction of the pollutants from leachate. Finally, (iv), the formed sludge is allowed to settle after which the supernatant is withdrawn for analysis. Fenton oxidation has been used successfully in the removal of pollutants from landfill leachate. In the treatment of Pulau Burung stabilized landfill leachate, Mohajeri et al. (2010) reported 78% and 58%, removal of colour and COD respectively. In terms of biodegradability improvement, BOD_5/COD ratios close to 0.5 after fenton oxidation have been reported Lopez et al. (2004). This overall removal of pollutants is achieved by coagulation-flocculation and/or oxidation and it depends on the reaction conditions such as pH and H_2O_2/Fe^{2+} ratio. Barbusi and Pieczykolan (2010) reported an optimum pH for fenton oxidation between 2 and 4 where they achieved up to 60% COD removal. This observation corroborated with that reported by Zhang et al. (2005) where 58% and 45% COD removal was achieved at an optimum pH of 2.5, and initial COD concentrations of 1000 mg/L and 2000 mg/L respectively. A pH of 3 favored the removal of 46% COD and 62% UV absorbance at 254 nm (Cortez et al., 2011). A further increase in pH led to a decrease in COD removal efficiency probably as a result of inhibition of H_2O_2 decomposition, deactivation of ferrous catalyst and/or scavenging by HCO_3^-, CO_3^{2-} which are dominant at alkaline pH (Deng and Englehardt, 2006). Singh and Tang (2013) investigated the impact of H_2O_2/Fe^{2+} ratio on fenton oxidation and found a very broad operational range of 0.5 to 60 (w/w). At this range, the COD removal efficiencies ranged between 31% and 95%. At low H_2O_2/Fe^{2+}, chemical coagulation is predominant. This is due to the formation of ferric ions by fenton mechanisms. The use of UV irradiation in the fenton process (photo-fenton) and production of H_2O_2 through the electrochemical process (electro-fenton) has shown great potential in COD removal efficiencies. Li et al. (2010b) reports up to 86% and 83% percentage of COD removal using photo fenton and electro-fenton respectively.

Photocatalysis can also be used to reduce COD concentration in leachate (Meeroff et al., 2012). At initial COD concentration ranging between 140 – 330 mg/L, over 70% COD removal efficiency was achieved when photocatalysis was carried out for 4 hours using 4 g/L of TiO_2 and UV intensity of 1960 µW/cm^2. Using photochemical technologies revealed that 35 – 57% COD removal efficiency could be obtained when landfill leachate (initial COD 1200 mg/L) is treated using 1-2 g/L TiO_2 and 500 µW/cm^2 UV intensity. Since high operation costs caused by high energy consumption is one of the major drawbacks of photocatalysis (Kurniawan et al., 2006b), the use of solar driven photocatalysis is of recent interest. An example is given in Rocha et al. (2011) where solar energy is used as a source of photons. Rocha et al. (2011) reports a decrease in dissolved organic carbon from 1200 mg/L to 900 mg/L in a leachate sample treated with 2721 µW/cm^2 . Further improvement of the photocatalytic process can be achieved by the addition of O_3 (heterogeneous photocatalytic ozonation) which favors the formation of more radicals compared to the TiO_2 / UV system only (Kurniawan et al., 2006b). The use of solar energy has also been explored with fenton oxidation. Da Costa et al. (2018) investigated the efficiency of solar photo fenton at pH 3, Fe^{2+}/H_2O_2 ratio of 1:5 and 60 minutes treatment time to treat leachate from Brazilian landfills. The COD and UV absorbance at 254 nm were reduced by 78 – 82% and 91 – 96.3% respectively in comparison to 19 – 53% and 17 – 43% respectively for fenton reactions without photo enhancement. This trend was also observed in the studies of Poblete et al. (2017) where a more heterogeneous system with solar/O_3/H_2O_2 exhibited better pollutant removals - 59.7% COD and 34.4% color – than 45% COD and 27.9% color in a solar/O_3 system.

In summary, Table 2.5 presents an overview of the performance of several AOP techniques in terms of COD removal (Kurniawan et al., 2006b).

Table 2.5: Performance of several AOP techniques in terms of COD removal, according to Kurniawan et al. (2006b)

Reactor type	Performance (% COD removal)
O_3	25-85
O_3/H_2O_2	28-50
O_3/UV	63
H_2O_2/UV	56-90
Fenton	52-85

2.1.4.6 Activated carbon adsorption

Technological assessment

Adsorption, a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid through physical and/or chemical interactions, is recognized as a widely employed method (Kurniawan et al., 2006b; Morawe et al., 1995). The popularity of activated carbon as an adsorbent is owed to its highly porous character and large surface area, controllable pore structure, thermostability, low acid/base reactivity, and high removal efficiency for a wide variety of organic and inorganic pollutants dissolved in aqueous media (Abbas et al., 2009). In practice, activated carbon adsorption is often used as a stage in an integrated chemical/physical/biological leachate treatment train. Further, it is often used simultaneously with a biological process and offers a number of advantages, such as enhancing nitrification efficiency, improving sludge dewaterability and removing refractory organic compounds (Aghamohammadi et al., 2007). Non-biodegradable organics, inert COD and color may be reduced to acceptable levels for biologically treated landfill leachate, and the existence of activated carbon is believed to contribute to a synergy effect for providing an attachment surface for bio-regeneration (microorganisms) and serving as a nucleus for the occurrence of floc formation (Cecen et al., 2003). The most commonly used adsorbent is granular activated carbon (GAC) or powder activated carbon (PAC) (Cecen et al., 2003; Mojiri, 2011; Renou et al., 2008). The main drawback of activated carbon adsorption is the need for frequent regeneration of columns or an equivalently high consumption of powdered activated carbon (PAC).

Application to landfill leachate

In most studies for purifying landfill leachate sample, activated carbon adsorption has also revealed the prominence in removal of essential amount of organic compounds and ammonium (Foo and Hameed, 2009). A widely reported case is that from the Goslar landfill in Germany where GAC was used to reduce the influent COD (940 mg/L) by 91% (Foo and Hameed, 2009). In a Greek landfill, PAC at a dosage of 6 g/L was successfully used to reduce the initial concentration of COD (5690 mg/L) by 95% (Kurniawan et al., 2006b). For an equal dose of GAC, Diamadopoulos (1994) managed to reduce the COD of landfill leachate from 1140 mg/L to 270 mg/L.

Li et al. (2010) presented a case study where combined use of 10 g/L PAC and coagulation-flocculation enhanced the removal of COD (from 2817 to 407 mg/L), Fe^{3+} (from 9.6 to 0.03 mg/L) and Pb^{2+} (from 289 to 7μg/L). Kargi and Pamukoglu (2004) investigated that PAC at a dose of 2 g/L improved COD and ammonium removal, resulting in nearly 86% COD and 26% ammonium removal. Kurniawan and Lo (2009) investigated H_2O_2 oxidation in combination with GAC adsorption and found removal efficiencies of 82% for COD and 59% for ammonium. Activated carbon had also successfully been used in the removal of heavy metals from leachate. Kurniawan et al. (2006a, 2006b, 2006c) reports a study where Cd^{2+}, Cu^{2+}, Cr^{3+}, Mn^{2+}, Pb^{2+}, and Zn^{2+} were removed from landfill leachate using a dosage of 2 g/L of GAC. A reduction of approximately 80-96% was achieved at an initial concentration of 84 mg/L. To counter the expensive costs associated with activated carbon, food wastes e.g. sugarcane bagasse, tamarind fruit seed, have been investigated as potential sources of activated carbon. With activated carbon from tamarind seed, Foo et al. (2013) achieved colour and COD reductions of 91 and 80% respectively. According to Shehzad et al. (2015) and the references there in, removal efficiencies ranging from 27 – 83% COD, 39.7 – 94.7% color and 46.7 – 79.6% ammonium can be achieved with activated carbon from food wastes. The differences in performance arises due to differences in leachate characteristics, activated carbon preparation and treatment conditions.

2.1.4.7 Membrane filtration

Technological assessment

A membrane could be defined as a material that creates a thin barrier capable of selectively resisting the movement of different constituents of a fluid and therefore affecting separation of the constituents (Visvanathan et al., 2000). Different membrane filtration techniques: microfiltration (MF) ultrafiltration (UF) nanofiltration (NF) and reverse osmosis (RO) are used in landfill leachate treatment (Abbas et al., 2009).

MF is employed to capture microorganisms, small particles, large molecules, emulsion droplets and large colloidal (Chang et al., 1996). This method is not suitable to be used alone but is recommended to be used as pretreatment process with other membrane processes (i.e. ultrafiltration, nanofiltration or reverse osmosis) or in combination with chemical treatment processes so as to remove suspended matters and colloids (Mojiri et al., 2013). UF is a selective process utilizing pressures up to 10 bar (Mojiri et al., 2013). It could be employed to eliminate the larger molecular weight components of leachate that tend to foul reverse osmosis membranes including organic biodegradable macromolecules and non-biodegradable ones (Rautenbach et al., 1997). Its separation is strongly dependent on the particle size of separated substances and the molecular weight cut-offs (MWCO) of the membrane (Pi et al., 2009). This process might prove to be useful as a pre-treatment method for reverse osmosis. NF has found a place in the removal of recalcitrant organic compounds and heavy metals from landfill leachate because of its unique properties (Calli et al., 2005; Ozturk et al., 2003; Urase et al., 1997). Unlike RO, NF has a looser membrane structure, enabling higher fluxes and lower operating pressure for the treatment of leachate (Trebouet et al., 2001). It has the ability to remove particles with a molecular weight higher than 300 g/mol and inorganic substances through electrostatic interactions between the ions and membranes (Abbas et al., 2009). Additionally, at higher leachate pH, e.g. pH 8, NF is typically negatively charged due to the deprotonation of the carboxylic groups on its surface. Therefore, DOM such as humic compounds which are smaller than the membrane pores but also negatively charged at this pH are rejected (Kurniawan et al., 2006b). For this reason, the high rejection rate for DOM and sulphate ions coupled with low rejection for chloride and sodium ions reduces the volume of concentrate. NF membranes are commonly made of polymeric films which have a molecular cut-off between 200-2000 g/mol (Renou et al., 2008). With high fluxes and the ability to operate over wide temperature and pH range, RO is another membrane filtration technique. With 98 – 99 % rejection for dissolved solids and metals RO can be used for the removal of heavy metals, suspended/colloidal materials and dissolved solids from landfill leachate (Kurniawan et al., 2006b) In spite of its high rejection rates, the drawbacks of RO include membrane fouling and its high-energy consumption (Liu et al., 2017).

Application to landfill leachate

An increasing number of leachate treatment plants have selected reverse osmosis technologies. With a system capacity of 500 m^3/d and a recovery rate of 80%, a two-stage RO system was able to achieve 99.9% removal efficiency for ions such as Ca^{2+}, Ba^{2+} and Mg^{2+} (Sír et al., 2012). A two-stage disc tube membrane was used to reduce the inlet COD and ammonium concentration from 1797 mg/L to less than 15 mg/L and from 366 to 9.8 mg N/L, respectively. The average rejection rates for salts and organic contaminants are about 99% (Peters, 1998). In the same study, the retention of both sodium and chloride was over 99%. Treatment of landfill leachate from a Swedish landfill resulted in a COD and ammonium reduction from 925 to less than 15 mg COD/L and from 280 to 16 mg N/L, respectively. The retention of both COD and ammonium was over 98% (Linde et al., 1995). The removal efficiencies of COD and NH_3-N from young landfill leachate were 96% and 97 %, respectively. 96–98% of COD removal in the leachate at operating pressure of 53 atm was achieved using a pilot-scale reverse osmosis unit (Chianese et al., 1999).

NF was used to reduce total Kjeldahl nitrogen (TKN) in leachate by 22% whereas the iron concentration was reduced by 99% at a cross flow velocity of 3 m/s, a pH of 8.3, and an applied pressure of 2MPa (Trebouet et al., 2001). Ince et al. (2010) reported 44% removal efficiency for TKN. The difference in removal efficiencies could have been due to use of different materials for the membrane as well as different operating conditions and leachate characteristics. A COD removal of 66% was achieved in a hybrid set up which included micro-filtration (Ince et al., 2010). This reduction was achieved when the cross flow velocity was set at 1 m/s, pH of 9.3, and applied pressure of 0.175 MPa.

Microfiltration (MF) and ultrafiltration (UF) membranes have also been used in leachate treatment albeit as a pretreatment step to remove colloids and suspended matter before RO or NF treatment although COD removal of 50% was obtained by using UF process alone (Deng, 2007). Pi et al. (2009) showed that COD of the leachate steadily decreased from 20 g/L to less than 3 g/L, and ammonium decreased from 368 mg/L to 259 mg/L in the UF process. Ameen et al. (2011) reported that MF decreased the turbidity, color, total suspended solids, total dissolved solids and volatile suspended solids in the leachate by 98, 90, 99, 14 and 20%, respectively.

The combination of membrane technologies with biological process also referred to as membrane bioreactors is used as an alternative to conventional biological processes. In a two stage membrane bioreactor with anoxic/oxic steps, the removal of COD and ammonium averaged at 80.6 and 99% respectively (Liu et al., 2017). The ability of an anaerobic membrane bioreactor to degrade UV absorbing compounds in leachate was investigated by Pathak et al. (2018). The two stage system – thermophilic followed by mesophilic steps - was able to reduce total UV absorbing compounds by 50% (Pathak et al., 2018).

2.1.4.8 Ion exchange treatment

Technological assessment

Ion exchange is a reversible process and may be accomplished with ion-exchange media which can be natural or synthetic in nature (Singh et al., 1999). It is a well-known technique for wastewater purification. However, there is little research towards the removal performance on landfill leachate using the technique. Kurniawan et al. (2006a, 2006b, 2006c) and Bashir et al. (2010b) reported ion exchange is not a well-studied method for removal of non-biodegradable organic compounds from landfill leachate and it is typically used as a polishing step for removal of ammonium, nitrate, and metals from leachate (Fernández et al., 2005; Primo et al., 2009). In the removal of nitrogenous nutrients such as ammonium, Unlike biological methods, ion exchange is able to handle high concentrations and abrupt changes in pollutant load with very high removals. There are a few recent studies that investigate ion exchange treatment of landfill leachate.

Application to landfill leachate

The application of ion exchange processes in municipal landfill leachate treatment was recently investigated (Bashir et al., 2011; Bashir et al., 2010a, 2010b). According to Bashir et al. (2011) cationic resin was an effective media for ammonium removal. At the optimum cationic dosage 69% colour, 38% COD and 92% ammonium removal was achieved. Equilibrium removal data for ammonium by cationic resin fitted well with Langmuir and Freundlich linear adsorption isotherms (Bashir et al., 2010a). Boyer et al. (2011) systematically evaluated magnetic ion exchange (MIEX) treatment of stabilized landfill leachate. The reduction in absorbance at 254 nm (57%) and dissolved organic carbon (34%) shows that MIEX-Cl resin is able to remove dissolved organic matter even from landfill leachate and steady-state dissolved organic matter removal of leachate by MIEX-Cl resin was achieved in 20 min, with no change in uptake between 20 min and 2 d of mixing. Singh et al. (1999) carried out a bench-scale study and found that the level of fluoride was reduced from approximately 10 mg/L to less than 1 mg/L. Natural media e.g. zeolites have also been used successfully to treat landfill leachate. From an influent concentration of 2292 mg NH_4^+ - N/L, removals of 17.68 mg NH_4^+ - N/g zeolite at pH 7 were obtained (Martins et al., 2017). Varied efficiency (1.08 – 56.3 mg NH_4^+ - N/g zeolite) of these zeolites to remove ammonium from landfill leachate have been reported (Martins et al., 2017). The high exchange capacities are a result of preconditioning the zeolite with e.g. sodium chloride solution before use.

One of the most significant drawbacks of ion exchange resin utilization in treatment processes is its cost (Grote and Schumacher, 1997). Other limitation is that, prior to ion exchange, appropriate pre-treatment system such as the removal of suspended solids from leachate is required.

2.1.4.9 Electrochemical treatment

Technological assessment

Electrochemical methods e.g. electrochemical oxidation and electrocoagulation are based on anodic and cathodic reduction of impurities present in waste water. The application of the techniques is to the treatment of colored effluent, removal of organic contaminants and for reducing the COD and ammonium concentrations of the effluent. Electrochemical oxidation of organic compounds from leachate is promising method of breaking down pollutants which are resistant to biological degradation (Mandal et al., 2017; Tatsi et al., 2003). Electrochemical methods have been studied in situations where traditional methods have been unable to achieve the satisfactory concentration limits or where they offer economic advantages (Deng and Englehardt, 2006; Ramprasad, 2012). The advantages associated with electrochemical methods include low or no sludge production and chemical reagents required (Dia et al., 2018).

Application to landfill leachate

Several researchers have employed an electrochemical method in reducing the COD, color, ammonium and other xenobiotic organic compounds such as 2-chlorophenol of leachate (Chiang et al., 1995a, 1995b; Panizza et al., 2000; Polcaro et al., 1999). All investigators found efficient removal of contaminant above mentioned in the leachate with the addition of chloride. Chiang et al., (1995a) indicated that the removal of COD was 52 % after 6 hours batch electrochemical oxidation and over 80% for ammonium. Polcaro et al. (1999) reported that electrochemical degradation of 2-chlorophenol was more efficient when chloride of approximately 1000 mg/L was added. During electro-oxidation of leachate, COD reduction efficiency ranges from 70% up to above 90%, and ammonium removal efficiency almost reaches 100% under appropriate conditions (Chiang et al., 2001; Ihara et al., 2004; Leu and Chang, 1999). For instance, electrochemical oxidation of leachate using a boron dipped diamond anode, current density 900 A/m^2 and chloride concentration of 2760 mg/L resulted in complete removal of original COD (3800 mg/L) and ammonium (1710 mg/L) (Mandal et al., 2017). Bashir et al. (2009) also reported COD and color removals of 67.6% and 83.7% respectively during electrochemical oxidation of landfill leachate. The result for removal of organic compounds in electro-oxidation of leachate is superior to those reported in coagulation-flocculation (Amokrane et al., 1997), light-enhanced oxidation (Ince, 1998), combination of UV and O_3/H_2O_2 (Qureshi et al., 2002), fenton process (Lopez et al., 2004) and other physical-chemical processes.

Post-treatment of biologically treated leachate with electrocoagulation using aluminium and iron electrodes, current densities ranging between 8 – 10 mA/cm^2 and treatment time of 20 minutes resulted in 65 – 70% COD and 80% α_{254} removals (Dia et al., 2017). With a low current density of 4.96 mA/cm^2 and longer treatment time of 90 minutes, the study of Li et al. (2011) resulted in minimal COD (50%) and ammonia (39%) removals. Regardless of the long treatment time, such a low current density is not enough to produce sufficient coagulating species.

As a summary for the more traditional processes, an overview of the performances is presented in

Table 2.6. During many years, the traditional processes including conventional biological treatments and classical physical-chemical methods were considered as the appropriate technologies for manipulation and management of high strength effluents like landfill leachates. The landfill operators selected suitable treatment processes (Table 2.6) according to the leachate characteristics. When, treating relatively young leachate, biological techniques can yield a reasonable treatment performance with respect to COD, ammonium and heavy metals. When treating stabilized (less biodegradable) leachate, physical-chemical treatments have been found to be suitable in order to remove refractory organic matter. Although the methods, to some degree, can effectively remove some nitrogen compositions and COD pollutions which can be seen from the Table 2.6, there are still many problems that occur.

For instance, the biological method of nitrification/denitrification is probably the most efficient and cost effective process to eliminate nitrogen from leachate (Sri Shalini and Joseph, 2013). However, biological treatment is hampered by the specific toxic substances (such as PAHs-polyaromatic hydrocarbons, adsorbable organic halogens, PCBs-polychlorinated biphenyls) and/or by the presence of bio-refractory organics (such as humic substances or surfactants). The efficiency of denitrification is reduced due to the limited level of biodegradable organics, in particular in stabilised landfills (Wiszniowski et al., 2006). On the other hand, the disadvantages of activated sludge processes are poor retention of solids, and large area and volume requirements (Visvanathan et al., 2004). Other methods such as reverse osmosis membrane filtration, active carbon adsorption only transfer the pollution from one stream to another and do not solve the environmental problem. Although advanced oxidation processes (AOPs) have been proposed in the recent years as an effective alternative for mineralization or partial degradation of recalcitrant organics in landfill leachate

(Wiszniowski et al., 2006), the investment cost is high.

Taking into account these problems, as well as the strict regulations for leachate discharge, leachate treatment plants are forced to integrate stages. The integrated chemical-physical or chemical-physical-biological processes (whatever the order) ameliorates the drawbacks of individual processes contributing to a higher efficacy of the overall treatment. This synergy created by combining different techniques forms an important part of this PhD thesis.

Table 2.6: Summary of performances of different traditional treatment techniques for landfill leachate treatment, according to Renou et al.(2008)

Process	**Average removal (%)**				
	BOD	**COD**	**Kjeldahl Nitrogen**	**Suspended Solids**	**Turbidity**
Coagulation-flocculation	–	40–60	<30		
Chemical precipitation	–	<30	<30		
Stripping	–	<30	>80	–	30–40
Aerobic biological treatment	>80	60–90	>80	60–80	–
Anaerobic biological treatment	>80	60–80	>80	60–80	–
Ultrafiltration	–	50	60–80	>99	>99
Nanofiltration	80	60–80	60–80	>99	>99
Reversed osmosis	>90	>90	>90	>99	>99

2.1.5 Combined Leachate Treatment Systems

The combination of two or more treatments proves to be more efficient and effective than individual treatment. This could be due to the fact that a two-step or three-step treatment has the ability to synergize the advantages of individual treatments, while overcoming their respective limitations. In the following, an overview of possible combinations is presented.

2.1.5.1 Physical-chemical leachate treatment

Physical-chemical treatment processes for young landfills leachate are not as effective as biological processes, whereas they are extremely efficient for stabilized leachate. The combination of treatment systems has been found to be suitable for the removal of refractory substances from stabilized leachate (Visvanathan et al., 2004). Not only that, but they are also as a refining step for biologically treated leachate. Prior to discharge, an additional effluent refining using physical-chemical treatment can be carried out on-site. The combined physical-chemical processes have been widely employed in landfill leachate treatment plants for COD removal. Table 2.7 lists treatment performance of some combined physicochemical leachate treatments reported in the literature.

Laboratory-scale experiments were conducted to study the combined performance of ammonium stripping and granular activated carbon (GAC) adsorption for the treatment of landfill leachate. The removal of COD and ammonium after ammonium stripping alone and its combination with GAC adsorption treatment was evaluated and compared, respectively. The combination of ammonium stripping and GAC adsorption using ozone-modified GAC demonstrated almost complete removal of COD (99.6%) and ammonium (99.9%) with an initial COD concentration of 30010 mg/L and ammonium concentration of 2.5 mg/L, compared to ammonium stripping alone (COD: 16%; ammonium: 97%) at the same initial concentrations with the following conditions: pH 11, 60 mL/min of flow rate and a temperature of 28°C. With the COD level of treated effluent at less than 200 mg/L, the results indicate that the combination of ammonium stripping and GAC adsorption was more effective than ammonium stripping alone for the removal of recalcitrant compounds from stabilized leachate. The application of the integrated process for leachate treatment was able to meet a stringent ammonium discharge standard of less than 5 mg/L, indicating that no further treatments would be required (Kurniawan et al., 2006a).

Another study of the treatment of mature leachate was conducted via air stripping followed by coagulation/ultrafiltration (UF) (Kewu and Wenqi, 2008). It was seen that the air stripping could obtain a removal efficiency of 89 % for ammonium. When the effluent of the air stripping process was treated by the single coagulation-flocculation process, the BOD_5/COD ratio increased from 0.049 to 0.138 with a $FeCl_3$ dosage of 570 mg/L, at pH 7.0,. A single UF process increased the BOD_5/COD ratio from 0.049 to 0.311. However, the combination of coagulation-flocculation and UF was found to increase the BOD_5/COD ratio from 0.049 to 0.423, and the final COD, BOD_5, ammonium and colour of the leachate were reduced from 18725 mg/L, 926 mg/L, 1868 mg/L and 12235 to 1023 mg/L, 2845 mg/L, 145 mg/L and 2056 mg/L respectively.

Table 2.7: Treatment performance of some combined physical-chemical treatment processes,

Type of combined treatment	**Leachate Age**	**Influent COD (mg/L)**	**% COD removal**	**Reference**
coagulation-flocculation + fenton	Old	417	73	Kurniawan et al. (2006d)
NF + coagulation-flocculation	Old	2150	80	Kurniawan et al. (2006b)
NF + PAC Adsorption	Old	1450	97	Kurniawan et al. (2006b)
ozone+GAC adsorption	Old	4970	90	Kurniawan et al. (2006d)
Coagulation-flocculation + ozonation	Old	3460	48	Kurniawan et al. (2006d)
NF + RO	synthetic landfill leachate	330	55	(Vogel et al., 2006)
Electrocoagulation + nanofiltration	Old	635.8	92	Mariam and Nghiem (2010)
Coagulation-flocculation + fenton	Old	5700	89	Amor et al. (2014)
Coagulation-flocculation + solar photo- fenton	Old	2400 (DOC)	75 (DOC)	Amor et al. (2014)
AC + solar/O_3/H_2O_2	NA	6660	70.8	Poblete et al. (2017)
AC + solar/O_3	NA	6660	59.1	Poblete et al. (2017)
AC + US + O_3	NA	6660	48.6	Poblete et al. (2017)
AC + US + O_3/H_2O_2	NA	6660	67	Poblete et al. (2017)

The overall performances for combined pretreatment of landfill leachate by air stripping for ammonium removal followed by coagulation–flocculation were recently evaluated (Abood et al., 2013). In these experiments the initial COD concentration was 2600-5500 mg/L, the initial ammonium concentration was 2200-3100 mg/L and the initial BOD concentration was 420 - 300 mg/L. The removal of COD, ammonium and BOD improved from 31%, 94% and 40%, respectively using ammonium stripping alone to 71%, 96% and 57% by using the combined treatments. The corresponding BOD_5/COD ratio was changed from 0.20 to 0.31. The results suggest that the coagulation-flocculation step enhanced ammonium stripping for the removal of organic compounds and NH_3-N from the leachate as well as increasing the biodegradability of landfill leachate.

An old landfill leachate was pre-treated in a pilot-scale aerated packed tower operated in batch mode for total ammonium nitrogen (TAN) removal. The stripped ammonia was recovered with a 0.4 mol/L H_2SO_4 solution, deionized water and tap water. $Ca(OH)_2$ (95% purity) or commercial hydrated lime was added to the raw leachate to adjust its pH to 11, causing removal of colour (82%) and heavy metals (70–90% for Zn, Fe and Mn). The 0.4 mol/L H_2SO_4 solution was able to neutralize 80% of the stripped ammonia removed from 12 L of leachate. The effectiveness of the neutralization of ammonia with deionized water was 75%. Treating 100 L of leachate, the air stripping tower removed 88% of TAN after 72 h of aeration, and 87% of the stripped ammonia was recovered in two 31 L pilot-scale absorption units filled with 20 L of tap water (Ferraz et al., 2013).

2.1.5.2 Combined physicochemical-biological leachate treatment

Numerous research studies on the leachate treatment using different types of combined physical-chemical and biological treatments have been performed (Goi et al., 2010; Tabrizi and Mehrvar, 2004; Umar et al., 2010). Table 2.8 shows the treatment performance of some combinations between physical-chemical and biological treatments reported in the literature.

Biological pretreatment are often applied as RO pretreatment (Baumgarten and Seyfried, 1996; Jans et al., 1992) for a better quality permeate from the RO unit and prolonged the life span of the RO unit by reducing fouling effects and treatment costs. On the contrary, lime coagulation appears a promising option for the pretreatment of biological techniques and the removal of colloidal particles and organic macromolecules. It is likewise possible to reduce the non-biodegradable organic matter that remains after biological treatment by adsorption with activated carbon (Kargi and Pamukoglu, 2004).

Table 2.8: Treatment performance of some combined physical-chemical and biological treatments

Type of combined treatment	**Initial concentration in leachate (mg/L)**		**Removal efficiency (%)**		**Reference**
	COD	**NH_3-N**	**COD**	**NH_3-N**	
UASB +RO	35000	1600	99	99	Jans et al. (1992)
Activated sludge + RO	1153	6440	99	99	Baumgarten and Seyfried (1996)
GAC + Nitrification	2450	830	55	93	Horan et al. (1997)
Repeated fed batch biological treatment + PAC	7000	700	94	30	Kargi and Pamukoglu (2004)
Lime coagulation + UASB	11247	598	80	2.5	Castrillón et al. (2010)
SBR + PFS coagulation + fenton + UBAF	3000	1100	97.3	99	Li et al. (2009)
Electrocoagulation + aerated biofiltration	1619	653 (NH_4^+-N)	63	99	Dia et al. (2018)
SBR + coagulation-flocculation	4975	1181	84.9	94	Yong et al., (2018)

PFS: polyferric sulfate
UBAF: upflow biological aerated filter
UASB: upfow anaerobic sludge blanket
RO: reverse osmosis
PAC: powdered activated carbon
SBR: sequential batch reactor

2.1.5.3 AOP-biological leachate treatment

AOPs' high oxidative capability and efficiency make it a popular technique in tertiary treatment in which the most recalcitrant organic and inorganic contaminants are to be eliminated. The increasing interest in water reuse and more stringent regulations regarding water pollution are currently accelerating the implementation and use of the combination of AOPs and biological processes. The use of AOP processes enhances the removal/conversion of recalcitrant contaminants (such as pharmaceuticals, pesticides and new emerging organic micropollutants) in the leachate into smaller and consequently more biodegradable intermediates.

Di Iaconi et al. (2006) reports the results of a laboratory scale investigation aimed at evaluating the effectiveness of mature municipal landfill leachate treatment by a biological stage, carried out in a biofilter with granular biomass (SBBGR), followed by a chemical oxidation step, performed using ozone or fenton, for further COD removal. The results show that the biological treatment was able to remove roughly 80% of COD in the leachate at an organic loading of about 1.1 kg COD/m^3.day. Ammonium removal efficiency was more than 20% because of the presence of high salinity and inhibitory compounds. When the leachate was pre-treated in order to reduce considerably the ammonium content, it was possible to reach organic loadings as high as 4.5 kg COD/m^3.day with a decrease in COD removal of only 10%. The biological treatment was characterized by a negligible sludge production. Ozone and fenton reagent were used to reduce the remaining COD content presumably made up of recalcitrant compounds. The treatment with ozone was able to remove only 33% of residual COD whereas using fenton reagents an 85% removal efficiency of COD was achieved.

Treatment with fenton process improved biodegradability from 0.3 to 0.65 and reduced toxicity by 50% which favored biological post treatment (Sivan and Latha, 2013). Fenton process was an efficient chemical pretreatment prior to anaerobic process. Anaerobic post treatment of fenton treated leachate at HRT 13 days and pH 7 further removed 90%, 98%, 28%, 70%, 40% and 78% COD, BOD, turbidity, nitrate, sulphate and TSS respectively. Combined chemical-biological process reduced COD, BOD, turbidity, nitrate, sulphate and TSS to levels 189 mg/L, 24 mg/L, 11 NTU, 48 mg/L, 170 mg/L and 68 mg/L respectively. In order to overcome the disadvantages of fenton process e.g. iron sludge production, electro- fenton has been adopted. Baiju et al. (2018) used electro- fenton in combination with biological processes to reduce the COD of leachate from 7184 mg/L to 192 mg/L achieving a removal efficiency of 97%. In comparison, with biological treatment only, 17% COD removal could be achieved. In this set-up, the electro- fenton step was used to convert recalcitrant compounds into more biodegradable components hence increase in biodegradability as shown by the improvement in BOD_5/COD ratio - 0.03 to 0.4. This study, gives a good example as to why this PhD thesis will consider the utilization of ozonated leachate in a prior biological step.

Anfruns et al. (2013) evaluated the suitability to couple the anammox process with advanced oxidation processes (AOPs) to treat mature landfill leachate with high nitrogen and non-biodegradable organic matter concentrations (2309±96 mg/N–TN and 6200±566 mg COD/L). The combination of a partial nitration-anammox system coupled with two AOP-based technologies (coagulation-flocculation and ozonation or photo- fenton) was assessed in terms of nitrogen and carbon removal. Total nitrogen removal efficiency within a range of 87–89% was obtained with both configurations without the need of any external carbon source. The COD removal efficiencies attained were 91% with coagulation-flocculation + ozonation and 98% with photo- fenton. The combination of partial nitritation-anammox system with photo- fenton treatment was more favorable than with coagulation-flocculation + ozonation treatment.

Applying the biological treatment prior or posterior to advanced oxidation processes-based technologies could give higher removal efficiencies. From a basic economical point of view and taking into account the results of the studies, the combination of biological treatment systems with AOP treatment was more favorable than other combinations. Table 2.9 shows the performance of integrated AOP and biological treatments in some countries.

Table 2.9: Integrated AOP and biological treatments, according to (Ai et al., 2017; Klauson et al., 2015; VanHullebusch and Oturan, 2011)

Location of Landfill	**Type of combined treatment**	**Coagulant/ Adsorbent/ Oxidant**	**Dose (g/L)**	**Ozone efficiency (mg O_3/mg COD)**	**Initial concentration in leachate (mg/L)**		**BOD/COD**	**Removal efficiency (%)**	
					COD	ammonium		COD	ammonium
Taiwan	coagulation-flocculation + Electro- fenton +SBR	$Fe(II)SO_4/H_2O_2$	0.75	-	1941	151	0.3	95	81
Hong Kong	UASB+Ozonation	O_3	0.05	16	15700	2260	0.06	93	NA
Hong Kong	UASB+Ozonation + fenton oxidation	O_3 ;$Fe(II)SO_4/H_2O_2$	0.05/0.3/0.2	25	15700	2260	0.06	99	NA
Kimpo (Korea)	fenton oxidation +Activated sludge	$Fe(II)SO_4/H_2O_2$	0.9/0.9	NA	7000	1800	0.15	98	89
Germany	Photochemical + Activated sludge	UV/H_2O_2	1 4	-	920	NA	0.005	89	NA
Fossalta (Italia)	Wet oxidation + Activated sludge	-	-	-	4140	998	0.46	NA	NA
Flanders (Belgium)	Ozone +activated sludge;	O_3;	2.8	3.7;	895	626	0.05	81	NA
	Ozone +activated sludge	O_3	0.05	2.0	2800	250	0.54	97	
Finland	Ozone +activated sludge	O_3	5.00	0.3	560	NA	0.06	95	NA
Teuftal (Switzerland)	Ozone +Nitrification	O_3	0.03	NA	1500	600	0.23	98	NA

Table 2.9 cont.

Location of Landfill	Type of combined treatment	Coagulant/ Adsorbent/ Oxidant	Dose (g/L)	Ozone efficiency (mg O_3 /mg COD)	Initial concentration in leachate (mg/L)		BOD /COD	Removal efficiency (%)	
					COD	ammonium		COD	ammonium
NA	Activated sludge + fenton	$Fe(II)SO_4/H_2O_2$	1/4/0.8(COD/ H_2O_2/Fe^{2+})	-	15700	840	0.69	94	56
NA	Activated sludge + fenton + activated sludge	$Fe(II)SO_4/H_2O_2$	1/4/0.8(COD/ H_2O_2/Fe^{2+})	-	6790	840	0.69	96	-
China	SBR + electro-fenton	$H_2O_2/Fe(II)SO_4$	12:1	-	2080	2875	NA	96.3	

NA: Not available

2.2 Conclusions

This comprehensive review discusses the merits that each technology possesses, promising features and potential problems. With the continuous hardening of the discharge standards in most countries and the ageing of landfill sites with more and more stabilized leachates that often need high investment cost to treat, any individual treatment process is not sufficient anymore to reach the level of purification needed to fully reduce the negative impact of landfill leachates on the environment. A combined treatment is indeed capable of improving the effluent quality and minimizing the residue generated at a lower treatment cost than an individual treatment.

The future research strategies for landfill leachate treatment could focus on the following points. (1) Every individual physical-chemical or biological systems should be optimized. (2) A selected treatment sequence to treat leachate of a particular age should offer the flexibility in adopting other unit operations or replacing some unit operations in favor of newer technologies. It is an important and necessary criteria in developing a treatment scheme for high organic, high ammonium leachate and leachate with variable characteristics at different time period. This should also be economically and technological feasible with a long-term sustainability. (3) A treatment train should be designed to be capable of coping with the changing leachate characteristics, possibly involving the use of primary (e.g. coagulation-flocculation), secondary (e.g. GAC), and tertiary (e.g. ion exchange)processes, for instance, explore the option of coupling different physical-chemical techniques to treat landfill leachate. (4) Due to the advantages provided by AOPs e.g. breakdown of recalcitrant compounds hence improved leachate biodegradability; special effort should be invested to the combination of AOPs such as ozonation with a biological process. Ozonation has the potential to improve the biodegradability of leachate which in turn can be used as a carbon source in the previous biological step. Their merits can then be compared with those of other conventional techniques such as coagulation-flocculation.

Chapter 3

Experimental set-ups and methods

3.1 Landfill leachate samples

Two specific types of landfill leachate were used in this work. First, biologically treated leachate was collected from the Intergemeentelijke Maatschappij voor Openbare Gezondheid (IMOG) municipal landfill treatment facility in Moen (Belgium) (Figure 3.1). IMOG is an inter-municipal co-operation that is responsible for the collection and safe disposal of waste in 11 municipalities in West-Flanders. IMOG runs four landfills which produce a total of 150 m^3 of leachate per day.

Figure 3.1: Birds eye view on the IMOG landfilling facility.

The produced leachate is treated on-site using both physical and biological techniques (Figure 3.2). Briefly, the leachate is first taken through a sedimentation and filtration unit to remove heavy material and suspended matter by gravity, after which any oily substances are skimmed off. The leachate is then loaded into two identical sequencing batch reactors (SBR) where the nitrification-denitrification process takes place. Here, methanol is added to satisfy the carbon requirements of the denitrification step. The biologically treated effluent subsequently flows over a floating macrophytic bed where suspended material from the biological treatment step is trapped by the plants. The leachate then flows over a stone/grind filter where iron is removed through the formation of iron hydroxide, after which it is sent through a fixed macrophytic bed for further polishing before it is finally passed through an activated carbon column where highly recalcitrant and persistent compounds are adsorbed in order to meet the Flemish environmental discharge limits specifically intended for IMOG.

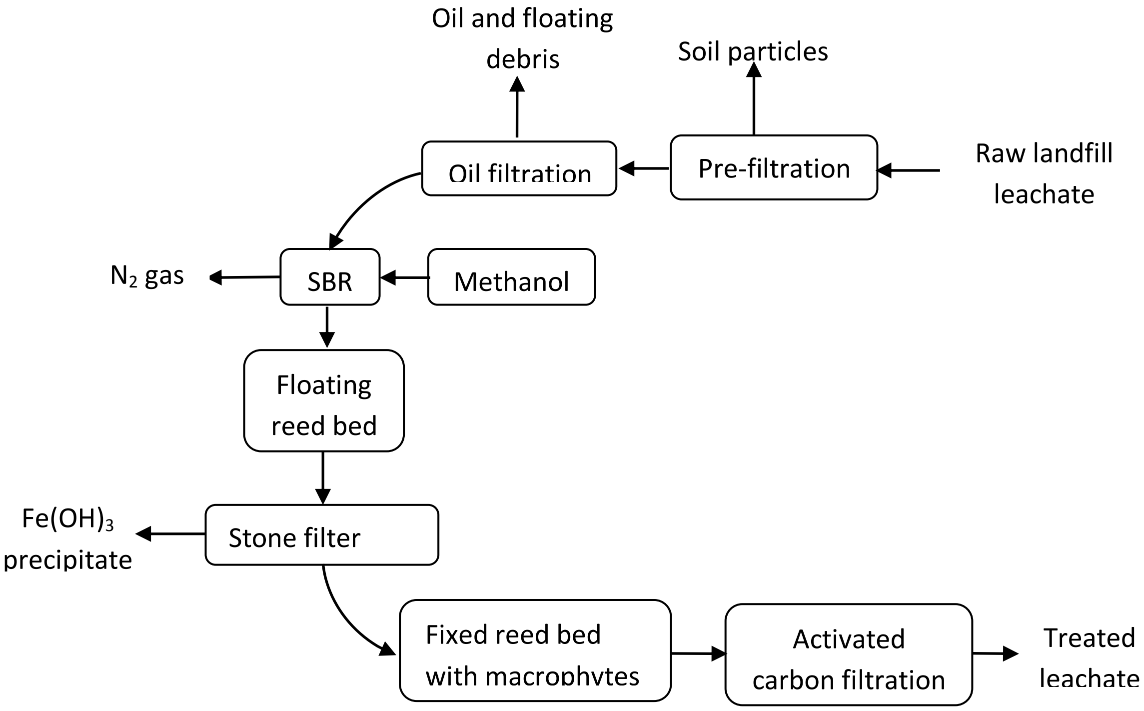


Figure 3. 2: Flow diagram of the landfill leachate treatment plant at IMOG

Second, raw landfill leachate was collected from the Vanheede landfilling facility in Roeselare (Belgium). This landfilling company accepts category two (domestic, non-hazardous, non-toxic industrial waste) and three (inert waste) wastes (Group Vanheede Environment, 2017), and does not have any on-site leachate treatment. As such, the produced leachate is stored in a tank and transported daily to an off-site treatment facility.

Both raw untreated leachate (Vanheede) and biologically treated leachate (IMOG) samples were collected in 20 L plastic containers previously washed and rinsed with distilled water. Samples from IMOG were collected in three periods between October 2012 – May 2013, September 2013 - January 2014 and October 2016 – January 2017. Leachate from Vanheede landfill was collected in the period between October 2014 – January 2015. The leachate samples were then immediately transported to the lab where they were stored at 4°C and analyzed within 24 hours. Measured values for the main leachate characteristics are listed in Table 3.1. Age of the landfills and type of wastes that were received by the two landfilling facilities are also indicated in Table 3.1.

Table 3.1: Physical-chemical characteristics of biologically treated and raw landfill leachates

Parameter	**Raw landfill leachate (IMOG)**	**Biologically treated leachate (IMOG)**	**Raw leachate (Vanheede)**
Age (years)	>10	Not applicable	>10
pH	7.8 – 8.2	8.0 – 9.1	7.7 – 8.1
COD (mg/L)	548.5 – 1826	315 – 1846	2365 – 4240
BOD_5 (mg/L)	94.3 – 281.9	20 – 50	38 – 45
BOD_5/COD	0.05 – 0.05	0.027 – 0.28	0.010 – 0.013
α_{254} (1/cm)	NA	2.92 - 8.5	14.5 - 20.2
NO_3^--N (mg/L)	3.5 – 17.2	3.9 – 19.5	12.1 – 16.3
NO_2^--N (mg/L)	0 – 65.6	0.3 – 0.7	NA
NH_4^+-N (mg/L)	244 – 627	2.4 – 9.2	1060 – 1950
Ni (mg/L)	0.094[a]	NA	2.1 – 4.3
Conductivity (mS/cm)	5.6 - 9.4	6.6 – 8.29	16.5 – 18.7
Wastes received by the landfills	Mixed wastes, incinerator ash, non-combustible materials	Not applicable	Domestic, inert and non hazardous industrial waste

[a] value from Dewandel et al. (2016)
NA: not available

Based on the age of the leachates, both leachates can be considered old. This is further supported by the pH which is above 7.5, the high ammonium concentration and the low biodegradability (Kjeldsen et al., 2002). The low biodegradability of both raw leachates show that they contain a lot of recalcitrant materials. The COD of IMOG leachate is lower than that from Vanheede, an indication that there could be more high molecular weight compounds in Vanheede than IMOG leachate. The nickel concentrations also vary between the two leachates with Vanheede having the highest concentration. The presence of heavy metals in landfills is as a result of the waste disposed therein. Looking at the waste received (industrial waste at Vanheede and mixed waste at IMOG Table 3.1) by the two landfilling facilities, leachate from Vanheede is more likely to have higher concentrations of nickel.

The physical-chemical processes taking place in the landfill can offer some explanation in the low concentration of nickel in the leachates. As the landfill ages, the concentration of heavy metals in the landfill leachate decreases due to mechanisms such as sorption and precipitation in the landfill. Waste disposed in the landfill contains soil and organic matter which have the ability to adsorb heavy metals. According to Bradl (2004), one of the most important parameters which determines the distribution of heavy metals between soil and water is pH. At pH above neutral, which is the pH of leachate from old landfills, soil has a very high sorptive capacity hence more heavy metals will be found in the soil as opposed to the landfill leachate. According to Christensen et al. (2001), sorption is an important attenuation process for heavy metals such as cadmium, copper, lead, nickel. At this point, it’s also important to note that one of the landfills at IMOG is a clay pit and clay has a very high sorption capacity.

The availability of heavy metals in landfill leachate is also governed by the formation of carbonates and sulphides. The sulphides and carbonates of heavy metals such as cadmium, copper, lead, nickel are insoluble in water. Precipitation reactions such as formation of hydroxides are also important in the reduction of chromium concentrations in old landfill leachate.

3.2 Treatment techniques

This section summarizes, for each of the investigated techniques, the experimental set-up and main conditions applied during the (post)-treatment of raw and biologically treated landfill leachate.

3.2.1 Ozonation

The ozonation of biologically treated leachate was performed using a lab-scale batch reactor (Figure 3.3) described by Audenaert et al. (2013) and Chys et al. (2015)

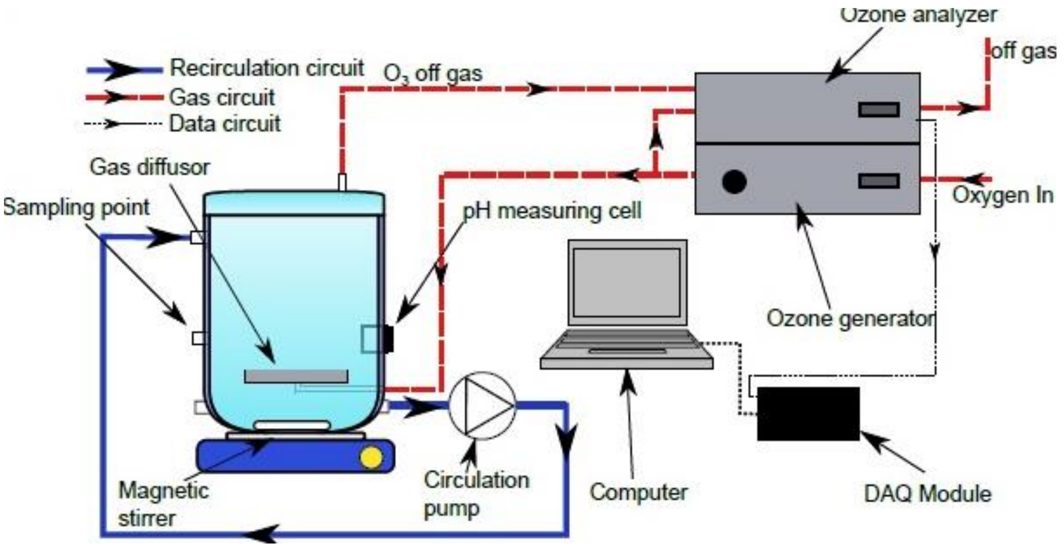


Figure 3.3: Lab-scale set up for the ozonation of biologically treated landfill leachate.

Ozone gas was generated by passing pure and dry oxygen gas through an Anseros COM AD-01-02 ozone generator. The generated ozone stream was bubbled for 60 minutes through 10 L of biologically treated leachate at a steady flow rate of 1 L/min and with an average ozone inlet concentration of 90.4 mg/L. This treatment time was chosen following preliminary studies discussed in Chapter 4, Section 4.3.1. All experiments were conducted at room temperature. The gaseous ozone concentration both at the inlet and outlet of the ozone reactor were monitored by means of an GM-OEM (Anseros) analyzer, and logged every second using a Cole-Parmer DAQ module (model No. FN-18200-00). This allowed mass balance calculations according to equation 3.1 to determine the transferred ozone dose.

$$TOD = {}^{Q_g}\!/_{V_L} \cdot \int_0^t \left(C_{g,i} - C_{g,o}\right) dt \qquad equation\ 3.1$$

with TOD (mg O_3/L) the transferred ozone dose per liter of treated leachate, calculated by integrating the difference between the constant inlet concentration ($C_{g,i}$) and the outlet concentration ($C_{g,o}$) during the applied time interval. Q_g (L /min) is the applied gas flow rate, and V_L (L) is the volume of leachate in the reactor. Samples were taken regularly to measure changes in the physical-chemical characteristics of the leachate samples according to the objectives of the experiment.

The efficiency at which the transferred ozone is used, e.g. for COD removal, could be calculated using equation 3.2.

$$Ozonation\ efficiency = {(COD_O - COD_t)}\Big/{(TOD - C_d)} \qquad equation\ 3.2$$

The change in COD content of the leachate is presented as the difference between the COD concentration at the beginning of the experiment and after a certain ozonation time (respectively COD_O and COD_t). C_d (mg O_3/L) is the dissolved ozone concentration, so that (TOD – C_d) is the ozone consumption due to reactions with leachate compounds, as well as through self-decomposition. As such, the ozonation efficiency is expressed as mg COD removed per mg O_3 consumed. Similar calculations can be done based on UV absorbance, leading to the ozonation efficiency defined as the decrease in absorption coefficient (cm^{-1}) per mg O_3 consumed.

3.2.2 Coagulation-flocculation

Coagulation-flocculation with ferric chloride ($FeCl_3$) and polyaluminium chloride (PACl) was carried out in a jar test apparatus. In a typical run, $FeCl_3$ and PACl were added at various doses (specified in the different experiments) to 500 mL of raw or biologically treated leachate, while stirring at 200 rpm for 1 min. The fast stirring was followed by slow stirring (40 rpm) for 20 min to facilitate floc formation. Finally, the sample was left to settle for 30 min. After the settling period, the supernatant was withdrawn by decantation for physical-chemical (i.e. COD, UV-VIS absorbance, nickel and ammonium content) and fluorescence analyses, depending on the objectives of the experiment and the type of leachate sample used. The coagulation-flocculation experiments were carried out at room temperature and without prior adjustment of the leachate pH. The settling ability of produced sludge was quantified using sludge volume index (SVI) (Clesceri et al., 1999).

3.2.3 Granular activated carbon adsorption

The adsorption experiments were conducted in a glass column with an internal diameter of 2.54 cm. To yield a bed height of 50 cm, 135 g of GAC (Organosorb 10® from Desotec, Belgium, with a mean particle diameter of 1.1 mm) previously washed and moistened with demineralised water was placed into the column. Pebbles were packed at the bottom to prevent wash out of the adsorbent. Leachate (raw, biologically treated, coagulated or ozonated samples) were passed through the column in a downward flow mode, at a flow rate of 9 mL/min resulting into an empty bed contact time of 30 min. The samples were collected at the column exit at different time intervals and analyzed for physical-chemical parameters (COD, UV-VIS absorbance, total nitrogen, nickel and ammonium content) and fluorescence excitation emission. To calculate the experimental adsorption capacity of the column q_{exp} (mg adsorbed/g GAC), the area (A) under the breakthrough curve obtained by plotting the adsorbed concentration C_{ads} (mg/L) against time (t) was integrated using equation 3.3 (Foo et al., 2013a).

$$q_{exp} = \frac{Q}{W}\int_{t=0}^{t} C_{ads}\,dt \qquad \textit{equation } 3.3$$

where Q is the volumetric flow rate (9 mL/min), W is the mass of the activated carbon (135 g), and t is the flow time (min).

3.2.4 Ion exchange

As an alternative for biological treatment, ion exchange was studied to capture ammonium from raw leachate, pre-treated with coagulation-flocculation + GAC or with GAC only. The strongly acidic commercial cation exchange resin Lewatit monoplus S108 (Lanxess, Belgium) was primarily used. Before use, 180 g of resin was preconditioned by washing and soaking overnight in demineralized water. The resin was then packed into a Pyrex column with an internal diameter of 2.54 cm. A layer of pebbles was packed at the bottom of the column to prevent resin wash out. The GAC effluent, still at a flow rate of 9 mL/min, was passed through the ion exchange column in a downward mode. Effluent from the ion exchange column was taken at regular intervals to primarily analyze ammonium, COD, UV-VIS absorbance, nickel and fluorescence excitation emission.

The used cation exchange resin was then regenerated with 2.74 M HCl solution, in order to elute the captured ammonium nitrogen. Regeneration was done in the downward mode at the same flow rate (9 mL/min) than that used during treatment, and was stopped after 3.2 BV. The concentration of ammonium in the regenerating solution was measured to determine the percentage of ion exchange regeneration.

3.2.5 Autotrophic nitrogen removal (ANR)

Though the focus of this work was on organic matter removal, one of the methods (ozonation) led to an increase in biodegradability. As such, it was of interest to study how the ozonated effluent affected biological steps. This was done by ozonating leachate which had been treated using autotrophic nitrogen removal processes. The ozonated effluent was then recirculated to the ANR step for further studies. Here, a brief description of the ANR set up is given. Details can be found in Gao et al. (2015a).

A cylindrical ANR reactor (internal diameter 12.7 cm) was packed with polyurethane foam (Recticel, Belgium) to hold biomass. Use of such a carrier is advantageous in a lab-set up as it provides a larger surface area for growth of micro-organisms and minimizes wash out of the important biomass in case of increased flows. However, at full scale level, suspended systems are used because they have a large surface area available for the proliferation of the micro-organisms. The reactor was filled with 2 L of activated nitrifying and denitrifying sludge from the IMOG landfill leachate treatment plant, and operated with real (undiluted) landfill leachate wastewater. During the course of operation, feeding of raw leachate only and raw leachate mixed with ozonated effluent was done semi-continuously, with a feeding phase of 6.5 min followed by a phase of 8.5 min without feeding. Each day, 3 L of influent was fed to the reactor resulting in a hydraulic residence time (HRT) of 2 days during the start-up period. The temperature was maintained at 35±1 °C (thermostatic bath, D-7633, Julabo Labotechnik GmbH, Germany), and the dissolved oxygen (DO) concentration was controlled automatically at 0.30–0.70 mg O_2/L during the start-up period using a labview PLC system and a Hach Lange LDO sensor.

3.3 Analytical methods

It is important to note that not all physical-chemical and fluorescence analyses were done on all collected leachate samples in this study. Particular analyses were performed depending on the specific objectives to be achieved and the type of leachate being used. These are explicitly mentioned in the respective chapters.

The COD of the leachate samples before and after treatment was determined using the colorimetric closed reflux method as described by Clesceri et al. (1999). The dissolved oxygen concentration used to calculate the BOD_5 of the raw (Vanheede) and biologically treated leachate (IMOG) was measured using an ISM Mettler Toledo digital sensor probe, according to the standard method (Clesceri et al., 1999). Analyses of ammonium, nitrate, and nitrite concentrations in raw and biologically treated leachate and nickel concentrations in raw leachate only were done with Hach Lange cuvettes (LCK 303, LCK 304, LCK 339, LCK 342, LCW 902 and LCK 337) and a DR2800 spectrophotometer according to the procedures outlined in the Hach Lange kits. Leachate pH was measured using a Hach HQ 40d multimeter and pH-electrode (Consort, type C830). The same type of multimeter was used for electrical conductivity (EC) measurements, whereas the turbidity was measured using a HI 98703 turbidity meter. UV-VIS absorbance between 200 – 800 nm was recorded using a Shimadzu 1600 spectrophotometer equipped with 1 cm quartz cuvettes. The absorbance at 254 nm was specifically used to evaluate the efficiency of the treatment techniques, because it is an indicator of compounds containing carbon to carbon double bonds and aromatic rings, which are ubiquitously present in landfill leachate. The absorbance at 436 nm was used as a reference for colour. Results based on absorbance measurements at 254 and 436 nm are further described using the absorption coefficient at 254 nm (α_{254}) and 436 nm (α_{436}). The above water quality parameters were done in duplicate. Fluorescence EEM analysis was carried out on diluted leachate samples (at least 10 – 200 times, to lower the fluorescence intensity and minimize inner-filtering effects) using a RF-5301 PC Shimadzu spectrofluorometer. Organic matter fluorescence in leachate was generated by scanning excitation wavelengths between 220 and 450 nm in 5 nm increments. Emitted fluorescence was detected at wavelengths between 280 and 600 nm at 1 nm intervals. A fluorescence spectrum of pure distilled water was recorded as a blank, and subtracted from the sample EEMs. Water Raman scans were generated at Excitation/Emission (Ex/Em) wavelengths of 350/365-450 nm. Integration of the area under the Raman signal allowed normalization of fluorescence intensities of EEMs to Raman units (R.U), giving the advantage that normalized data can be quantitatively reproduced by another spectrofluorometer (Nieke et al., 1997). For correcting the inner filter effects, the absorbance of the leachate samples was measured using a Shimadzu 1600 UV-VIS spectrophotometer at 200 – 800 nm. Samples diluted with distilled water were mixed thoroughly to ensure homogeneity.

The SVI of the samples treated by coagulation-flocculation was calculated as a ratio between the 30 minutes settled sludge volume and amount of sludge formed (Clesceri et al., 1999). To obtain the settled sludge volume after 30 minutes (SSV_{30}), 50 mL of the remaining sludge was settled for 30 minutes in a cylindrical flask after which the volume of wet sludge at the bottom was determined (Jamali et al., 2009). The total amount of formed sludge was calculated after drying a 50 mL aliquot at 105°C (Clesceri et al., 1999).

PART II: Biologically treated landfill leachate

Chapter 4

Ozonation of Biologically Treated Landfill Leachate: Efficiency and Insights in Organic Conversions

Redrafted after:

Michael Chys, Violet A. Oloibiri, Wim T.M. Audenaert, Kristof Demeestere, Stijn W.H. Van Hulle (2016) Ozonation of biologically treated landfill leachate: ozone efficiency and insights on organic conversions. Chemical Engineering Journal, 277, 104-111.

Contribution of Violet Oloibiri: performing the experiments and writing part of the manuscript that has been included in this PhD

Abstract

Biologically stabilized landfill leachate contains a significant amount of recalcitrant organic matter, often expressed as chemical oxygen demand (COD). To meet regulatory requirements, (a combination of) advanced treatment techniques such as ozonation. However, the mechanisms occurring during ozonation of the complex matrix are not well understood. Therefore, transformations were studied (in a lab-scale semi-batch reactor) into detail based on COD measurements and UV-visible spectral calculations. First of all, a declining initial COD (COD_0 from 1846 to 112 mg/L) resulted in a decreasing trend of α_{254} removal efficiency (respectively from 0.015 to 0.0042 cm^{-1} absorption decrease/mg O_3) which was not seen for COD removal efficiency (no clear trend noticeable; average of 0.34 mg COD removed/mg O_3). For low COD_o, the amount of most reactive moieties is less, resulting to further reactions with the formed intermediates. A more alkaline pH resulted in a higher production of hydroxyl radicals ($HO^{\bullet}$). Hence more COD was removed at higher pH values.

4.1 Introduction

Due to both low investment and exploitation costs, landfilling of waste is historically widely employed (Renou et al., 2008). Nowadays, landfilling is mostly replaced by alternatives but currently existing landfills still pose a serious environmental burden because of the generation of leachates. These leachates have a distinctive character and contain a high concentration of (recalcitrant) organic compounds (e.g. amines, alcohols, aliphatic compounds, carboxylic acids), often expressed as Chemical Oxygen Demand (COD) (Kjeldsen et al., 2002). Biological processes such as conventional activated sludge (CAS) processes are commonly employed for leachate treatment but are seriously hampered by their inability to degrade the large content of bio-recalcitrant organic matter (e.g. humic and fulvic acids) (Di Iaconi et al., 2006). Furthermore, nutrient imbalances such as high ammonium, low phosphorus and biologically degradable carbon content frequently occur in landfill leachate and make it difficult to maintain proper biological treatment and decent effluent quality. Therefore, post-treatment of biological effluents is still necessary to further remove organic matter (Cassano et al., 2011; Zhao et al., 2012). The aforementioned limitations of biological techniques in addition to restrictive environmental legislations and the need for cost-effective treatments have led to an increased interest in the use of advanced oxidation processes (AOPs) such as fenton, photocatalysis, UV/H_2O_2 and ozonation as a valuable addition to conventional treatment techniques (Abbas et al., 2009; Chys et al., 2015a; Cortez et al., 2010a; de Morais and Zamora, 2005; Del Moro et al., 2013; Di Iaconi et al., 2012; Silva et al., 2004)

Research comparing different AOPs showed that especially ozonation could be an (economically) favorable technique (Abbas et al., 2009; Chys et al., 2015a; Cortez et al., 2010a). However, oxidation techniques are not suitable as a replacement for a biological treatment or too expensive as a final polishing step (Chaturapruek et al., 2005). Ozonation after CAS processes as a preceding step to granular activated carbon treatment might therefore be a more cost-effective alternative. Chys et al. (2015a) obtained a decrease in total operation expenses from 1.32 to 1.20 €/m^3 of treated leachate by adding an ozonation step before activated carbon filtration (Chys et al., 2015a). Additionally, ozonation has also shown to convert recalcitrant compounds into smaller and more biodegradable components improving the overall leachate biodegradability, often expressed as BOD_5/COD (Chaturapruek et al., 2005; Cortez et al., 2010; Marttinen et al., 2002). Mainly an increase of hydroxyl and carboxylic groups were found as main by-product formation during leachate ozonation (Monje-Ramirez and Orta de Velásquez, 2004). Contrastingly, as leachate is highly toxic from nature, it has mostly been noticed that ozonation did not lead to an increase (and even a decrease) of toxic compounds (Poznyak et al., 2008).

The characteristic fluctuation of the load and type of organic matter present in landfill leachate directly impacts the ozonation process and all downstream processes. Although much information is already available for low strength wastewater streams (e.g. secondary effluent of municipal wastewater treatment plants (WWTPs)) (Audenaert et al., 2013), studies about the oxidative treatment of high strength wastewater streams such as biologically treated landfill leachate to understand the occurring reactions are rather scarce. A more profound knowledge is needed for successful implementation of advanced processes in full-scale treatment trains.

Organic matter significantly impacts the process performance as it directly reacts with produced hydroxyl radicals ($HO^\bullet$) and ozone itself. Additionally, higher concentrations of organic matter would increase the ozone demand. Next to the organic matter, ozone reaction pathways (and formation/consumption of $HO^\bullet$) are directly influenced by pH. Ozone has the ability to efficiently oxidize organic matter at slightly alkaline pH, which is the typical pH of most (biologically treated) landfill leachates. Operating ozonation at alkaline pH favors the production of $HO^\bullet$ which can accelerate the removal of recalcitrant organic matter. For instance, Cortez et al. (2010) reported up to 36% COD removal at pH 9 compared to 23% COD removal at pH 3.5. (Li et al. (2010b) observed 87-100% color removal when oxidizing landfill leachate at slightly alkaline pH.

To increase the knowledge on the ozonation of high strength wastewater as part of a complete treatment train, conducting a parameter study on critical factors such as initial COD concentration and initial leachate pH should allow for a better understanding of the effect of these factors on treatment performance. Therefore, the objectives of this research are to evaluate the role of initial pH, organic matter content and the related ozone doses while assessing the specific ozonation efficiency.

4.2 Materials and Methods

The biologically treated leachate used in this study was sampled from IMOG after the nitrification denitrification step. The leachate characteristics are mentioned in Table 3.1. To account for different operational conditions, the initial leachate pH and COD were altered at the beginning of different experiments. H_2SO_4 or NaOH were added to respectively lower and increase the initial pH. A minimum of pH 7 and maximum of pH 10 were chosen as literature (Cortez et al., 2010) suggests that no clear benefits can be obtained outside this range. The natural pH of the leachate samples was around 8.4. Nevertheless, it is known that leachate has a high buffering capacity because of its very complex nature (as a mixture of organic and inorganic compounds). However, ozonation around pH 7 and 10 will give more insights into the working mechanism. It was already stated that an increased pH leads to a higher rate constant for direct ozone reactions and appearance of $HO^{\bullet}$ radicals and vice versa at lower pH (Beltran, 2004). Variations in initial COD (COD_0) were obtained by dilution of leachate with demineralized water. Ozonation of landfill leachate at various aforementioned conditions was done according to the procedures outlined in Chapter 3, Section 3.2.1. Samples were regularly taken during a time frame of 60 minutes, accounting for different applied ozone doses (0.13 – 1.51 mg O_3/mg COD_0). This time (60 minutes) was determined based on preliminary studies (see Section 4.3.1 of this chapter). Mass balance calculations of ozone in the gas phase allowed to estimate the transferred ozone dose (TOD) following equation 3.1 whereas the efficiency with which the transferred ozone is utilized was calculated using equation 3.2. The performance of ozonation was monitored using COD, α_{254} and α_{436}.

4.3 Results And Discussion

4.3.1 Ozonation performance in time

The time of ozonation, and consequently the ozone dose, is an important parameter in the oxidative conversion (i.e. partial transformation) of organic pollutants in landfill leachate. During a preliminary experiment in which oxidative treatment was conducted for 4 hours, a decrease of COD (up to 23%), α_{254} (up to 58%) and α_{436} (up to 69%) was observed (Figure 4.1a) with a TOD ranging up to 820 mg O_3/L or 0.44 mg O_3/mg COD_0. The higher removal rate for α_{254} and α_{436} compared to COD can indicate that these relative low ozone doses (some authors - Li et al., 2010b; Monje-Ramirez and Orta de Velásquez, 2004) mention dosages up to 3.5 or more mg O_3 /mg COD_0) are mainly resulting in selective conversion of the organic material. Ozone is known to have a great affinity towards components containing electron rich moieties, inherent to the structure of humic acids absorbing around the wavelength of 254 nm. At higher wavelengths (e.g. α_{436}) the removal rate was even higher which can be a result of the transformation of components absorbing at higher wavelengths into components absorbing at lower wavelengths. This phenomenon corresponds with earlier studies on leachate (F. Wang et al., 2004) and secondary WWTP effluent (Audenaert et al., 2013; Nöthe et al., 2009).

The use of low ozone doses is also supported by the high ozonation efficiency (0.52 mg COD removed/mg O_3) after 4 hours of ozonation (0.44 mg O_3 /mg COD_o; Figure 4.1b). This is within the range reported in literature as ozonation efficiency ranges from 0.19 to 0.81 mg COD removed /mg O_3 while related ozone dosages range from 0.18 – 1.7 mg O_3 /mg COD_0 respectively (Di Iaconi et al., 2012; Li et al., 2010b; Renou et al., 2008). As the ozonation efficiency based on COD increased in time (Figure 4.1b), the maximum ozonation efficiency based on α_{254} (0.0151 cm^{-1} absorption decrease /mg O_3) and α_{436} (0.003 cm^{-1} absorption decrease /mg O_3) was already obtained after respectively 30 and 120 minutes of ozonation (Figure 4.1b). The difference in maxima is most likely again attributed to the fact that ozone will preferentially attack electron rich moieties first.

Nevertheless, an increased ozonation time relates to a high ozone dose and therefore to higher operational costs as will be further explained in Chapter 7.

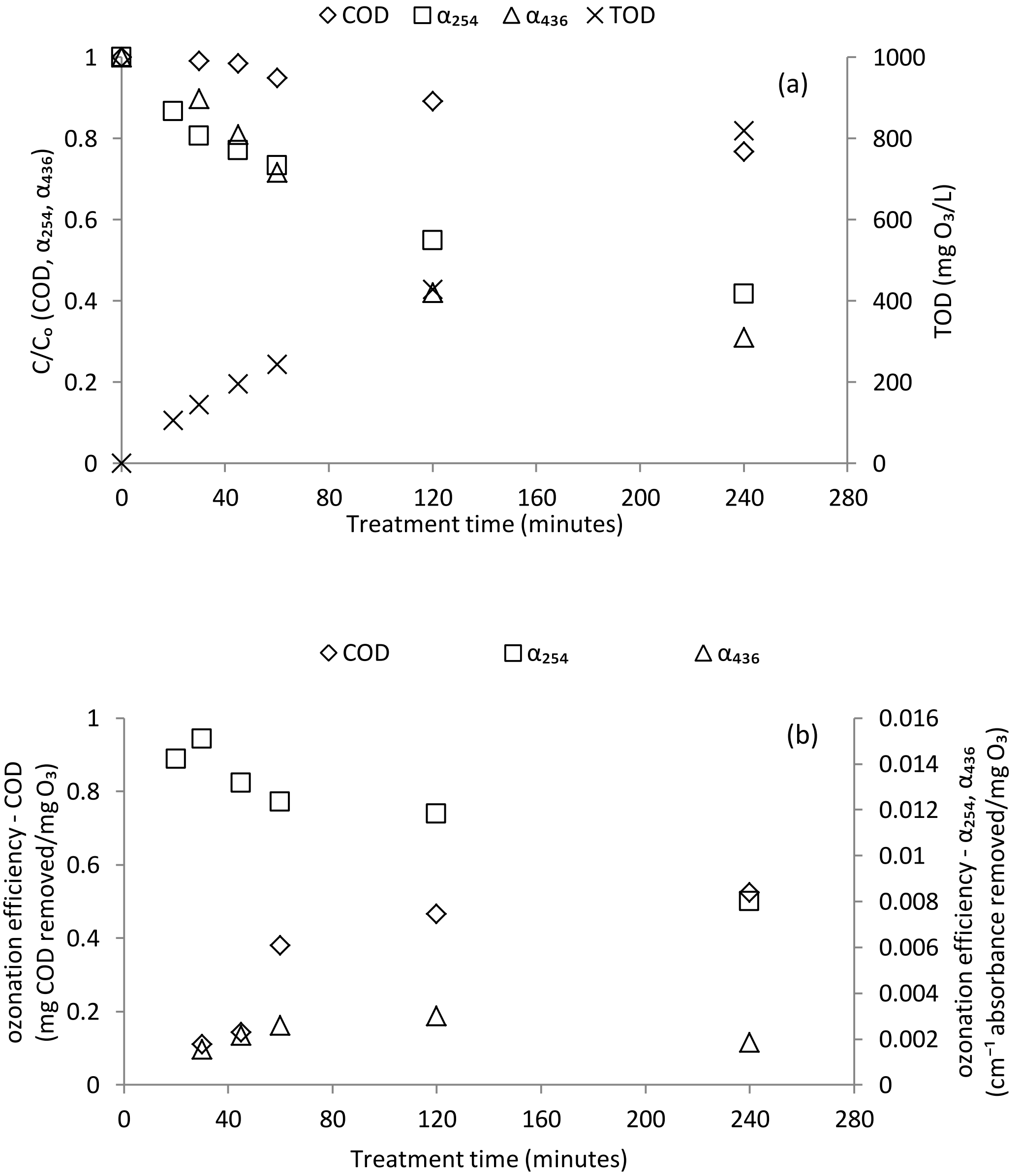


Figure 4.1: (a) TOD (up to 820 mg O_3 /L) and relative evolution of COD (COD_o = 1864 mg /L), α_{254} ($\alpha_{254,\ o}$ = 11.23 cm^{-1}) and α_{436} ($\alpha_{436,\ o}$ = 2.21 cm-^{1}); and (b) COD, α_{254} and α_{436} based ozonation efficiency in time during ozone treatment. (The COD based values after 20 min (1918 mg / L and - 0.68 mg COD removed /mg O_3) are not displayed on respectively (a) and (b) as an error due to the sensitivity of the analyses occurred)

4.3.2 Variation of initial COD and pH

Landfill leachate is characterized as a very fluctuating water stream, especially with respect to pH and COD content (Renou et al., 2008). Therefore, either the initial pH or COD_o were altered during different experiments of which a summarizing overview is presented in Table 4.1. In total, seven experiments are performed of which experiments 1, 2, 3, 4 and 7 are related to different initial COD concentrations (COD_o obtained by dilution). Experiment 5 to 7 are related to a different initial pH (altered by adding H_2SO_4 or NaOH). Small COD_o differences were not found to have an influence on the obtained results and conclusions.

In comparison to the TOD, the measured dissolved ozone was very low, i.e. mostly less than 1% of the TOD was retained as dissolved ozone concentration (C_d). This shows that most of the transferred ozone was immediately consumed due to the abundance of highly reactive moieties. The only exception occurred at very low COD_0 (112 mg/L; C_d = 10% of TOD after 60 minutes of ozonation) as most likely all reactive moieties were rapidly attacked by ozone and only slowly or non-reactive species were remaining (Table 4.1, exp. n°1).

The percentage removal in organic matter decreased at higher initial leachate COD. At higher COD concentrations, organic matter available in the leachate undergoes partial mineralization leading to the formation of intermediates which still contribute to the overall COD. However, since ozonated leachate is normaly further polished with a GAC step, then partial mineralization as opposed to complete mineralization is sufficient. With respect to pH, better percentage removals were obtained at more alkaline pH due to the presence of hydroxyl radicals which oxidise organic matter unselectively .

Table 4. 1: Summary of the obtained results after 60 minutes of ozonation for varying initial COD and pH conditions

Parameter	**Unit**	**Time (min)**	**Experiment n°**						
			1	**2**	**3**	**4**	**5**	**6**	**7**
COD	mg/L	0	112	288	502	825	1392	1623	1846
		60	62.9	237	401	767	1176	1549	1754
	Δ COD		49	51	101	58	216	74	92
	% removal		44	18	20	7	16	5	5
α_{254}	cm^{-1}	0	0.84	1.45	3.73	8.04	8.17	9.59	11.2
		60	0.19	0.30	1.77	4.36	4.53	5.96	8.25
	Δ α_{254}		0.65	1.15	1.96	3.68	3.64	3.63	2.95
	% removal		76.8	79.0	52.5	45.8	44.6	37.9	26.5
α_{436}	cm^{-1}	0	0.07	0.20	0.25	0.68	0.75	1.52	2.21
		60	0.01	0.04	0.03	0.18	0.28	0.78	1.58
	Δ α_{436}		0.06	0.16	0.22	0.5	0.47	0.74	0.63
	% removal		86	80	89	73	63	49	29
pH	-	0	8.5	8.0	8.4	8.4	10.0	7.1	8.4
		60	7.4	7.9	7.7	8.0	9.8	7.9	8.1
TOD	mg O_3 /L	60	169	183	208	240	274	228	243
	mg O_3/mg COD_o	60	1.51	0.63	0.42	0.29	0.20	0.14	0.13
C_d	mg O_3 /L	60	17.0	0.46	1.08	0.95	1.03	1.44	1.42

1,2,3,4,7: experiments investigating the effect of initial COD concentration
5,6,7: experiments to study change in pH

A comparison between the ozonation efficiencies of the different experiments was made in Figure 4.2. Concerning variations of COD_o, the specific ozonation efficiency for COD somewhat fluctuated within the range of 0.24 – 0.49 mg COD removed/mg O_3 but no clear trend could be distinguished (Figure 4.2a). Contrastingly, an increasing trend was clearly observed when considering the ozonation efficiency based on α_{254}. Most likely, the ozonation of leachate containing a higher COD_o will be dominated by conversions of the organic matrix (due to reactions with electron rich moieties) leading to the formation of intermediates. These can still contribute to the measured COD concentration but may have an altered UV-VIS absorbance character. For lower COD_o, the amount of most reactive moieties is logically lower, presumably resulting to more reactions with formed intermediates using a similar ozonation time (this leads to a higher relative ozone dose for lower COD_o (mg O_3 /mg COD_o)). The lower specific α_{254} decrease (cm^{-1} absorption decrease/mg O_3) at low COD_o (0.42 compared to 1.23 at the highest COD_o) supports this reasoning since α_{254} is known to represent very reactive moieties. The specific decrease of both α_{254} and α_{436} are showing a similar trend, which is however less pronounced for α_{436} as the moieties absorbing at this wavelength are exhibiting less absorbance compared to those for α_{254}.

Compared to the observations at varying COD_o, opposite findings were obtained for a change in initial pH. Figure 4.2b clearly indicates a higher COD based ozonation efficiency (up to 0.79 mg COD removed /mg O_3) at pH 10 compared to lower pH values. However, the α_{254} and α_{436} ozonation efficiency show no clear difference among the different initial pH values, which is in agreement with Cortez et al. (2010). Various reasons can explain these findings. Firstly, applying ozonation at a highly alkaline leachate pH of 10 will most probably lead to a faster ozone decomposition and therefore a significant enhancement of $HO^{\bullet}$ production, which is a more reactive and unselective species compared to ozone itself. At pH 7 or 8.4, the dominance by $HO^{\bullet}$ is less pronounced (less indirect promotion of $HO^{\bullet}$) (Gottschalk et al., 2000). Secondly, it is possible that at lower pH, organic pollutants are shifted towards their non-ionized forms (e.g. pKa-values of humic acids ranges mostly between 2 to 8 (Fukushima et al., 1996; Klučáková and Kolajová, 2014). This results in a lower reactivity towards ozone compared to the ionized or dissociated form (Audenaert et al., 2013; Ntampou et al., 2006). Formed intermediates, contributing to the measured COD concentration, can have a lower absorbance compared to their parent components. Further reaction of these intermediates will presumably affect the measured COD concentration but into a much lesser extent α_{254} and α_{436}.

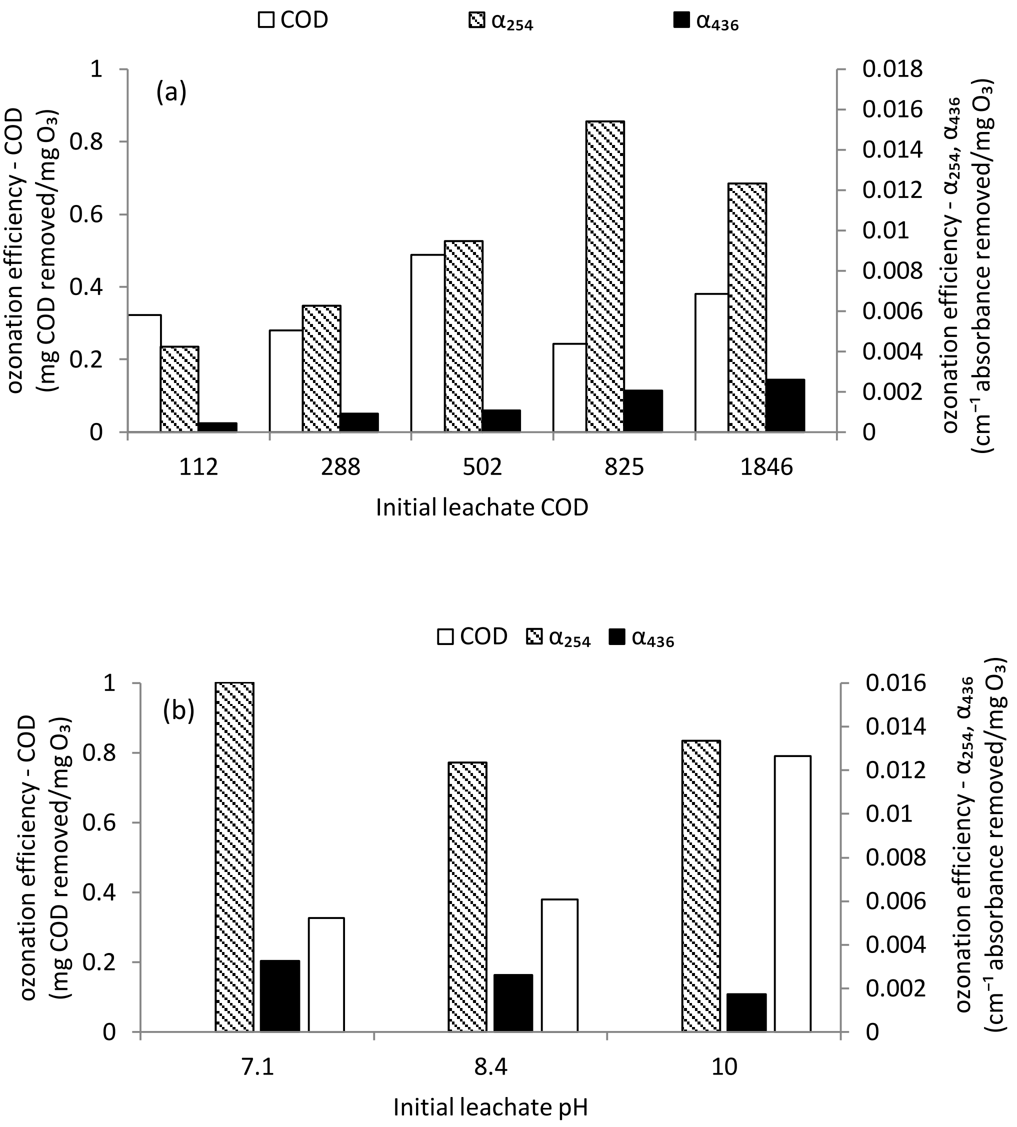


Figure 4.2: COD, α_{254} and α_{436} based ozonation efficiency related to variations in COD_o (a, pH = 8.3 ± 0.2) and initial pH (b, COD_o = 1620 ± 227 mg/l after 60 minutes of ozonation

The conversions of the recalcitrant material will also affect the occurring pH. In general, especially the alteration of the initial pH seemed to influence the pH variation during ozonation. Overall, a small decrease ($\Delta pH = -0.1$ to -0.7 for 6 out of 7 experiments) could be observed (see Table 4.1), except at pH 7 where an increase of pH ($\Delta pH = +0.8$) was obtained. During ozonation, carboxylic acids are known to be formed (Smith, 2011). However, due to possible mineralization, CO_2 might be formed and removed (by gassing-out) by the continuous supply of an ozone/oxygen-gas mixture.

Both processes have an opposite effect on the pH and may keep each other in balance, which is the best exemplified by the rather constant pH measured during ozonation at starting pH 10 (ΔpH = -0.1). At neutral pH (pH 7), the dissociation equilibrium of carbonates will enable a more pronounced CO_2 formation (carbonates are accumulating at alkaline pH) and stripping will be more significant. This might explain the small increase of pH.

4.4 Conclusions

In this chapter, the influence of different process variables on the ozonation of biological treated landfill leachate and the occurring transformations was studied. Using relatively small ozone doses (maximum 1.5 mg /O_3 mg COD_0), decreases in α_{254} and α_{436} were higher than for COD, as most likely the process was dominated by fast oxidation of reactive organic moieties (O_3 firstly reacts with electron rich moieties). Furthermore, a more alkaline environment led to an increased $HO^\bullet$ production hence higher ozonation efficiencies with regards to COD. Nevertheless, the removals obtained by ozonation alone are minimal as such follow up studies – Chapter 5 and 6 will focus on coupling ozonation with a polishing step e.g GAC to further increase the removal of pollutants originally in leachate or formed during oxidation.

Chapter 5

Integration of autotrophic nitrogen removal, ozonation and activated carbon filtration for treatment of landfill leachate

Redrafted after:

J.L. Gao, V. Oloibiri, M. Chys, Stijn De Wandel, B. Decostere, W. Audenaert, Y.L. He, S.W.H. Van Hulle. (2015) Integration of autotrophic nitrogen removal, ozonation and activated carbon filtration for treatment of landfill leachate. Chemical Engineering Journal, 275, 281-287

Contribution of Violet Oloibiri: performing the physical-chemical experiments and writing the related part of the paper

Abstract

The aim of this study was to determine an appropriate combination for effective and economical COD and nitrogen removal from landfill leachate. Biological (nitrogen) treatment was performed with the autotrophic nitrogen removal (ANR) process. The (post-) treatment performances of (i) ozonation (O_3) alone, (ii) adsorption to granular activated carbon (GAC) alone, (iii) the combination of O_3 and GAC and (iv) an integrated approach with continuous recirculation of ozonated ANR effluent were investigated. It was observed that ANR post-treatment with ozonation was able to remove only 15.2 % of residual COD and 14.0 % of total nitrogen in the effluent after 60 min treatment time whereas using activated carbon a 73.6 % removal efficiency of COD and 17.3 % of total nitrogen were achieved. The best performance was obtained for an ANR post-treatment combination of ozonation + GAC, after ozonation, GAC ensured high removal for both COD and total nitrogen. When different ratios of ozonated effluent were mixed with the influent of the ANR, it was found to be possible to reach COD removal as high as 40% with a slight decrease in nitrogen removal of around 70-80% compared to respectively 5.31 % and 85.9 % when no ozonated leachate was recycled to the ANR reactor. Taking the overall performance and operational expenses into account, a combination of ANR biological treatment and its different (post-) treatments (ANR + oxidation +GAC) results in a good performance and a lower cost compared to traditional treatment.

5.1 Introduction

As already mentioned in Chapters 1 and 2 landfill leachate is a high strength wastewater whose disposal without treatment possess environmental risks Many treatment options (or their integrated technologies) were utilized by landfill operators for economically efficient treatment of landfill leachate (Chapter 2)

Presently, biological treatments are usually preferred over physical-chemical ones (Henze et al., 2001) because of its economics, simplicity and efficiency for the removal of ammonium and/or as a first stage of young leachate treatment. However, these techniques can be limited by refractory compounds. In such a situation, one way to overcome such operational problems is to assess the potential of non-biological treatment processes to remove the biorecalcitrant material and improve leachate treatment. And for this reason, a combination of several treatment methods is usually applied. The most common post-treatments – as mentioned in Chapter 2 include reverse osmosis, coagulation-flocculation, evaporation, incineration, activated carbon adsorption and chemical oxidation (such as ozonation) (Di Iaconi et al., 2006). The latter two are the attractive methods and particularly interesting in recent years.

Granular activated carbon, in combination with biological pretreatment has already been implemented (Chys et al., 2015a). In most cases, activated carbon adsorption has allowed sufficient removal of organic compounds (non-biodegradable organics and inert COD), color and other toxic substances to acceptable levels from biologically treated landfill leachate. Morawe et al. (1995) showed activated carbon could reduce the concentration of the non-biodegradable organic and chlorinated organic compounds, as well as the color to an acceptable level. However, high cost caused by high activated carbon consumption for the significant quantities of components in the leachate samples indicated that an intermediate treatment would be required to reduce the organic load and/or enhances the biodegradability in an economical efficient way (Chys et al., 2015a). Ozone was reported capable of oxidizing the large refractory organic molecules (up to 10^4 g/mol), found in leachates, to smaller more biodegradable molecules even to their highest stable oxidation states (producing water and carbon dioxide) (Tizaoui et al., 2007). In Chapter 4, the results already showed that ozonation has the capacity to oxidise recalcitrant organic matter in landfill leachate achieving removal efficiencies of 23% COD 58% α_{254} when the treatment time was 240 minutes. Other studies such as Derco et al. (2002) reported that ozone alone ensured a COD reduction of approximately 60% after about 10 to 11.5 h ozonation time.

The treatment of biologically treated landfill leachate using GAC treatment or ozonation has previously been investigated. Several sites use a combination of biological treatment and activated carbon adsorption as illustrated in the literature review Chapter 2. Other configurations, for example “Bio–O_3–Bio” have been used for the treatment of leachates (Gottschalk et al., 2000). Only limited research was performed however on the possible synergistic coupling of an oxidative process with GAC treatment for treatment of biologically landfill leachate (Chys et al., 2015a). With such combinations both COD as well as nitrogen removal can be achieved.

In this study, biological treatment is firstly established and performed by autotrophic nitrogen removal (ANR). ANR combines the partial nitrification process (conversion of ammonium to nitrite) with the Anammox process which converts ammonium and nitrite on an almost equimolar basis to nitrogen gas (Gao et al., 2015; Van Hulle et al., 2010). ANR biological treatment has future prospects of wide application as the cost of nitrogen removal can be significantly decreased (Gao et al., 2015). The process has a certain level of efficiency in nitrogen and biodegradable organic matter removal, but it was not able to remove any of the refractory organic compounds still present additionally, complete removal of nitrogen compounds was not possible (Gao et al., 2015). Therefore, in the study, several post-treatment methods were then evaluated in terms of reduced organic load, decreased amount of nitrogen components and increased leachate biodegradability. Given the potential of ozonation to reduce organic matter in landfill leachate as shown in Chapter 4 coupled by other merits described in the literature review Chapter 2; such as ability to increase biodegradability of leachate, ozonation was chosen as one of the post-treatment techniques of biologically treated leachate. Additionally granular activated carbon (GAC) was chosen due to its aforementioned merits. Ozonation, GAC adsorption were used as single steps, in combination (O_3 prior to GAC) and in a system involving recirculation of ozonated effluent into the ANR system.

5.2 Materials and methods

Raw leachate used in this study was sampled from IMOG. The specific characteristics of leachate before and after the ANR step are given in Table 5.1.

Table 5.1: Physico-chemical analysis of the used landfill leachate.

Parameter	**Range**	
	Raw leachate (influent of ANR)	**Biologically treated leachate (effluent of ANR)**
COD (mg/L)	548.5-1826	427-869
BOD_5 (mg/L)	94.3-281.9	1.15-9.95
N-NH_4^+ (mg/L)	244-627	0.08-186
N-NO_2^- (mg/L)	0-65.6	0.21-145
N-NO_3^- (mg/L)	3.5-17.2	30.9-110
Ec,(µS/cm^2)	5590-9360	11
pH	7.8-8.2	7.02-9.21

ANR treatment of leachate was done according to the steps outlined in the Chapter 3 – Methodology. Raw leachate was mixed gradually with ozonated ANR effluent at ratio of 0 , 1/10 , 1/4 and 1/2 volume ratio during the course of the experiments. The effect of ozonation on ANR effluent and effluent recirculation was studied. Post-treatment of ANR effluent with ozonation and GAC filtration (Figure 5.1)were performed according to the set up and respective conditions outlined in Chapter 3. Leachate was sampled after 60 minutes ozonation for COD, UV-VIS absorbance with specific attention to 254 nm, ammonium, nitrate, nitrite and pH. For GAC adsorption; COD, Total nitrogen, ammonium, nitrate, nitrite were monitored.

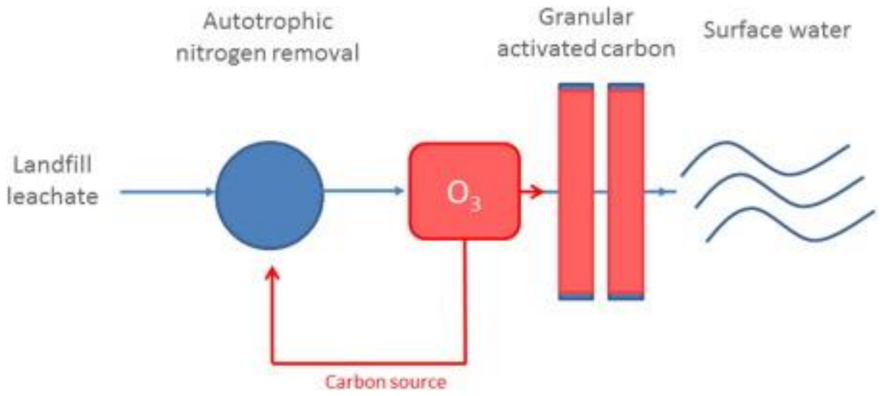


Figure 5.1: Shematic representation of the post-treatment of biologically treated landfill leachate with ozonation and GAC

5.3 Results and discussion

5.3.1 Ozonation results

The effluent generated in the ANR reactor was treated with ozone. Table 5.2 presents the results of transferred ozone dose, COD and α_{254} removal efficiencies, as well as the pH, ammonium, nitrite and nitrate variations before (i.e. in the effluent of ANR) and after ozonation for 60min treatment. Transferred ozone dose and ozonation efficiency were calculated according to equation was calculated according to equation 3.1 or equation 3.2 respectively:

Looking at Table 5.2, which represents experiments with different initial COD concentrations, the absolute removal of organic matter does not provide a clear picture on the removal of organic matter from landfill leachate. However, looking at the percentage removals, it was observed that COD removal efficiencies increased at lower initial COD concentration. The highest removal efficiency of 32.6% was corresponded with the lowest initial COD concentration (427 mg/L). At higher COD concentrations (736-812.1 mg/L), the removal was less than 10%, suggesting a number of recalcitrant compounds, other organic and/or inorganic pollutants in the final effluent was high and was still present after ozonation. This trend is in agreement with the observations in Chapter 4 when considering the procentual removal of COD. Whereby less than 10% COD reductions was achieved when the initial COD concentration was greater than 800 mg/L. Decreasing of the α_{254} was shown to occur faster than COD and the removal efficiency ranged between 36.8% and 55.2%. The absorbance at 254nm (α_{254}) has been reported to be a qualitative indicator of aromatic and unsaturated compounds present in wastewater (Imai et al., 1998; Sevimli, 2005). This results supports the observation that aromatic compounds and other unsaturated compounds which have maximum absorbance at 254nm are easily ozonated but generate low reactivity intermediates that react more slowly and are resistant to further oxidation such as aldehydes which contribute to COD instead of CO_2 as mentioned above (Tizaoui et al., 2007). At a COD concentration of 869.1 mg/L, 18.9% of COD removal and 51.8 % of α_{254} removal was obtained, which is caused by a higher transferred ozone dose compared to the other experiments

Values of the ammonium, nitrate, nitrite and pH are also given in Table 5.2. Ozonation can potentially catalyse chemical nitrification (Haag et al., 1984) and the reaction for chemical nitrification is that ammonium and nitrite are oxidized by ozone to nitrate. During the experiment, with pH values of 7.14 - 9.2 as shown in Table 5.2, the ammonia oxidation rate can be considered relatively low (Langlais et al., 1991) which is the case for biologically treated effluents used in this study. Nevertheless, still some conversion of ammonium to nitrate can be seen. The overall nitrogen removal was 10.4-24.6% at the end of the experiment. The slight decrease in pH value during the course of ozonation can be ascribed to formation of acidic by-products. For example, carboxylic acids and aldehydes produced by direct ozonation reactions (Kurniawan et al., 2006d) In sample 3, because of relatively high levels of ammonium and nitrite, a significant increase in pH was observed. The increase in pH can be attributed to stripping of ammonia and (produced) volatile fatty acids (Frontistis et al., 2008).

Ozonation of ANR effluent with pH 7 (e.g. experiment 4) led to a decrease in pH contrary to what was observed in Chapter 4. At such a lower TOD (130 mg O_3/L) partial mineralization is dominant hence formation of carboxylic acids is favoured hence the decrease in pH.

A simplistic economical analysis of the operating costs associated to ozonation studied, was performed. The calculated costs, based on 60 min of operating time and considering (i) ozone power consumption was 12 kWh/kgO_3 (Chys et al., 2015a), (ii) the cost of electricity was 0.12 euro/kWh (Chys et al., 2015a;

Van Hulle and Ciocci, 2013) are summarized in Table 5.2. Details on the operating cost calculations are covered in Chapter 7 which deals with economic considerations.

Table 5.2: Evolution of TOD, COD and α_{254} removal efficiencies, as well as pH, nitrite, nitrate and ammonium concentrations after 60 min of ozonation.

Parameters	**1**	**2**	**3**	**4**	**5**	**6**
Initial COD (mg/L)	426.6	736.8	762	784.7	812.1	869.1
Δ COD	139	64	73	50	62	164
COD removal (%)	32.6	8.7	9.6	6.4	7.6	18.9
Initial α_{254} (cm^{-1})	5.19	13.9	12.0	15.1	14.2	14.1
Δ α_{254}	3	5	4	7	8	7
α_{254} removal (%)	51.1	37.4	36.8	43.4	55.2	51.8
Initial NH_4^+-N(mg/L)	59.8	2.74	186	1.53	3.05	2.14
NH_4^+-N (mg/L)	39	1.46	179	0.27	1.71	1.12
Initial NO_2^--N (mg/L)	4.83	0.26	145	1.38	0.28	0.21
NO_2^--N (mg/L)	0.14	0.038	0.18	0.01	0.053	0.038
Initial NO_3^--N (mg/L)	110	45.5	30.9	49	57.7	66.1
NO_3^--N (mg/L)	114	37.8	145	36.4	50.4	51.7
TN removal (%)	12.3	14.1	10.4	24.6	10.1	19.8
Initial pH	7.386	7.249	9.2	7.14	8.26	8.17
pH	7.081	6.224	9.4	6.18	7.43	6.88
TOD (mg O_3/L)	130	240	380	130	300	480
TOD (mg O_3/mg COD_o)	0.3	0.3	0.50	0.17	0.37	0.55
Cost (€/m)	0.19	0.35	0.55	0.19	0.43	0.69
Ozonation efficiency (mg COD removed/mg O_3)	1.03	0.26	0.19	0.37	0.21	0.34
Cost (€/kg removed COD)	1.39	5.43	7.58	3.87	6.97	4.18

As shown in Table 5.2, the calculated cost was between 0.19 and 0.69 euro/m^3 leachate (1.39-7.58 euro/kgCOD removed) for different samples in the experiment. The lowest cost was 0.19 euro/m^3 leachate (1.39 euro /kgCOD removed) obtained for the COD concentrations of 426.6 mg/L. The higher TOD value corresponds to the higher COD and/or high ammonia nitrogen concentration or nitrite in ANR-treated effluent. Results reveal that the operation of the ANR process influences the performance of the ozone process. It is very important for ozone experiment to achieve steady-state effluent in the ANR biological treatment. These results further show that higher TOD attracts higher treatment costs.

The biodegradability of the effluent was measured after 60 min of ozonation to assess the absolute increase with ozone treatment as a function of initial COD and the results obtained are compiled in Figure 5.2. As shown in Figure 5.2, after ozonation, the BOD_5/COD ratio varied from 0.001-0.002 to 0.01- 0.06. Generally, the ratio becomes higher by reducing the initial COD, especially when it is lower than 1500 mg/L, which indicates that ozonation becomes more efficient in improving biodegradability in lower concentrations of biologically stabilized leachate (Hamidi and Salem, 2015). BOD_5 increased by about 943% at 426.6 mg/L, 134-282% at 700-800 mg/L. The raise in BOD_5 can be due to the transformation of the refractory large compounds into smaller and more biodegradable products (Wang et al., 2004). Though the BOD_5/COD is still considered low its increase indicates that the leachate can undergo microbial oxidation more easily than before.

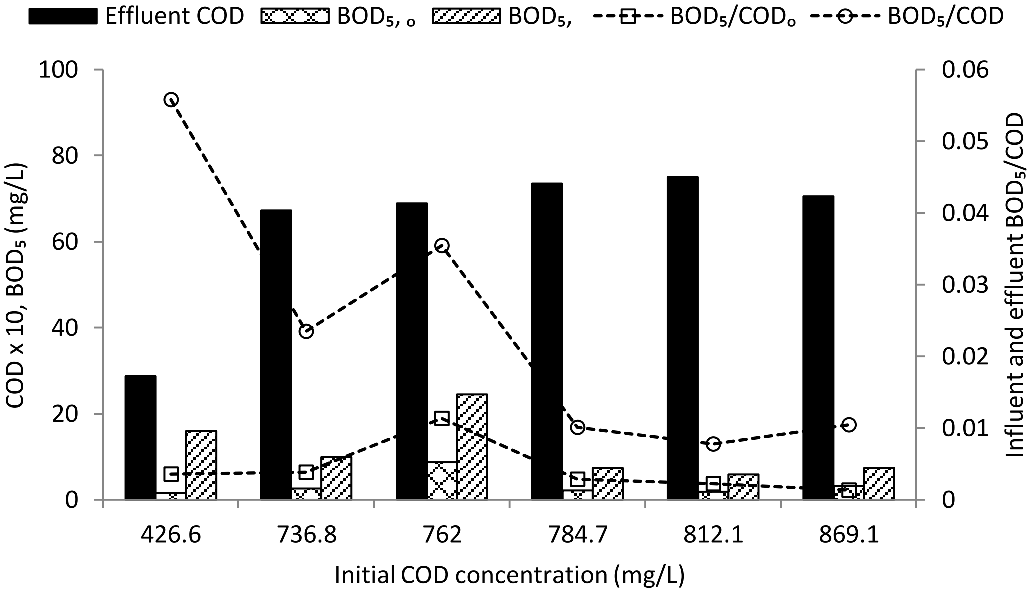


Figure 5.2: The COD, BOD_5 and the ratio of BOD_5/COD before and after ozonation of ANR- effluent.

Ozonation aided colour removal as the leachate colour changed from brown (initial conditions) due to the presence of humic substances to light yellow after a short period of ozonation. This agrees with the behaviour of ozonation towards color contributing components (absorbance at 436 nm) described in Chapter 4. UV-VIS absorbance measurements for sample 1 (Figure 5.3a) indicate that the ozone treatment step is clearly effective for removing constituents that are strongly absorbing at 254 nm (Figure 5.3a) and the 400-800 nm range, which overlaps with the visible spectrum (Figure 5.3b). There was a direct attack of ozone in the chromophoric parts during the ozone treatment (Gottschalk et al., 2000). Additionally, it is also clear that very little divergence in the absorbance measurements of the raw compared to the biological treated samples was obtained at almost all wavelengths.

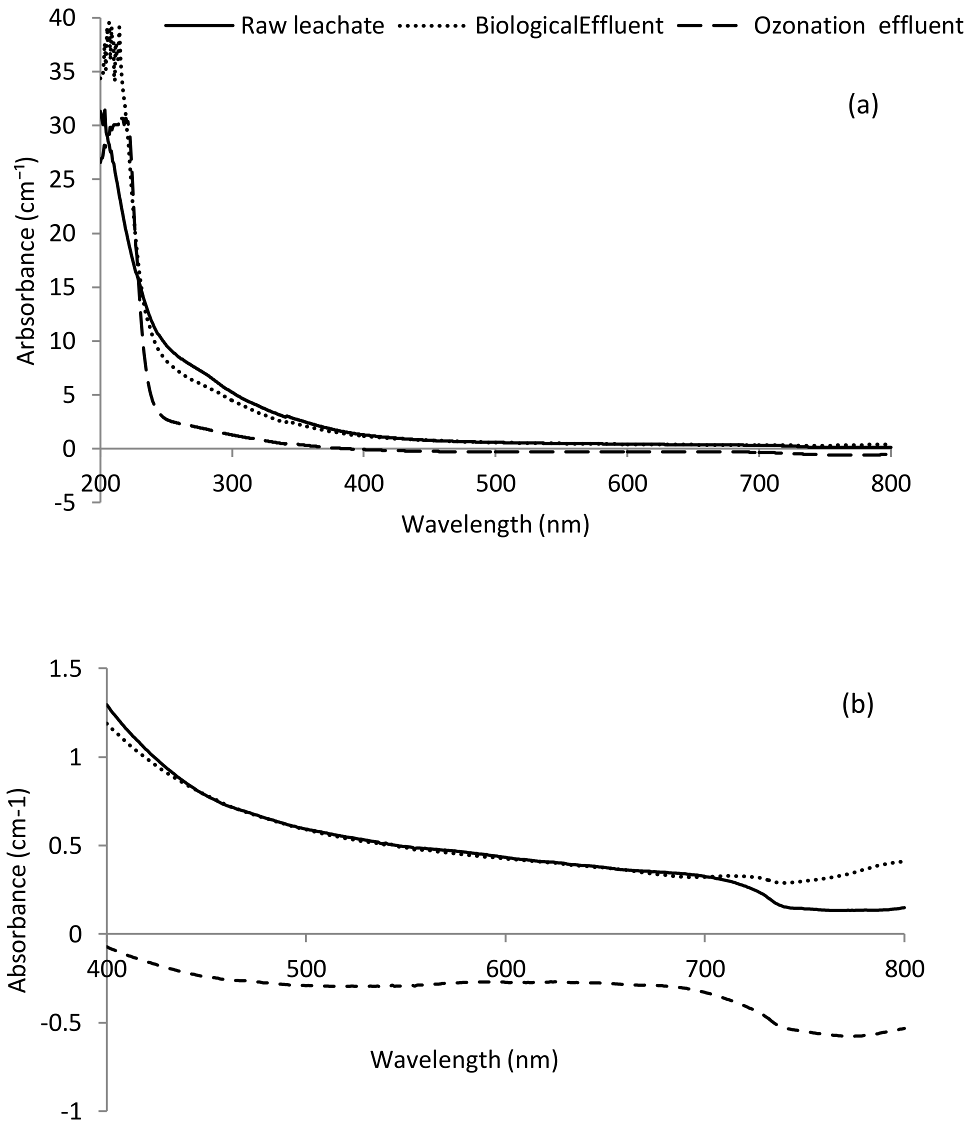


Figure 5.3: Effect of ozonation treatment on UV-VIS absorbance of biologically treated landfill leachate from (a) 200 – 800 nm and (b) special focus on the VIS region 400 – 800 nm.

5.3.2 GAC adsorption of biologically treated and/or ozonated leachate

A series of column experiments were performed using sample 1, 3 and 6 to evaluate the feasibility of carbon adsorption as a post treatment process. Effluent concentration from all columns was plotted against number of filtered bed volumes generating breakthrough curves. The results of the treatment efficiency according to COD are presented in Figure 5.4 . The results show an early breakthrough followed by a quick rise in the relative concentration of the effluent (C_e/C_o). It can be observed from Figure 5.4 that within the first 0.5 BVs, GAC adsorption controlled the removal of organic matters from the leachate in all columns and ion-exchange for nitrogen compounds (Appendix 1). Between 0.5 BVs and 1 BVs, GAC adsorption played equally important roles on different COD concentrations. After 1 BVs, the outlet concentration strongly increased, indicating that a slow adsorption was taking place (Kurniawan et al., 2006d). In the column 1, because of the low concentration of COD in sample 1, the COD removal was still kept at around 80% after 4 BVs and the effluent concentration achieved a pseudo-steady state. Compared to GAC adsorption for only biologically treated leachate, GAC showed slightly higher adsorption capacities of COD (Figure 5.4) in column operation for ozonated leachate. This could be proved once more by the fact that ozone oxidation could react with some of the recalcitrant organic compounds in the biologically treated leachate, breaking them down into smaller components which can access the GAC pores easily (Chys et al., 2015b). The lower COD concentration of sample 1, could have enabled an increased ion-exchange capacity for nitrogen, which caused the significant increasing of nitrogen removal by the GAC column (Appendix 1). Nevertheless, GAC is not an efficient method in removal of nitrogenous compounds compared to biological or ion exchange.

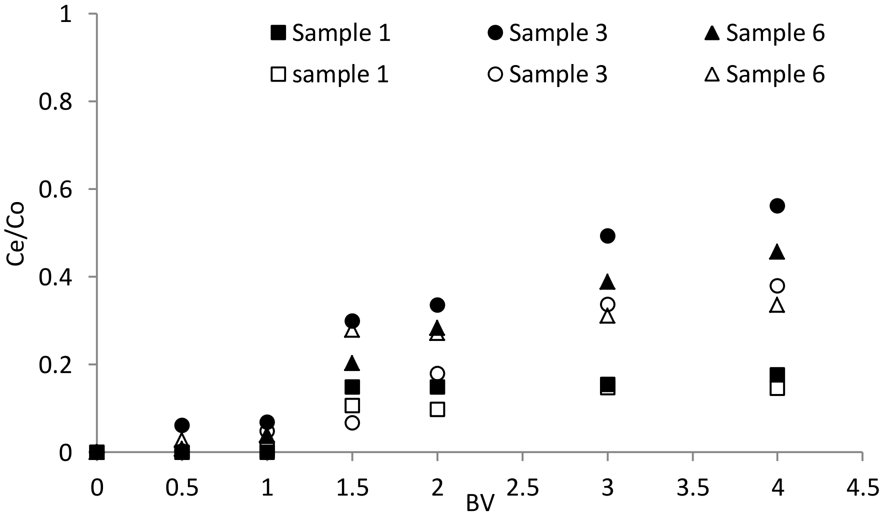


Figure 5.4: The plots of COD (a) versus filtered bedvolumes, (■, ● and ▲) represents GAC adsorption of biologically treated leachate; (□, ○ and △) represents GAC adsorption of ozonated leachate.

In order to assess additional cost related to GAC, the specific values of 1.32 €/m^3 was used as the cost for single treatment of leachate with GAC treatment (Chys et al., 2015b)According the discharge limit specifically for IMOG, column tests were evaluated as soon as the effluent COD reached the discharge limit of 250 mg/L. From Figure 5.5 it can be seen that the GAC lifetime lengthened after ozonation (especially for sample 3 and 6) and is 1.3-1.5 times that of biologically treated leachate that is not ozonated. Due to the enhanced GAC lifetime after ozonation, the GAC cost could be drastically decreased as 0.88-1.02 € /m^3.

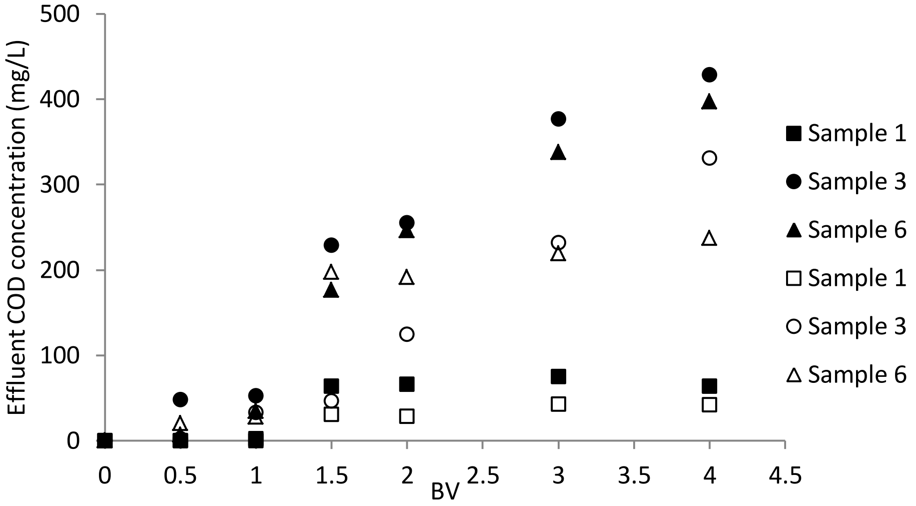


Figure 5.5. The plots of effluent COD concentration versus filtered bedvolumes, (■, ● and ▲) represents GAC adsorption of biologically treated leachate; (□, ○ and △) represents GAC adsorption of ozonated leachate.

5.3.3 Combining biological treatment with ozonation as post-treatment: -recycling of ozonated ANR effluent to the influent

Ozone was confirmed capable of decomposing large recalcitrant compounds into smaller more biodegradable molecules, which can be removed more easily in a subsequent biological system. Therefore, ozonation of ANR effluent and recirculation of ozonated effluent to the ANR step (Figure 5.1) were carried out after about 2 years of operation of the ANR reactor. During this 2 year (683 working days) the ANR reactor was fed only with raw leachate, in order to achieve improved effluent quality.

The ozonated (ozonation time of 60 minutes) ANR effluent was progressively added to the ANR influent in order to get a progressive adaptation of biomass to the mixture of raw leachate and ozonated effluent, as well as to minimize possible inhibition phenomena. Before recycling of the ozonated effluent to the ANR reactor, as shown in Figure 5.6, higher rates of TN (average 85.9 %)

rather than COD removals (average 5.31%) were observed, which is consistent with the well-known behavior of an ANR system. After recycling of ozonated effluent to the ANR reactor, as expected, COD removal increased to 12.9% (Figure 5.6) and the total nitrogen (TN) removal was as high as before and remained on average 87.5% (Figure 5.6). Such a behaviour can be explained by the nitrate recirculation and the effective biodegradation of residual recalcitrant compounds and their oxidation products formed during ozonation. When 1/10 volume ratio of the ozonated effluent was added, the biodegradable materials were utilized by the heterotrophic bacteria present (but perhaps not active) in the ANR reactor. Heterotrophic denitrification in the leachate took place and made significant contributions to the heterotrophic route of COD removal and nitrogen removal. This allowed better effluent quality, with relatively lower nitrogen (Figure 5.6) and COD content. During recirculation of ozonated leachate to the biological step, the flow rate remains the same and the nitrogen load decreases since the influent is diluted with treated leachate (appendix 3). The ozonated leachate contains less nitrogen than that in the ANR reactor. This observation is also true for COD however, the decrease is not as much as that experienced by nitrogen. Due to the large decrease in nitrogen to the ANR, the carbon to nitrogen ratio increases from 1.0 when no ozonated effluent is added to 2.4 when 50% of ozonated effluent is recirculated this in turn favours denitrification process.

When the ozonated effluent volume ratio in the feed was increased from 1/10 to 1/4 and further to 1/2, final COD removal was always increasing. COD removal percentages increased with the higher amount of ozonated leachate and the removal efficiency was finally increased to approximately 40%. Whereas the total nitrogen removal started to decrease during the earliest part of the subsequent periods, later it increased and reached a total nitrogen removal percentage of mean 70%-80%. The relatively lower total nitrogen removal after changing the influent conditions may be attributed to adaptation of the biomass. Also, the heterotrophic metabolism could have caused deceleration of the autotrophic metabolism responsible for nitrification/denitrification, i.e the autotrophic bacteria could be inhibited. These effects on the whole could have been responsible for the total nitrogen removal reduction.

At the same time, according to appendix 2, it could be observed that the effluent ammonium and nitrite concentrations were similar between before and after adding ozonated effluent and always were quite low. But the nitrate concentration in the effluent, tends to decrease after addition of ozonated effluent. This may further confirm that denitrification exists in the ANR reactor.

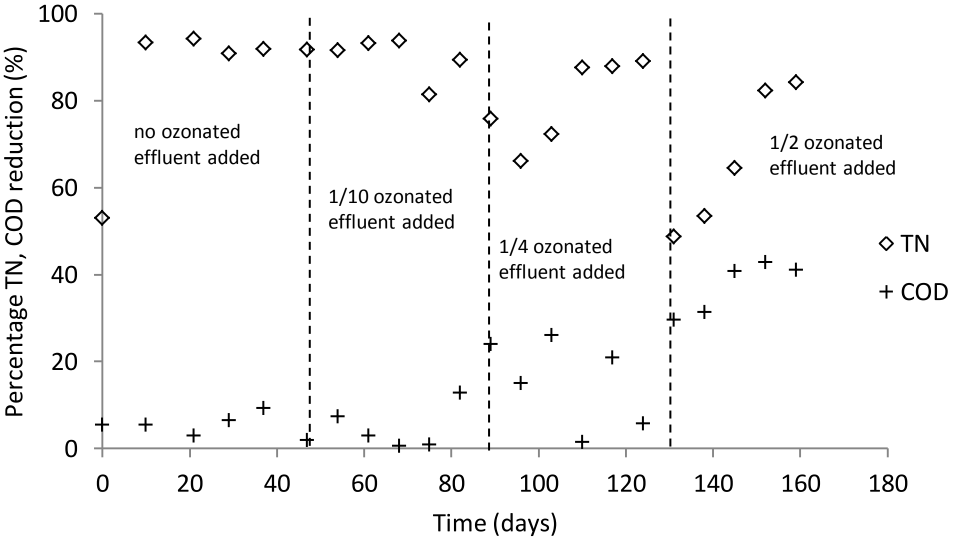


Figure 5.6: Change in ANR efficiency in terms of COD and total nitrogen removal efficiency due to recirculation of ozonated ANR effluent. Days 0 – 47 no ozonated effluent, 48 – 89 ozonated effluent at ratio 1/10, 90 – 131 ozonated effluent at ratio 1/4, 132 – 159 ozonated effluent at ratio 1/2

5.3.4 Evaluation of the combined treatment train

COD and nitrogen removal values were calculated and compared in the laboratory-scale integration treatments system with the experimental results. Ozonation alone as a single post-treatment for biologically treated leachate, as Table 5.3 shows, results in minimal COD removal. The effluent COD concentrations are still higher than the specific discharge limit set fo IMOG (250 mg/L). Probably since the relatively low ozone doses used encourage partial mineralization. The by-products of this oxidation process still contribute to the overall COD. Moreover, even after subsequent recirculation of the ozonated leachate to the ANR step that is ANR + O_3 + ANR treatment, the effluent COD were still higher than the specific standard set for IMOG (344 – 484 mg/L). GAC on the other hand shows higher COD removals. As will be revealed in Chapters 8 and 10, GAC unselectively removes organic matter from landfill leachate hence the higher efficiencies The calculation on removal efficiencies was conducted at the end of GAC lifetime. However, the most interesting result of combination of ozonation and GAC, is that after O_3, the GAC remarkably improved COD removal, as already reported by Chys et al. (2015a). Likewise, from integration treatments system point of view, the results of Table 5.3 also put in evidence that the ANR+O_3+GAC achieved the higher removal of both nitrogen and COD among all integration treatments systems. The removal of COD and total nitrogen from effluent would be up to 78.4% and 82.6% respectively . Combination of ANR + O_3 + GAC was able to treat leachate for more than 3.5 BV before the discharge limit was surpassed. On the other hand, effluent COD from the ANR + GAC treatment chain passed the 250 mg/L after 2 BV

The costs of treating landfill leachate are very site-specific because of the variable quality and quantity of leachate and also the available (treatment) infrastructure, knowledge and experience with certain techniques at the landfill. The preliminary cost analysis presented in Table 5.3, is performed based on the removal efficiency of the separate post-treatment techniques and cost factors related to full-scale installations (obtained in previous studies (Chys et al., 2015a; Gao et al., 2015)). This should give a first indication of operational costs that can be expected. More detailed information on the cost calculations are available in Chapter 7.

For the recycling ozonated ANR effluent to the ANR reactor system (O_3^c +ANR), due to the different proportions of ozonated leachate added (1/10, 1/4 and 1/2 volume ratio), the treatment cost could be calculated as (0.04+ratio*0.19) giving 0.06, 0.09 and 0.14, respectively. As such, the overall treatment train - ANR+O_3^c+ANR - resulted in the lowest treatment cost per m^3 of treated leachate. Next to this treatment train, the combination of ANR and ozonation (ANR + O_3) also seems to be a cost effective alternative with the low treatment cost between 0.23 (0.04 + 0.19) and 0.73 (0.04 + 0.69) €/m^3. Conversely, by the values in Table 5.3,it was clear that the use of a combined ANR and

GAC treatment (ANR+GAC) or (ANR+ O_3+GAC) treatment implied higher costs (up to 1.36 or 1.75 € m^{-3}). Nevertheless, this technique (ANR+ O_3+GAC) may be considered as most cost effective due to its both high COD and nitrogen removal, if the remaining organic load was considered from an effluent quality perspective. Furthermore, these costs are much lower than other studies that have applied ozone to landfill leachate most probably because the applied ozone dosage is much lower in this study (<0.55 mg O_3/mg COD_o compared to 20 mg O_3/mg COD_o) (Anfruns et al., 2013).

Table 5.3: Performance of the integration treatment processes tested and their operational costs assessment.

Treatments	**Performance (average removal (%))**		**Operating costs (€ /m^3)**
	Nitrogen	**COD**	
ANR	74.0	13.2	0.04[a]
O_3 (treatment time for 60 min)	14.0	15.2	0.19-0.69
GAC[b]	17.3	73. 6	1.32
GAC (after O_3)	42.5	76.0	0.88-1.02
Recycling ozonated ANR effluent to the ANR reactor (O_3[c]+ANR)	87.5;75.3;71.1	8.1; 16.5; 39.1	0.06-0.11; 0.09-0.21; 0.14-0.39
Total (ANR+ O_3)	**80.4**	**26.8**	**0.23-0.73**
Total (ANR+GAC)*	**66.4**	**81.4**	**1.36**
Total (ANR+ O_3+GAC)*	**78.4**	**82.6**	**1.11-1.75**
Total (ANR+ O_3[c]+ANR)	**90.5; 83.9; 82.8**	**27.1; 40.9; 52.1**	**0.14-0.19; 0.17-0.29; 0.22-0.47**

[a] Operational cost of ANR based on the data from Gao et al. (2015); [b] The removal rate of nitrogen and COD was calculated at the end of GAC lifetime i.e when COD less than 250 mg O_2/L; [c] The proportions of O_3 effluent were 1/10,1/4 and 1/2 volume ratio respectively; * Leachate treatment trains whose effluent COD were below 250 mg/L

5.4 Conclusions

This work focused on investigation of feasibility of different treatment procedures for removal of pollution (COD and nitrogen compounds) from landfill leachate. As indicated in this research, the main conclusions and suggestions for future studies are:

Final COD removal was always quite low and at the same time, nitrogen removal was always unsatisfactory in ozonation. Considering this, in any case, ozonation alone is further confirmed not to be a sufficient for post-treatment of biologically treated landfill leachate . However, ozonation was able to enhance the biodegradability. BOD_5/COD ratio increased from 0.001-0.002 to 0.01- 0.06.

When mixing the ozonated ANR effluent into the ANR reactor, the highest nitrogen and COD removal of 93.8% and 42.9% were obtained respectively at 1/10 and 1/2volume ratios, compared to 93.4% and 9.3 % when no recirculation was performed.

Adsorption to activated carbon is a necessary final polishing step removing a significant amount of organics

When combining ANR, ozonation and GAC an overall removal performance for nitrogen and COD of 78.4% and 82.6% can be obtained. Considering the technical performance and cost assessment, the results of this work demonstrate that landfill leachate can be effectively and economically treated by this combination.

Chapter 6

A comparative study on the efficiency of ozonation and coagulation-flocculation as pre-treatment to activated carbon adsorption of biologically stabilized landfill leachate

After:

Violet Oloibiri, Innocent Ufomba, Michael Chys, Wim Audenaert, Kristof Demeestere, Stijn W. H. Van Hulle (2015) A comparative study on the efficiency of ozonation and coagulation–flocculation as pretreatment to activated carbon adsorption of biologically stabilized landfill leachate. Waste Management, 43, 335 – 342.

Contribution of Violet Oloibiri: Designing the experiments and writing the manusript

Abstract

The present work investigates the potential of coagulation-flocculation and ozonation to pretreat biologically stabilized landfill leachate before granular activated carbon (GAC) adsorption. Both iron (III) chloride ($FeCl_3$) and polyaluminium chloride (PACl) are investigated as coagulants. Better organic matter removal is observed when leachate was treated with $FeCl_3$. At a dose of 1 mg $FeCl_3$/mg COD_o (COD_o: initial COD content), the COD and α_{254} removal was 66% and 88%, respectively. Dosing 1 mg PACl/mg COD_o resulted in 44% COD and 72% α_{254} removal. The settle-ability of sludge generated by PACl leveled off at 252 mL/g, while a better settle-ability of 154 mL/g was obtained for $FeCl_3$ after dosing 1 mg coagulant/mg COD_o. For ozonation, the percentage of COD and α_{254} removal increased as the initial COD concentration decreased. Respectively 44% COD and 77% α_{254} removal was observed at 112 mg COD/L compared to 5% COD and 26% α_{254} removal at 1846 mg COD/L. Subsequent activated carbon adsorption of ozonated, coagulated and untreated leachate resulted in 77%, 53% and 8% total COD removal after treatment of 6 BV. Clearly showing the benefit of treating the leachate before GAC adsorption. Mathematical modeling of the experimental GAC adsorption data with Thomas and Yoon-Nelson models show that ozonation increases the adsorption capacity and breakthrough time of GAC by a factor of 2.5 compared to coagulation-flocculation.

6.1 Introduction

The generation of landfill leachate is an inevitable consequence of municipal solid waste landfilling. Due to the leachate characteristics mentioned in Chapter 1, If not properly collected and treated, landfill leachate can contaminate surface water, ground water and soils. To prevent this, collection, treatment and safe disposal of leachate is mandatory.

Several methods are used to treat landfill leachate. Biological techniques such as sequential batch reactor (SBR), aerated lagoons, activated sludge, up-flow anaerobic sludge blanket (UASB) – discussed in Chapter 2 are preferred in the treatment of young leachate due to their economic competitiveness (Kheradmand et al., 2010; Zhao et al., 2012). However, conventional biological methods are inefficient in the treatment of stabilized leachate. This is due to the low biodegradability ($BOD_5/COD < 0.1$), high ammonia nitrogen (> 400 mg/L), and low phosphorus content of stabilized leachate (Abbas et al., 2009; Amokrane et al., 1997; Kim et al., 2007; Li et al., 2010b). Therefore, to achieve the required discharge limits, post treatment of biological effluent is required. Post treatment of biological effluent is preferred because all chemicals and energy used in treatment are aimed at removing the bio-recalcitrant fraction. These post treatment techniques are described in detail by in Chapter 2.

Adsorption is commonly used in the post treatment of biologically treated landfill leachate (Foo and Hameed, 2009). This is due to its large specific surface area, thermo-stability and fast adsorption kinetics. Furthermore, activated carbon is highly versatile in the removal of a wide range of organic and inorganic pollutants regardless of their concentrations (Turki et al., 2013).the good performance of GAC is already seen in Chapter 5 whereby GAC adsorption of biologically treated leachate resulted in up to 73% COD removal. Renou et al. (2008) also reports 85% decrease of COD after adsorption of biologically treated leachate. Despite the advantages offered by activated carbon, the operation and regeneration costs are high, which results in increased treatment costs (Chys et al., 2015a) or even forms a barrier for its application (Foo and Hameed, 2010).

Because of its simplicity in operation and implementation, coagulation-flocculation has been employed successfully in treatment of stabilized leachate (Wang et al., 2009). Coagulation-flocculation facilitates the removal of organic matter and other pollutants from landfill leachate by use of coagulants. However, sometimes moderate COD removal and sludge production are mentioned as drawbacks (Li et al., 2010b). Aluminium sulphate, polyaluminium chloride, ferrous sulphate, and ferric chloride are the most commonly used coagulants (Amokrane et al., 1997). Coagulation-flocculation of leachate was shown to remove, up to 87% suspended solids (Li et al., 2010b) and 100% of leachate color (Tatsi et al., 2003). Survey of literature revealed that the efficiency of the coagulation-flocculation technique depends on the type of coagulant, coagulant concentration, pH, temperature e.t.c (Rui et al., 2012). Color reduction, organic matter and heavy metals removal provide valuable information in judging the suitability and effectiveness of coagulation-flocculation in treating landfill leachate. However, few works focus on certain aspects such as settle-ability of produced sludge which is of importance if certain units such as clarifiers are to be added into the treatment train.

As already discussed in Chapter 2 and practically seen in Chapter 4 and 5, ozonation can oxidize recalcitrant organic substances such as humic acids due to its strong oxidizing potential (E^O=2.07V) (Cortez et al., 2010).

At alkaline pH, in combination with oxidants such as H_2O_2, ozone produces hydroxyl radicals (Tizaoui et al., 2007). Hydroxyl radicals have a higher oxidizing potential (E^O=2.80), are non-selective in nature, and thus can rapidly oxidize organic compounds which oxidize slowly with ozone. (Chapter 4). Furthermore, ozonation facilitates the conversion of complex high molecular weight compounds into simple and more easily biodegradable compounds. This in-turn increases the biodegradability of the leachate (Chapter 5)

(Bila et al., 2005; Chaturapruek et al., 2005). Recirculation of such ozonated effluent into a biological unit shows improved removal efficiency of biological systems and reduced ozone consumption of leachate during subsequent ozonation (Chapter 5) and (Chaturapruek et al., 2005). Application of ozonation is however limited by the high operating costs especially when higher doses are required. For instance, ozonation of 1 m^3 of leachate at pH 3.5 and 743 mg/L initial COD costs 64 € to remove 1 g of COD (Cortez et al., 2010). To achieve 10% COD removal from landfill leachate (initial COD 729 mg/L) 3.1 € was required (Chys et al., 2015a).

Combination of adsorption with either coagulation-flocculation or ozonation can reduce the drawbacks of a single process. For instance, coagulation-flocculation can be used to remove moderate COD hence reducing the COD load to the activated carbon. Subsequently, this reduces the amount of activated carbon consumed. The feasibility of such a combined set up was reported by Li et al. (2010b). In their study, the COD removal increased to 80% after combined treatment as opposed to 70% when only coagulation-flocculation was used. Granular activated carbon adsorption of ozonated leachate resulted in total COD reduction from 3135 mg/L to 270 mg/L. Furthermore, a reduction in iron from 12.6 mg/L to 0.27 mg/L and a total elimination of nitrites was achieved (Cataldo and Angelini, 2013). This synergy was also demonstrated in the study discussed in Chapter 5

Several studies (Asakura and Matsuto, 2009; Foo et al., 2013b; Papastavrou et al., 2007) use batch adsorption to evaluate the performance of activated carbon. Batch adsorption studies provide vital equilibrium data on removal of pollutants from landfill leachate, and is a fast and easy way to collect preliminary data on activated carbon adsorption as will be illustrated further in this PhD (Chapter 8). However, column adsorption studies provide a more realistic representation of the use of carbon adsorption in real practice. Furthermore, column studies are more useful in studying the uneven flow patterns, non-equilibrium conditions, recycling and regenerating aspects associated with GAC adsorption (Sivakumar and Palanisamy, 2009). Moreover, column studies are effective in studying the impact of pretreatment techniques on the operating time of activated carbon. For instance (Kurniawan et al., 2006c) uses column studies to demonstrate a 4 times improvement in breakthrough time of COD from GAC, when ozonated leachate is treated using ozone modified GAC. To compare the effect of different types of treatment on the operation time of an activated carbon bed, (Ramirez Zamora et al., 2000) utilized coagulation-flocculation and fenton oxidation as pre-treatment steps before fixed bed activated carbon adsorption. Results showed that the operation time of the activated column fed with coagulation-flocculation effluent was extended by a factor of 1.3 compared to the column fed with fenton oxidation effluent. Therefore, coagulation-flocculation of leachate results in less activated carbon columns used, and as such less operational costs. However, the costs incurred in disposal of the large amounts of sludge formed from coagulation-flocculation and fenton oxidation can nullify the benefit of saved costs.

Based on the discussion above it can be concluded that there is a need for a technique which provides optimum removal efficiency while extending the operation time of the activated carbon step as already seen in Chapter 5. It is in this regard that a comparative study on ozonation and coagulation-flocculation is presented in which both techniques are combined with a granular activated carbon (GAC) column for efficient removal of organic matter. The pretreatment steps will be evaluated based on their removal efficiency and their effect on activated carbon column properties. Specifically, evaluation of the pretreatment steps and their combined use with GAC will be based on COD and α_{254} removal. Attention will also be paid to the settle-ability of the sludge produced during coagulation-flocculation. The Thomas and Yoon-Nelson adsorption model will be used to predict the effect of ozonation and coagulation-flocculation on adsorption capacity and breakthrough time of the activated carbon column.

6.2 Materials and method

The leachate used in this study was sampled from IMOG after the nitrification denitrification stage, in the period between September 2013 and January 2014. The main characteristics of the biologically treated leachate sampled from IMOG are summarized in Table 3.1.

Coagulation-flocculation with ferric chloride ($FeCl_3$) and polyaluminium chloride (PACl) was carried out at various coagulant concentrations (50 – 1400 mg/L) following the procedure outlined in the Chapter 3. The supernatant was withdrawn for pH, turbidity, COD and UV–VIS measurements and subsequent carbon adsorption. The remaining sludge was sampled for sludge settling measurements.

The ozonation of biologically treated leachate at different initial COD concentrations was performed using a lab scale batch reactor described Chapter 3. Low leachate COD concentrations were achieved by diluting the initial sample accordingly using distilled water. Ozonated leachate was sampled after 60 minutes to determine changes in COD, UV- VIS absorbance at 254 nm and dissolved ozone.

Effluents from the coagulation-flocculation and ozonation steps were further subjected to GAC adsorption in a fixed column (Figure 6.1). Leachate samples were collected at the GAC column exit at different time intervals and analyzed for COD and UV VIS absorbance at 254 nm. The column was stopped after 6 hours which corresponds to 12 BV. The breakthrough point was set as 50% of inlet concentration, this was enough to determine any improvements in the properties of the GAC using the breakthrough curve. The efficiency with which GAC is used was determined by calculating the adsorption capacity according to equation 3.1.

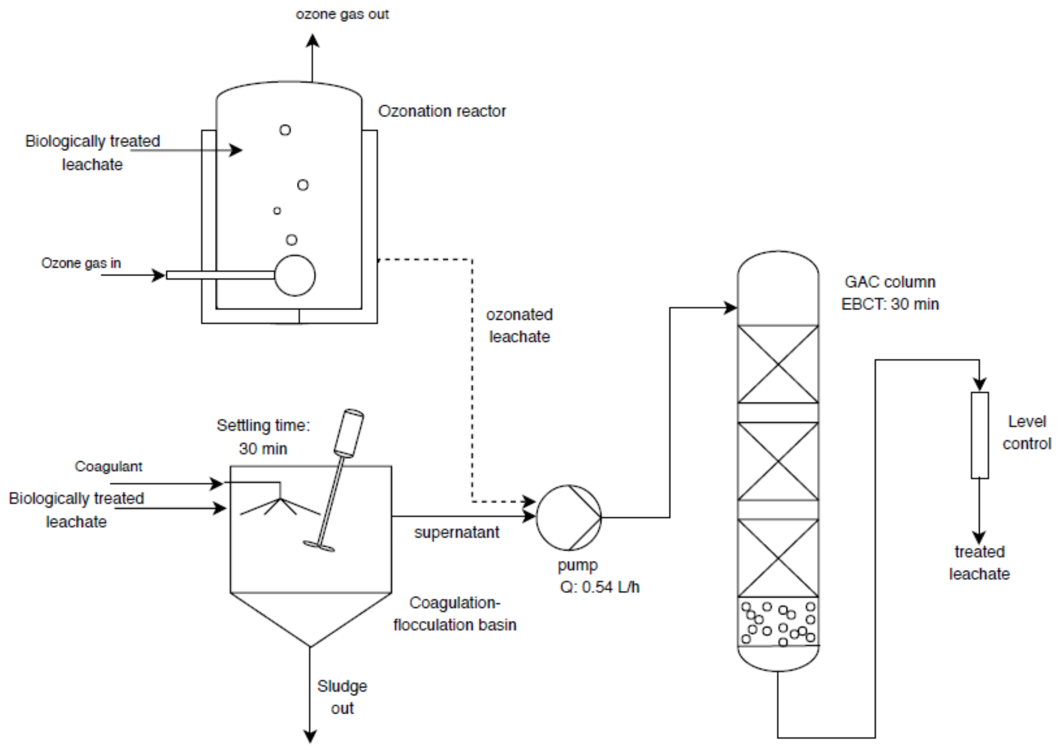


Figure 6.1: Flow diagram of the coupling of ozonation or coagulation-flocculation with granular activated carbon adsorption for post-treatment of biologically treated landfill leachate

6.3 Results and discussion

6.3.1 $FeCl_3$ and PACl performance in the treatment of landfill leachate by coagulation-flocculation

The coagulant dose of $FeCl_3$ and PACl varied from 0.03 – 1.0 mg coagulant /mg initial COD concentration (COD_o). Increasing the concentration of both coagulants consistently improved the COD removal efficiency achieving 58% COD removal at a coagulant concentration of 1000 mg/L (0.72 mg coagulant/mg COD_o) (Figure 6.2). Further increase in $FeCl_3$ concentration up to 1400 mg/L (1 mg $FeCl_3$/mg COD_o) resulted in 66% COD removal, whereas higher PACl concentrations (1400 mg/L, 1 mg PACl/mg COD_o) did decrease the COD removal efficiency to 44%. This could result from re-stabilization of colloidal particles triggered by the increasing coagulant concentration (Vedrenne et al., 2012). Figure 6.2 also shows an increasing α_{254} reduction at higher coagulant concentration (Figure 6.2). For $FeCl_3$, up to 88% α_{254} reduction is noted when the coagulant concentration was 1400 mg/L (1 mg $FeCl_3$/mg COD_o). For PACl, the maximum α_{254} reduction of 72% was achieved already at 1000 mg/L PACl (0.72 mg PACl/mg COD_o). Comparing the results of both parameters, it is clear that coagulation-flocculation is more effective in removing compounds with aromatic groups and carbon to carbon double bonds than in reducing bulk COD, being in agreement with other studies on coagulation-flocculation used for the treatment of leachate and surface waters (Comstock et al., 2010; Lanciné et al., 2008; Zhang and Wang, 2009).

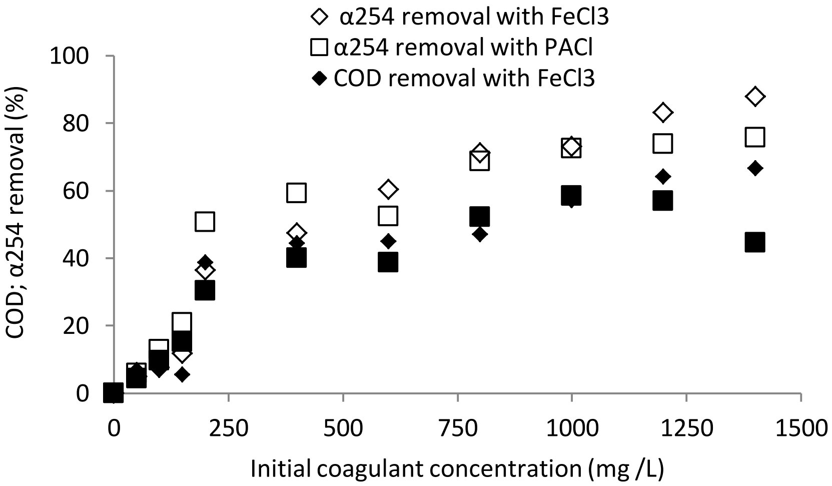


Figure 6.2: Percentage COD and α_{254} reduction for $FeCl_3$ and PACl as a function of coagulant dose (initial conditions: COD 1378 mg/L, α_{254} 8.24/cm, pH 7.9)

The turbidity of leachate treated with $FeCl_3$ changed gradually from 39.5 to 1.1 NTU at the highest coagulant concentration. With PACl, only 200 mg/L (0.15 mg PACl/mg COD_0) was required to reduce the turbidity to 7.2 NTU. A further increase in PACl coagulant concentration did not yield significant changes in turbidity. Given the acidic nature of $FeCl_3$ and PACl (Amokrane et al., 1997), the pH of the leachate samples treated with $FeCl_3$ and PACl at 1400 mg/L (1 mg coagulant/mg COD_o) dropped from 7.9 to 5.4 and 7.5, respectively.

When compared with literature, the obtained coagulation-flocculation results follow reported trends whereby the performance of iron salts is higher than that of aluminum salts. Approximately 70% and 30% COD reduction was achieved when stabilized leachate with 5350 mg/L initial COD was treated with 1000 mg/L (0.18 mg coagulant/mg COD_o) of respectively $FeCl_3$ and $Al_2(SO_4)_3$ without pH control (Tatsi et al., 2003). The result achieved with $FeCl_3$ is much higher than that obtained in this study, which is most probably because of different leachate characteristics. The landfill leachate used by Tatsi et al. (2003) had a very high COD concentration (5350 mg/L) which can be an indication of the big amounts of high molecular weight compounds (humic compounds) present in the leachate. The COD mentioned above is at least 4 times higher than that of the leachate used in this chapter (1378 mg/L), hence the difference in COD removal. Moreover, it is possible that there is also a difference in the molecular weight of humic compounds present in the leachate of Tatsi et al. (2003) and that used in this chapter.

When turbidity is considered, usage of 500 mg Fe^{3+}/L (0.04 mg Fe^{3+}/mg COD_o) resulted in 90.3% turbidity removal. To achieve 97.7% turbidity reduction; 4000 mg/L PACl (0.3 mg PACl/mg COD_o) was required (Marañón et al., 2008).

Several authors have focused on the volume of sludge generated during the treatment of landfill leachate by coagulation-flocculation (Gotvajn et al., 2009; Marañón et al., 2008; Tatsi et al., 2003). However, this does not provide any information on the settle-ability of the generated sludge which is an important parameter when designing secondary units such as clarifiers. Figure 6.3 shows that the SVI of both coagulants first increases and then levels off at higher coagulant concentrations. This might be the result of sweep coagulation which is promoted at high doses, leading to a high flocs concentration (Duan and Gregory, 2003) and SVI. The high SVI of PACl could also be attributed to the presence of the polynuclear species $Al_{13}O_4(OH)_{24}^{7+}$ commonly referred to as Al_{13}. This Al_{13} is one of the hydrolysis products of PACl and consists of a central tetrahedral AlO_4^{5-} surrounded by 12 Al octahedral with shared edges. At high coagulant concentrations, Al_{13} causes colloids and natural organic matter (NOM) to reverse charge and re-stabilize, leading to the formation of small Al_{13}-NOM flocs which cannot be removed easily by settling (Yan et al., 2008) and thus yields a high SVI. A maximum SVI of 154 mL/g and 252 mL/g was achieved when leachate was treated with 1000 mg/L (1 mg coagulant/mg COD_o) $FeCl_3$ and PACl, respectively. When using activated sludge, a SVI below 150 mL/g is an indicator of good settling properties (Janczukowicz et al., 2001). As such, the settle-abilty of the sludge generated by $FeCl_3$ can be considered to be appropriate, whereas PACl generates poorly settling sludge which might be difficult to clarify.

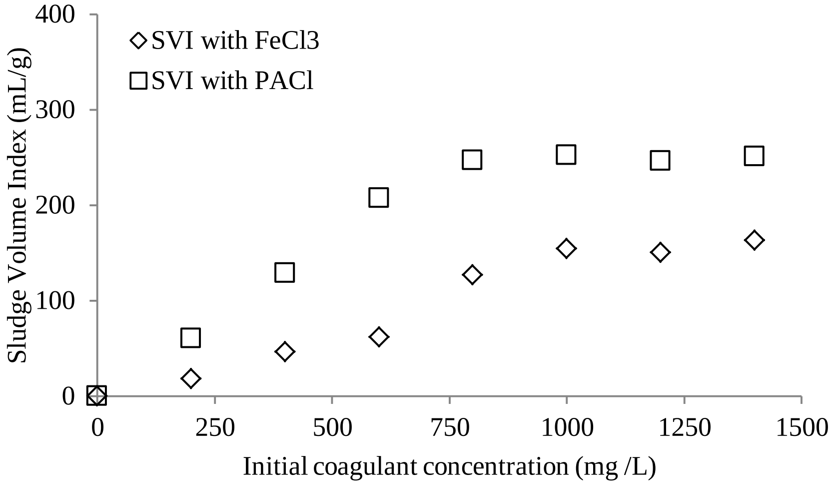


Figure 6.3: Settling characteristics of the sludge produced during $FeCl_3$ and PACl treatment of leachate at different coagulant doses (initial conditions: COD 956 mg/L, pH 7.9)

Given the high percentage of COD and α_{254} removal, high turbidity reductions and the good settling characteristics of sludge generated by $FeCl_3$, the effluent from the $FeCl_3$ process was used in subsequent adsorption studies. A sufficiently high concentration (1200 mg/L, 0.87 mg $FeCl_3$/mg COD_o) was selected to ensure proper COD removal.

6.3.2 Ozonation performance in the treatment of landfill leachate

The initial leachate COD plays an important role in determining the organic matter removal efficiency of ozonation. As the initial leachate COD increases, the percentage COD removal efficiency decreases. This is in agreement with the trend reported in Chapter 5. For instance, after 60 minutes of ozonation, 44% COD reduction was achieved at an initial COD concentration of 112 mg/L while only 5% COD removal was obtained at 1846 mg/L. The limited COD removal at high leachate COD concentration might result from the high amount of recalcitrant compounds and the high concentrations of scavengers such as inorganic carbon which consume produced hydroxyl radicals. The ozonation efficiency - calculated according to equation 3.2 shows no clear relationship with the initial COD concentration in accordance with Chapters 4 and 5. The ozonation efficiency ranged between 0.23 and 0.71 mg COD removed/mg ozone, which is of the same order as the values reported in literature (0.3 – 0.5 mg COD removed / mg ozone) (Tizaoui et al., 2007). Also the percentage α_{254} reduction decreases at higher initial leachate COD concentrations. Up to 77% and 26% α_{254} reduction was achieved at 112 mg/L and 1846 mg/L, respectively. Due to the electrophilic nature of ozone, compounds with aromatic and C=C groups are easily oxidized to UV insensitive and saturated intermediates, which still contribute, however, to the overall COD. This explains why relatively higher α_{254} reductions are observed compared to COD removal (Imai et al., 1998).

6.3.3 Surrogate parameters for the follow up and control of the GAC pretreatment processes

The measurement of common parameters such as COD, total organic carbon (TOC) and dissolved organic carbon (DOC) for organic matter characterization can be time and cost consuming. Therefore, simple and accurate surrogates are required to facilitate a quick monitoring of the organic matter concentration during leachate treatment. In this chapter, UV-VIS absorbance was explored as a possible surrogate measurement for COD. However, other methods such as fluorescence excitation emission matrix are available as will be discussed later (Chapter 8 and 10). Absorbance in the near UV (200 – 380 nm) and at 465 nm (representative wavelength for the visible region) were correlated with COD concentrations of leachate treated with $FeCl_3$ and PACl coagulation-flocculation (Campagna et al., 2013). For $FeCl_3$, over 0.90 R^2 values (n = 12) were obtained when the COD concentration was correlated with UV absorbance at 254, 265 and 320 nm (Figure 6.4).

For PACl, also a reasonable correlation (R^2 = 0.89; n= 12) was achieved at 254 and 265 nm (results not shown). Overall, Figure 6.4 shows the potential of α_{254} as a viable surrogate parameter for COD concentrations in coagulated leachate. However, at higher wavelengths (465 nm), a rather low correlation (R^2 = 0.85 for $FeCl_3$ and R^2 = 0.72 for PACl) and small changes in absorbtion coefficient indicate that compounds absorbing light in this region are poorly removed by coagulation-flocculation compared to those in the UV region.

The potential of α_{254} as a surrogate for COD in treated leachate is confirmed by considering the results obtained during ozonation. Figure 6.5 shows that COD concentrations correlate well with α_{254} (R^2 = 0.89, n = 38). The intercept of the trend line suggest that elimination of bulk organic matter in the leachate starts at the same time as the reduction of α_{254} (Gerrity et al., 2012).

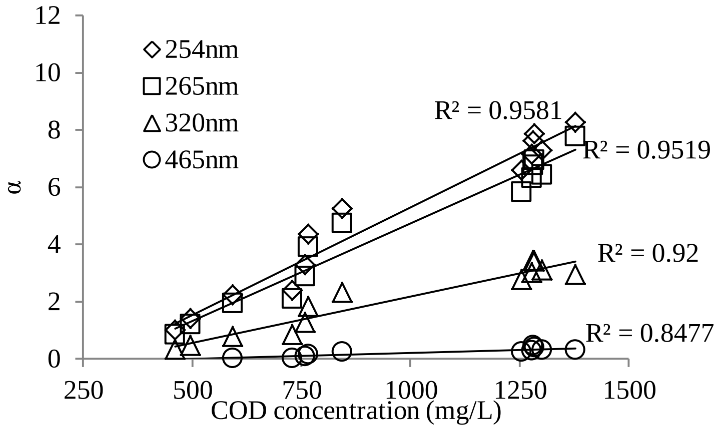


Figure 6.4: Correlation between absorption coefficient at various wavelengths and COD concentration for $FeCl_3$ treated leachate (initial conditions: COD 1378 mg/L, α_{254} 8.24 cm-1 pH 7.9)

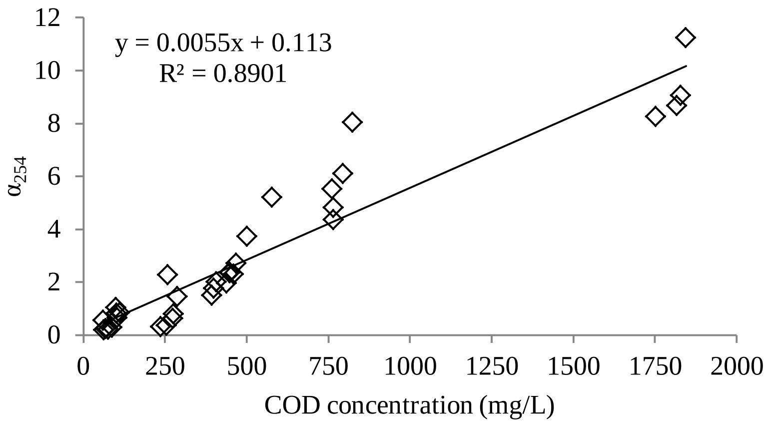


Figure 6.5: Correlation between α_{254} and COD concentrations for ozonated leachate (ozonation time: 60 minutes)

6.3.4 Post-treatment of coagulated and ozonated effluent using granular activated carbon adsorption

Table 6.1 depicts the COD and α_{254} removal efficiencies obtained when untreated (biologically treated leachate), coagulated and ozonated leachate are further treated using GAC adsorption. Untreated landfill leachate contains high molecular weight compounds which do not fit in the pores of the GAC as a result of their size or structural orientation. This leads to a limited adsorption capacity, as exemplified by only 20% COD and 8% α_{254} reduction achieved after 3 hours of GAC treatment (6 BV). The GAC also showed fast breakthrough when loaded with untreated landfill leachate, i.e. after 30 minutes and 45 minutes, corresponding to 1.0 and 1.6 BV, with respect to COD concentration and α_{254} respectively. This is 9 and 7 times faster than the COD and α_{254} breakthrough of ozonated effluent, and 2 and more than 7 times faster than the COD and α_{254} breakthrough of $FeCl_3$ coagulated leachate (Figure 6.6 and 6.7). The above GAC breakthrough time of COD from ozonated leachate are higher than those of the Chapter 5. This is because the biologically treated leachate was ozonated at a higher dose (0.48 mg O_3/mg CODo) and the effluent COD concentration of the ozonated effluent is much lower than that in Chapter 5 (samples 3 and 6)

No significant difference was observed in COD removal when treating the landfill leachate by only ozonation or coagulation-flocculation (Table 6.1). Comparable to Chapter 5, 4BV GAC adsorption of leachate with a low COD concentration resulted in 74%. Up to 3 hours GAC adsorption (6 BV) of ozonated effluent resulted in a COD reduction of 66%, whereas the COD level in the coagulated effluent decreased by 33% by subsequent adsorption. Moreover, the GAC column operated approximately 4.5 times longer before COD breakthrough when treating ozonated rather than coagulated leachate. The overall performance of the ozonation-adsorption treatment in terms of COD removal (i.e. 77% removal after 3 hours of GAC operation) is better than with the coagulation-flocculation and adsorption sequence where the overall removal was 53% (Table 6.1). After about 6 hours (12 BV) of GAC adsorption, however, comparable COD removal was obtained for untreated, coagulated and ozonated leachate in term of both removal efficiency (average 18 %, Figure 6.6) and removal rate (63 mg/L.hr, Figure 6.8). The total adsorption capacity of the GAC for COD, expressed by q_{exp} determined from equation 3.3, was the highest (3.6 mg/g) for ozonated leachate compared to 2.3-2.4 mg/g for both untreated and coagulated leachate (Table 6.2). This can be explained by the production of smaller and more easily adsorbable compounds during ozonation. The small size of the ozonation products increases their surface area for adsorption and their accessibility to the GAC micropores (Ramirez Zamora et al., 2000). In contrast, coagulation-flocculation is only efficient in removing humic acids, whereas fulvic acids remain in the leachate still reducing the adsorption capacity of GAC.

In terms of α_{254}, ozonation applied as a single treatment is slightly more efficient than coagulation-flocculation (71 versus 60% reduction). However, GAC treatment of the ozonated effluent resulted in a relatively low additional α_{254} reduction (63%) after 3 hours (6 BV) and breakthrough after 12 BV. Adsorption of coagulated effluent resulted in a nearly complete (99%) α_{254} removal and no breakthrough was observed within the experimental period neither with $FeCl_3$ (Figure 6.7) nor with PACl (data not shown). GAC adsorption is thus more efficient in reducing α_{254} from leachate pretreated with coagulation-flocculation than with ozonation. Though ozonation of bulk organic matter leads to the production of smaller compounds which are easily adsorbed (Ramirez Zamora et al., 2000), the by-products from oxidation of aromatic sites and carbon to carbon double bonds are very hydrophilic thus poorly adsorbed by GAC. On the contrary, infra-red analysis of the chemical composition of the coagulated effluent reveals the presence of amines and aliphatic compounds (Monje-Ramirez and Orta de Velásquez., 2004). Hydrophobic compounds are easily adsorbed onto GAC hence better reduction of α_{254} from coagulated effluent.

Table 6.1: Percentage COD and α_{254} removal obtained with ozonation, coagulation-flocculation and 3 hours of GAC adsorption both as single and combined treatments

Treatment	**Single treatment**			**Single treatment + GAC Adsorption**		**% Total removal**
	Influent	**Effluent**	**% removal**	**Effluent**	**% removal by GAC only**	
COD (mg/L)						
Biologically treated leachate	612	-	-	485	20	20
Coagulated leachate - $FeCl_3$	612	428	30	287	33	53
Ozonated leachate	578	394	31	133	66	77
α_{254} (cm^{-1})						
Biologically treated leachate	5.51	-	-	5.05	8	8
Coagulated leachate - $FeCl_3$	5.51	2.18	60	0.02	99	99
Ozonated leachate	5.19	1.49	71	0.54	63	90

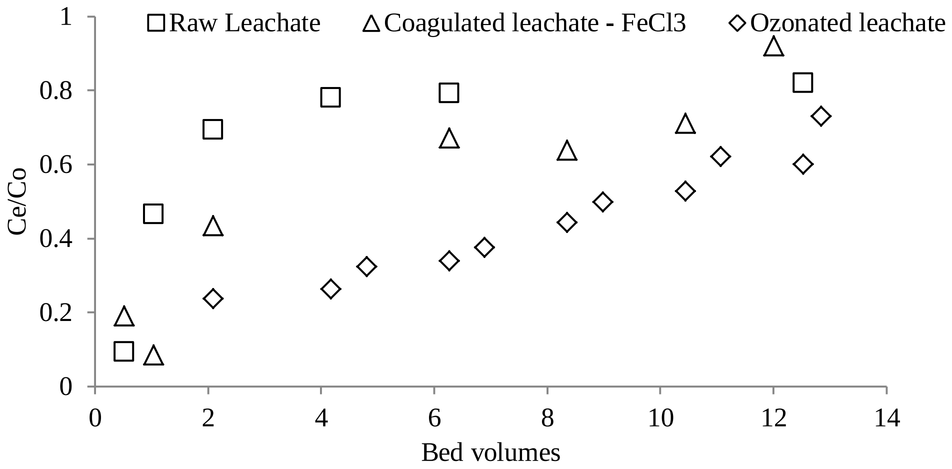


Figure 6. 6: GAC breakthrough curves for COD in biologically treated landfill leachate, FeCl3-coagulated effluent and ozonated effluent. (column influent COD: 612 mg/L for biologically treated landfill leachate, 428 mg/L for coagulated effluent, 394 mg/L for ozonated effluent; coagulant concentration: 1200 mg/L (1.96 mg $FeCl_3$/mg CODo); ozone dose 0.48 mg O_3/mg CODo)

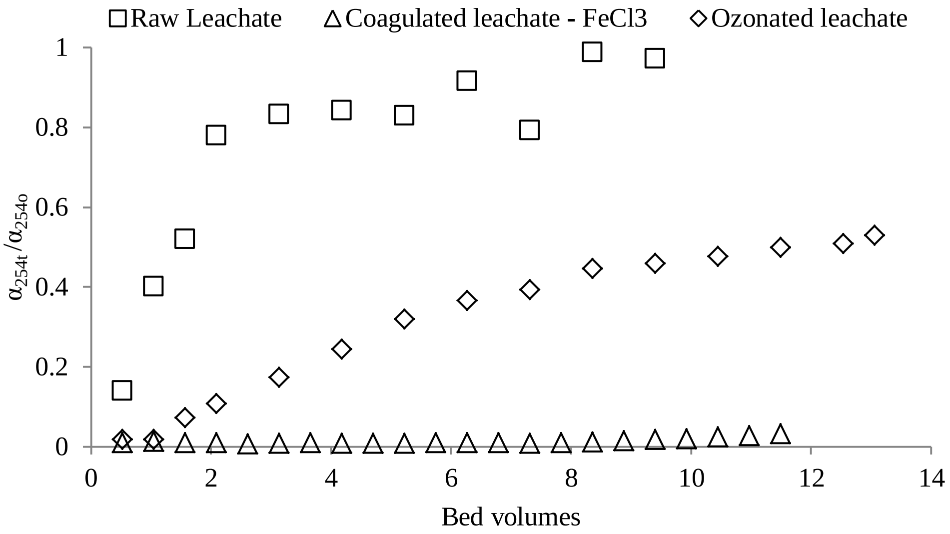


Figure 6.7: GAC breakthrough curve for α254 in biologically treated laandfill leachate, coagulated effluent and ozonation effluent . (Column influent α_{254}: 5.51 for biologically treated landfill leachate, 2.18 for coagulated effluent, 1.49 for ozonated effluent; coagulant concentration: 1200 mg/L (1.96 mg $FeCl_3$/mg COD_o), ozone dose 0.48 mg O_3/mg COD_o)

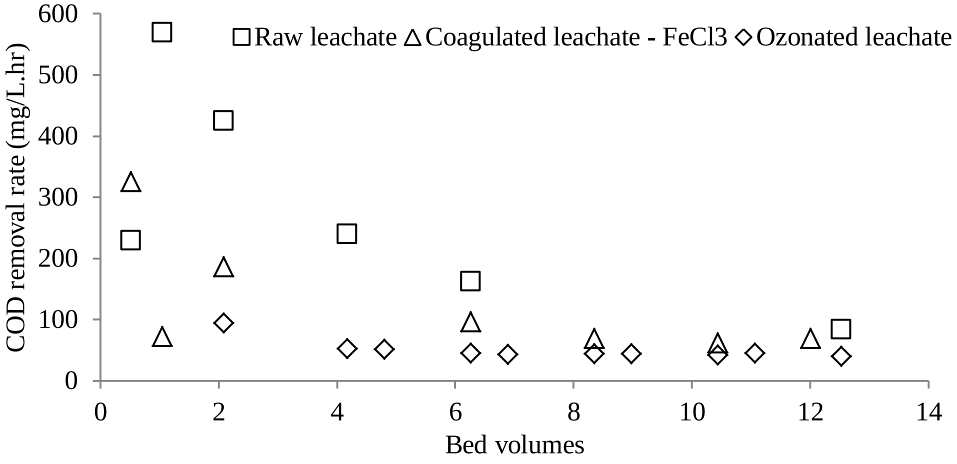


Figure 6.8: COD removal rate in the GAC column for biologically treated landfill leachate, coagulated effluent and ozonation effluent (column influent COD: 612 mg/L for biologically treated landfill leachate, 428 mg/L for coagulated effluent, 394 mg/L for ozonated effluent; coagulant concentration: 1200 mg/L (1.96 mg $FeCl_3$/mg CODo), ozone dose 0.48 mg O_3/mg CODo)

Successful optimization of the design and operation conditions of a fixed bed activated carbon column requires sufficient information on the breakthrough behavior and the adsorption capacity of GAC. However, the experimental determination under varying conditions is expensive and time consuming (Xu et al., 2013) and necessitates the application of mathematical models. In the present study, the Thomas model is used to determine the adsorption capacity and rate constant of the activated carbon column (Xu et al., 2013). Next to that, the Yoon-Nelson model is used to determine breakthrough time due to its simple nature not requiring detailed data on adsorbent and adsorbate characteristics (Xu et al., 2013)

The Thomas model assumes both Langmuir kinetics for equilibrium and second order reversible reaction kinetics (Khraisheh et al., 2010). The Thomas model is adequately described by the following equation

$$In\left(\frac{Co}{Ce}-1\right)=\frac{k_{TH}*\,q_{TH}*W}{Q}-k_{TH}*Co*t \qquad equation\ 6.1$$

where C_o is the influent COD concentration (mg/L), C_e the effluent COD concentration at a given time (mg/L), k_{TH} the Thomas rate constant (mL/mg.hr), q_{TH} the adsorption capacity (mg/g) as predicted by the

Thomas model, W is the mass of GAC (g), t is the flow time (hr), Q is the volumetric flow rate (mL/minute). A linear plot of In (C_o/C_e -1) versus time was used to determine the values of q_{TH} and k_{TH}.

The Yoon-Nelson model is a concise model which assumes that the decrease in probability of an adorbate to be adsorbed is proportional to the probability of its adsorption and breakthrough from the adsorbent (Xu et al., 2013). The Yoon-Nelson model is described by

$$In\left(\frac{Ce}{Co-Ce}\right) = k_{YN} * t - \tau * k_{YN} \quad equation\ 6.2$$

where k_{YN} is the Yoon-Nelson rate constant (1/hr), τ is the time (hr) required to reach breakthrough concentration. A linear plot of In (C_e/C_o-C_e) versus time was used to determine k_{YN} and τ.

Considering the results presented in Table 6.2, the Thomas model predicts that the GAC adsorption capacity for COD improves when leachate is pretreated by coagulation-flocculation and particularly ozonation. A 4 and 1.3 times higher adsorption capacity is obtained for ozonated and coagulated leachate respectively compared to untreated leachate. The q_{exp} and q_{TH} for untreated leachate are in good agreement. On the contrary, the q_{TH} value for ozonated and coagulated effluent deviated from q_{exp} by a factor of 2.4 and 1.5 respectively. During adsorption, other processes such as interphase mass transfer and axial dispersion might occur. This might limit the potential of Thomas model to predict the adsorption capacity of GAC for COD, as is shown by the low R^2 values for untreated and coagulated leachate and deviation between q_{exp} and q_{TH} value for ozonated and coagulated effluent. (Khraisheh et al., 2010).

According to the Yoon-Nelson model, pretreatment of landfill leachate before GAC adsorption results in longer breakthrough times also as experimentally seen in Chapter 5. The breakthrough time of the GAC for COD removal in ozonated leachate is a factor 4 to 5 longer (11.5 BV versus 2.5 BV, Table 6.2) than with untreated leachate. Meanwhile, the breakthrough time of GAC for COD increased by a factor of 1.8.

The improvement as a result of using coagulation-flocculation is higher than that reported by Ramirez Zamora et al. (2000). Furthermore, in contrast to Ramirez Zamora et al. (2000) our study found ozonation – an AOP better in increasing the breakthrough time of GAC than coagulation-flocculation. The Yoon-Nelson model also suggests that the rate at which the GAC column removes COD from the ozonated effluent was lower (0.27 hr^{-1}) than that of the untreated leachate (1.03 hr^{-1}). This is in agreement with the results shown in Figure 6.8, where the COD removal rate of the ozonated effluent is consistently the lowest among the three samples. This might be attributed to the differences in influent concentrations. A high influent COD concentration increases the concentration gradient between the bulk solution and the adsorbent. This creates a large driving force that increases the flux of molecules from the leachate to the adsorption sites hence, the high COD removal rate (Sivakumar and Palanisamy, 2009; Sugashini and Begum, 2013).

Table 6.2: Thomas and Yoon-Nelson column kinetic parameters for GAC adsorption of COD from coagulated and ozonated effluent

	Initial COD concentration into the column (mg/L)	**q_{exp} (mg/g)**	**Thomas Model**			**Yoon-Nelson**			
			q_{TH} (mg/g)	**Rate constant k_{TH} (mL/mg.hr)**	**R^2**	**τ (hr)**	**τ (Bed volumes)**	**Rate constant k_{YN} (hr^{-1})**	**R^2**
Biologically treated leachate	612	2.3	2.82	1.69	0.61	1.2	2.5	1.03	0.61
Coagulated leachate – FeCl3	428	2.4	3.59	2.17	0.73	2.1	4.4	0.93	0.73
Ozonated Leachate	394	3.6	8.64	0.68	0.91	5.5	11.5	0.27	0.91

6.4 Conclusions

The present study clearly shows the added value of combined treatment trains for the purification of biologically stabilized leachate. While removal efficiencies with GAC adsorption as a single technique did not exceed 8% and 20% for α_{254} and COD, respectively, the organic matter removal from landfill leachate could be clearly improved by adding an ozonation or coagulation-flocculation step before GAC.

Overall removal of 99% α_{254} and 53% COD was achieved by applying $FeCl_3$ coagulation-flocculation prior to GAC adsorption. Coagulation-flocculation with $FeCl_3$ was found to be more favorable than with PACl as it showed higher COD, α_{254} and turbidity removal next to better settling characteristics of the produced sludge. Ozonation as a single treatment could only remove 31% of COD. However, up to 77% COD removal was obtained with an ozonation/GAC sequence.

Experimental and modeled data revealed that pretreatment of leachate before GAC polishing increases both the adsorption capacity and operation time of a GAC column toward COD removal. Ozonation of leachate as a pretreatment step improved the adsorption capacity and operation time of a GAC column toward COD four folds. For coagulation-flocculation, the adsorption capacity and breakthrough time were extended by a factor of 1.2 and 1.7 respectively. This result is of main importance for the cost-effective implementation of GAC-based treatment strategies for high strength landfill leachate. Since longer operation times translate into low GAC consumption hence less operation costs.

Chapter 7

Removal of organic matter and ammonium from landfill leachate through different scenarios: operational cost evaluation in a full-scale case study of a Flemish landfill

After:

Violet Oloibiri, Michael Chys, Stijn DeWandel, Kristof Demeestere, Stijn W. H. Van Hulle (2017). Removal of organic matter and ammonium from landfill leachate through different scenarios: operational cost evaluation in a full-scale case study of a Flemish landfill. Journal of Environmental Management, 203, 774 – 781

Contribution of Violet Oloibiri: performing some of the experiments used in this chapter and writing the manusript

Abstract

Several scenarios are available to landfilling facilities to effectively treat leachate at the lowest possible operating cost. In this study, the performance of various leachate treatment sequences to remove COD and nitrogen from a leachate stream and the associated cost are presented. The results show that, to achieve 100% nitrogen removal, autotrophic nitrogen removal (ANR) or a combination of ANR and nitrification – denitrification (N-dN) is more cost effective than using only the N-dN process (0.58 €/m^3) without changing the leachate polishing costs associated with granular activated carbon (GAC). Treatment of N-dN effluent by ozonation or coagulation-flocculation led to the reduction of the COD concentration by 10% and 59% respectively before GAC adsorption. This reduced GAC operating costs and subsequently reduced the overall operating costs by 7% (ozonation) and 22% coagulation-flocculation. On the contrary, using fenton oxidation to reduce the COD concentration of N-dN effluent by 63% increased the overall operating costs by 3%. Leachate treatment sequences employing ANR for nitrogen removal followed by ozonation or fenton or coagulation-flocculation for COD removal and final polishing with GAC are on average 33% cheaper than a sequence with N-dN + GAC only. When ANR is the preceding step and GAC the final step, choice of AOP i.e., ozonation or fenton did not affect the total operating costs which amounted to 1.43 (ozonation) and 1.42 €/m^3 (fenton). In all the investigated leachate treatment trains, the sequence with ANR + coagulation-flocculation + GAC is the most cost effective with an operating cost of 0.94 €/m^3.

7.1 Introduction

Landfilling remains the primary disposal method for municipal solid waste in developed and developing countries (Tizaoui et al., 2007). As a result of ground water intrusion, rainfall percolation and moisture present in the waste, deposits of toxic waste waters called landfill leachate are generated. Release of this leachate into the environment without proper treatment poses considerable risks to human and ecosystem health. The European Union council directive of 1999/31/EC requires landfill operators to undertake proper leachate treatment during the entire life cycle of a landfill to prevent any possible negative effects to the environment (Council of the European Union, 1999). In Flanders (the Northern part of Belgium), this EU directive is reflected in Flemish environmental regulations VLAREM II.

Several conventional as well as advanced treatment processes have been tested and are used to treat leachate (Chapter 1) To meet the strict quality standards for the direct discharge of leachate into surface water, it is widely accepted that a combination of chemical (coagulation-flocculation, advanced oxidation processes (AOPs), physical (adsorption, membrane filtration, air stripping) and biological steps are to be used as already exemplified in Chapter 5 and 6. Often, the potential techniques for treatment of landfill leachate are evaluated based on their ability to reduce the pollutant load. This is clearly seen in the literature review Chapter 2 and other review papers (Kurniawan et al., 2006b; Renou et al., 2008). Other important factors used to evaluate the suitability of a technique for treatment of landfill leachate include available operational experience, energy requirements, process reliability and related environmental impacts (Van Hulle et al., 2010). Regardless of the aforementioned criteria, the most crucial factor used in selection of the best available techniques is cost (Van Hulle et al., 2010). The total costs for landfill leachate treatment include capital and operating costs. In lab scale leachate studies, focus is mainly put on operating costs to assess the economic implication of implementing a given technology. This is because operation and maintenance of a leachate treatment sequence accounts for 40-60% of total investments costs (IPPC, 2007). This constitutes 50 – 67% of total landfilling costs (IPPC, 2007). Therefore, the importance of an economic assessment of the operating costs of the proposed leachate trains cannot be over emphasized. Given the importance of costs involved in operating a landfill leachate treatment plant, this PhD thesis focused on operating costs only.

On a large scale, landfill leachate treatment costs are directly affected by environmental concerns (Figure 7.1) (Bisung et al., 2015). The environmental concerns are in turn driven by the available technology and its efficiencies, operating conditions and environmental discharge standards. These three factors directly affect the quality of landfill leachate discharged into the environment and impose a cost to the treatment of landfill leachate.

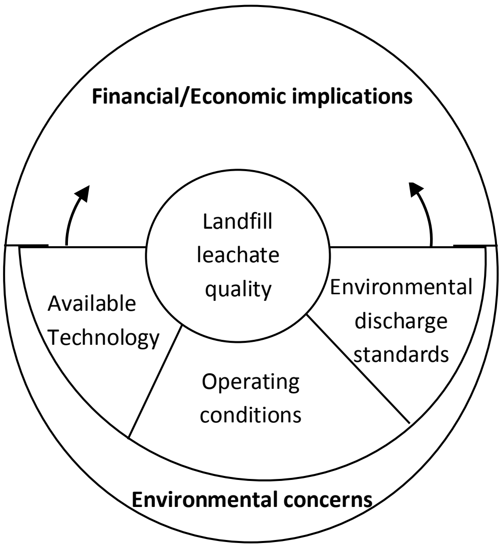


Figure 7.1:The factors directly affecting landfill leachate quality and their relationship with environmental concerns and costs

In view of their economy, several treatment plants incorporate a biological step as initial treatment step (Chapter 2, (Behzad et al., 2011). Indeed, a survey of 166 leachate treatment plants by (Alvarez-Vazquez et al. (2004) showed that 72% of the schemes had a biological method such as aerobic lagooning, activated sludge, and up-flow anaerobic sludge blanket. These biological processes make use of the nitrification-denitrification (N-dN) mechanism for nitrogen removal. Micro-organisms involved in N-dN processes are readily hampered by high concentrations of ammonium (500 – 2000 mg/L) present in leachate(Kjeldsen et al., 2002). For instance, after a long hydraulic residence time of 20 days, only 20% ammonium could be removed during N-dN in a sequencing batch biofilter granular reactor (Di Iaconi et al., 2006). Besides, additional carbon sources are required to aid the nitrification-denitrification process (Chys et al., 2015a). As an alternative biological method, leachate treatment facilities are now employing full autotrophic nitrogen removal (ANR) processes (Gao et al., 2015a). Depending on the operating conditions, ANR processes can achieve up to 90% nitrogen removal (Anfruns et al., 2013). This is evidently exemplified by the studies in Chapter 5 where by an average removal of 85.9% of total nitrogen was achieved. Moreover, compared to nitrification-denitrification methods, ANR is known to consume 60% less oxygen and 40% less or no organic carbon and is therefore characterized by less operational costs (Van Hulle et al., 2010). On the other hand, operational problems and long start up periods of ANR processes (Van Hulle et al., 2010) have led to the use of chemical techniques such as struvite precipitation. Ozturk et al. (2003) showed that 90% of ammonium can be removed from landfill leachate with an influent ammonium concentration of 2240 mg/L. The related cost amounts to 4.45 €/m^3 after considering the economic value of the struvite.

For removal of non-biodegradable (organic) matter present in the effluent of biological techniques, generally activated carbon adsorption is used. However, this also results in high operating costs as a large amount of activated carbon is necessary to remove the recalcitrant COD in the leachate. Difficulties and high costs associated with regeneration of used activated carbon further limit its application in landfill leachate treatment. Advanced oxidation processes (AOPs) are reported as the most effective method in degradation of recalcitrant organic matter, and hence pose a possible alternative to activated carbon (Anfruns et al., 2013; Kurniawan et al., 2006d). Anfruns et al. (2013) reported up to 98% COD and 87% total nitrogen removal when an Anammox process is coupled with photo- fenton in treatment of landfill leachate. However, the chemical and energy requirements for

AOPs are very high with respect to the total operating costs (Table 7.1). In the combined treatment of landfill leachate using sequencing batch reactor (SBR), coagulation-flocculation, fenton and up-flow biological aerated filters, 30% of the operating costs were attributed to reagents for the fenton step (Li et al., 2009). Reagents for the photo- fenton step in the study of Anfruns et al. (2013) cost 6.61 €/m^3, which is 92% of the total operating costs. A parallel configuration with ozonation used 4.04 €/m^3 for ozone production from a total operating cost of 7.72 €/m^3 (Anfruns et al., 2013). Efforts to lower the energy costs of AOPs, have focused on natural solar energy as a cheaper and sustainable alternative energy source (De Torres-Socías et al., 2015; Rocha et al., 2011; Silva et al., 2016). Based on UV radiation distribution in certain geographical locations, the sole use of solar radiation is not feasible as the land requirements for installing compound parabolic collectors (CPCs) is impractical (43,173 m^2) where land is scarce and expensive (Silva et al., 2016). Furthermore, CPCs are expensive (349 €/m^2) and constitute a cost of at least 24% of the total unitary (€/m^3) operating costs (De Torres-Socías et al., 2015). Table 7.1 gives a summary of the operating costs implications for adopting different technologies for COD removal (unless otherwise stated) from landfill leachate.

The importance of cost in treatment of landfill leachate is clearly seen in Gupta and Singh (2007). In this study, a cheap treatment sequence (1.12 €/m^3) with a methane phase bed reactor, leachate recycling unit and soil column is recommended for use as opposed to one with an activated carbon (2.8 €/m^3) as the final polishing step; which is however more effective in COD, BOD_5 and suspended solids removal. This illustrates the need to balance economic and technical performance criteria that often is required in practice.

Table 7.1: The operating costs of treatment of landfill leachate using different technologies either as a single step or combined, to achieve the indicated organic carbon removal.

Treatment process	**Influent COD (mg/L)**	**% COD removal**	**Chemical costs (€/m^3)**	**Energy costs (€/m^3)**	**Sludge disposal costs (€/m^3)**	**Total operating costs (€/m^3)**	**Reference**
Physical-chemical processes							
Coagulation + GAC	23700	99				16.56	Kılıç et al. (2007)
Lime treatment + air stripping	23700	19				4.6	Kılıç et al. (2007)
UF + RO (BW) membranes	1700	99				0.97	Ozturk et al. (2003)
UF + RO (SW) membranes	3000	89				0.74	Ozturk et al. (2003)
Advanced oxidation processes							
O_3	545(TOC)	59(TOC)	105	272		377	Bauer and Fallmann (1997)
O_3	743	23-40				11.0-11.7	Cortez et al. (2010)
O_3	340	18 – 49				5.52 – 6.17	Cortez et al. (2011)
O_3/H_2O_2	340	27 – 72				5.8 - 6.1	Cortez et al. (2011)
O_3/H_2O_2	743	30 – 63				11.7-12.5	Cortez et al. (2010)
$O_3/H_2O_2/Fe^{2+}$	2180	64				5.9	Amr et al. (2013)
O_3/UV	545(TOC)	61(TOC)	69.7	272		342	Bauer and Fallmann (1997)
UV/H_2O_2	545(TOC)	13(TOC)	5.96	136		142	Bauer and Fallmann (1997)
Fenton	340	46				1.3	Cortez et al. (2011)
Fenton	1403	79				2.85	Canizales et al. (2013)
photo- fenton	545(TOC)	60(TOC)	6.11	56.7		62.8	Bauer and Fallmann (1997)
photo- fenton	6200	98	6.66	0.02	0.5	7.18	Anfruns et al. (2013)
photo- fenton	6200	90	4.15	0.009	0.5	4.66	Anfruns et al. (2013)
Solar photo- fenton	545(TOC)	60(TOC)	6.11	0		6.11	Bauer and Fallmann (1997)
Solar photo- fenton	11 (DOC)	27 (DOC)	31	0.1		31.1	De Torres-Socías et al. (2015)
Coagulation-flocculation + O_3	6200	91	0.93	4.04	2.75	7.72	Anfruns et al. (2013)
US+ O_3	6660	14.7	0.0	15.5		15.5	Poblete et al. (2017)
US + O_3/H_2O_2	6660	33.8	18.6	15.5		34.1	Poblete et al. (2017)

Table 7.I continued

Treatment process	**Influent COD (mg/L)**	**% COD removal**	**Chemical costs (€/m^3)**	**Energy costs (€/m^3)**	**Sludge disposal costs (€/m^3)**	**Total operating costs (€/m^3)**	**Reference**
Solar/O_3	6660	27.9	0.0	3.2		3.2	Poblete et al. (2017)
Solar/O_3/H_2O_2	6660	34.4	24.7	3.2		28.0	Poblete et al. (2017)
AC + US+ O_3	6660	48.6	41.4	30.5		71.9	Poblete et al. (2017)
AC + US + O_3/H_2O_2	6660	67	60.0	30.5		90.5	Poblete et al. (2017)
AC + Solar/O_3	6660	59	41.4	12.1		53.5	Poblete et al. (2017)
AC + Solar/O_3/H_2O_2	6660	70	66.1	18.2		84.4	Poblete et al. (2017)
Combined biological and chemical processes							
SBBGR + Solar photo- fenton	2900	94.8	2.76	0.84	0.53	4.1	Cassano et al. (2011)
SBBGR + Solar photo- fenton	2900	85	1.89	0.84	0.53	3.26	Cassano et al. (2011)
SBBGR + O_3 + Solar photo-fenton	2900	95.3	3.28	1.18	0.36	4.8	Cassano et al. (2011)
SBBGR + O_3	2900	95	3.36	2.18	0.2	5.7	Cassano et al. (2011)
SBBGR + O_3	2900	85	1.86	1.18	0.2	3.24	Cassano et al. (2011)
SBBGR + O_3	2900	82				4	Di Iaconi et al. (2011)
SBR + Solar photo- fenton	1200 (DOC)	57(DOC)				14.7	Silva et al. (2016)
SBR + Solar photo- fenton	1200 (DOC)	80(DOC)				11.5	Silva et al. (2016)
SBR + coagulation-flocculation + fenton + UBAF	3000	97	1.26	1.22		2.48	Li et al. (2009)
Struvite + RAS	5700(SCOD)	24(SCOD)	2.01	0.43	0.93	3.37	Kochany and Lipczynska-Kochany (2009)
fenton + RAS	5700(SCOD)	66(SCOD)	7.22	0.34	0.52	8.11	Kochany and Lipczynska-Kochany (2009)
MPB + LRU + Chemical precipitation	4016	95				4.90	Gupta and Singh (2007)
MPB + LRU + Aerated lagoon	4016	97				0.84	Gupta and Singh (2007)
MPB + LRU + Soil column	4016	98				1.12	Gupta and Singh (2007)
MPB + LRU + Activated carbon	4016	99				2.8	Gupta and Singh (2007)

Conditions such as seasonal variations in leachate quality, which might become even more pronounced as a result of climatological changes, can have a significant impact on leachate treatment costs. For instance, the chemical oxygen demand concentration in leachate increases on average from 4539 mg/L (wet season) – 9004 mg/L (dry season) (Kawai et al., 2012). This in turn increases the chemical demand in case of chemical treatment and consequently increases the operational costs. A discussion of how the chemical demand affects costs can be found in Chapter 10. Also the implementation of more stringent environmental discharge standards impose great costs for treatment (H. Li et al., 2009). This is clearly shown by the study of Cassano et al. (2011). The operational costs for treatment of leachate (initial COD 2900 mg/L) using SBBGR and solar photo-fenton to a discharge limit of 500 mg/L was lower (3.2 instead of 4.1 €/m^3) than that required to treat the same leachate to meet a discharge limit of 160 mg/L. This trend is confirmed by Silva et al. (2016) who reported total operating costs of 7.2 and 11.7 €/m^3 for treating leachate using solar photo-fenton to discharge standards of 1000 and 150 mg/L, respectively. In essence a small increment in treatment costs (38%) can improve COD removal by 85% and help landfilling facilities avoid costs associated with discharging treated leachate to sewers for further treatment (Silva et al., 2016).

Landfill operators have minimum or no control over strict discharge standards and seasonal variations. Therefore, to alleviate the environmental concerns, associated with landfill leachate, they must constantly review their treatment processes and in certain cases incorporate other techniques or totally overhaul their system. Notwithstanding, the choice must allow the operators to comply with the environmental discharge standards at the lowest possible costs. From this perspective, this Chapter presents the results of a case study investigating how the choice of technology affects the leachate quality and treatment costs. Though an ideal economic assessment would include capital costs, for simplicity of the study, only operating costs associated with chemicals, energy and sludge disposal are taken into account. Labour was not included in the operating costs calculations since it was assumed that each integrated set up would need more or less the same amount of personel.

Three possible scenarios consisting of eight treatment sequences (Figure 7.2) are considered, using the leachate treatment scheme applied at IMOG (Intergemeentelijke Maatschappij voor Openbare Gezondheid) (Chys et al., 2015a; Gao et al., 2015a) - a landfill facility in Flanders - as a starting model. In scenario 1, the effect of complete or partial replacing the classic nitrification-denitrification (N-dN) by autotrophic nitrogen removal (ANR) specifically partial nitritation/anammox, while keeping the subsequent GAC-step is investigated. Scenario 2 investigates the incorporation of additional techniques, namely ozonation, fenton and coagulation-flocculation, into the IMOG treatment chain. In scenario 3, the potential of a sequence of ANR, followed by either ozonation or fenton oxidation or coagulation-flocculation and granular activated carbon adsorption to treat stabilized landfill leachate, is evaluated.

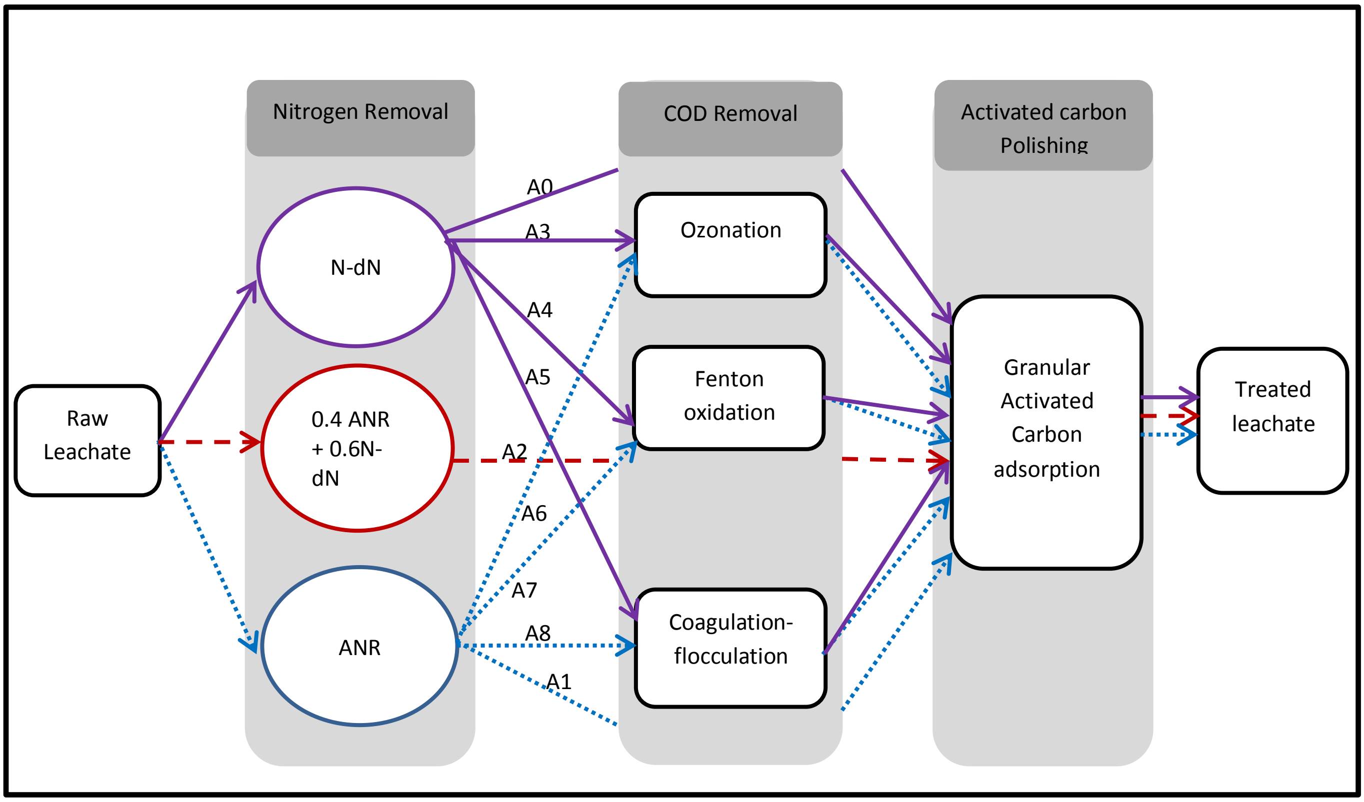


Figure 7. 2: Possible leachate treatment sequences for treatment of raw landfill leachate

7.2 Methodology

7.2.1 Landfill leachate characteristics

The leachate considered in this study is that from IMOG. Characteristics of the raw and biologically treated leachate reported in Table 3.1

7.2.2 Experimental design and cost evaluation

Data used in this study are selected from experimental studies carried out previously by our research group, which are described below. A total of eight leachate treatment sequences (Figure 7.2; Table 7.2) are described and compared with the existing sequence at IMOG. The treatment sequence as it is installed now at IMOG is denoted as A0. Apart from their good performance in pollutant removal, the alternative techniques investigated (i.e., ANR, ozonation, fenton and coagulation-flocculation) were selected based on site specific situations such as availability of space and infrastructure.

Table 7.2: Leachate treatment sequences described in this study

Scenario	Alternative	Sequence
	Alternative 0 (A0)	N - dN + GAC
Scenario 1	Alternative 1 (A1)	ANR + GAC
	Alternative 2 (A2)	ANR + N - dN + GAC
Scenario 2	Alternative 3 (A3)	N – dN + Ozonation + GAC
	Alternative 4 (A4)	N – dN + fenton oxidation + GAC
	Alternative 5 (A5)	N – dN + coagulation-flocculation + GAC
Scenario 3	Alternative 6 (A6)	ANR + Ozonation + GAC
	Alternative 7 (A7)	ANR + fenton + GAC
	Alternative 8 (A8)	ANR + coagulation-flocculation + GAC

In the first scenario; ANR is employed in complete or partial nitrogen removal from landfill leachate in place of N-dN. Descriptions of the ANR lab scale set-up and varying operating conditions are outlined in the methodology Chapter 3. In this study, cost calculations of the biological processes consider the methanol, electricity consumed during aeration only and sludge generated.

In scenario 2 and 3, N-dN or ANR effluent is treated separately using ozonation, fenton oxidation and coagulation-flocculation, before GAC adsorption. The perfomance of these three techniques is based on COD removal.

For fenton oxidation, leachate pH variations and optimum concentration for Fe^{2+} and H_2O_2 for leachate treatment are described in detail by Chys et al. (2015a). The optimum conditions for leachate treatment were at pH 6, H_2O_2/Fe^{2+} of 1.5 and 30 minutes reaction time. Since at pH 6 coagulation is a significant mechanism in fenton oxidation, the effect of coagulation-flocculation only on leachate treatment was investigated. Ferric chloride ($FeCl_3$) and polyaluminium chloride were used in coagulation-flocculation of landfill leachate. To create conditions similar to fenton oxidation, coagulation-flocculation experiments at leachate pH 6 were done and are described by Chys et al. (2015a) For operating cost calculations, the cost for chemicals consumed in the three techniques i.e. ozonation, fenton oxidation and coagulation-flocculation and energy involved in ozone generation are considered.

For GAC, the operating costs calculations only considered the cost of the adsorbent.

7.3 Results and Discussion

7.3.1 Scenario 1: Changing one biological process for another: nitrification-denitrification versus ANR

Nitrification-denitrification (N-dN) is a robust biological technique that removes ammonium from landfill leachate. From the leachate characteristics shown in Table 3.1 Chapter 3, N-dN is efficient in reducing the ammonium concentration in landfill leachate below the specific Flemish discharge limit for IMOG (5 mg/L). Values above 5 mg/L are from samples collected during the winter period when biological reaction rates are lowered by cold temperatures. The poor BOD_5 is an indication that the denitrification stage is driven by an external source of carbon. Most leachate treatment plants employ methanol as an external carbon source. Assuming a stoichiometric methanol dosage of 2.47

g CH_3OH/ g N_{NO3^-} (3.7 g COD/g N_{NO3^-}) (Gao et al., 2015a) to achieve a 100% total nitrogen removal from a leachate stream containing 60 kg N/d (influent concentration 0.4 kg N/m^3 * flow rate 150 m^3/d), the methanol costs are 0.4 €/m^3. For aeration costs, it is assumed that 1 kg nitrogen consumes 4 kg oxygen (Gao et al., 2015a). Given an oxygen efficiency of 1.8 kg O_2/kWh and an electricity cost of 0.1 €/kWh, the aeration costs amount to 0.09 €/m^3. During N-dN, 0.44 kg $COD_{biomass}$ is produced per cubic meter of leachate. Taking into account a sludge disposal costs of 0.2 €/ kg $COD_{biomass}$ (Gao et al., 2015a), the total sludge disposal costs are 0.09 €/m^3. As such, the total operating costs of the N-dN process are 0.4 + 0.09 + 0.09 = 0.58 €/m^3 (31,755 €/year). As predicted, up to 71% of the total operation costs is spent on methanol, which is the main reagent. Similar observations are reported by Cassano et al. (2011). Methanol consumption in the treatment of landfill leachate using N-dN in a sequencing batch biofilter granular reactor accounted for 60% of the total operating costs. In comparison, only 18% and 7% of the total costs were attributed to aeration and sludge disposal respectively (Cassano et al., 2011). To achieve the discharge limits for COD (250 mg/L), further treatment of the biological effluent using GAC adsorption implies an additional operating cost of 1.32 €/m^3 (72,270 €/year). Therefore, the total operating costs for leachate treatment using A0, consist of N-dN and GAC, is calculated to be 1.9 €/m^3 (104,025 €/year).

To reduce the operating costs, it is important that the addition of the external carbon source is reduced while increasing the nitrogen removal efficiency. To achieve this, ANR has been considered, involving partial oxidation of ammonium into nitrite to achieve a theoretical nitrite versus ammonium ratio of 1:1 (Veys et al., 2010), next to the anammox process where ammonium is used as an electron donor and nitrite as an electron acceptor to produce nitrogen gas (Liang and Liu, 2008; Van Hulle et al., 2010). Lab scale operations showed that the ANR reactor is sensitive to changes in hydraulic retention time (HRT), nitrogen loading rate, dissolved oxygen and temperature. At a HRT of 2 days, the nitrogen removal efficiency varied between 14% and 45%. Instances of poor performance corresponded with reduced nitrogen loading rates of 153 mg N/L.d) compared to the initial rate of 238 mg N/L.d and nitrite concentrations of 253 mg/L in the effluent. Nitrite concentrations above 100 mg/L are known to inhibit the Anammox process (Xu et al., 2010). Increasing the HRT to 3 days raised the nitrogen removal efficiency to 72%. A decrease in nitrite concentrations in the effluent below 20 mg N/ L was also observed. Optimizing the HRT (3 days), nitrogen loading rate (257 mg N/L.d) and dissolved oxygen concentrations (0.3 – 0.5 mg O_2/L) in the reactor led to the effluent ammonium and nitrate concentrations dropping below 25 mg N/L.d and 23 mg N/L.d respectively hence a total nitrogen removal efficiency of 55% is achieved (Gao et al., 2015a). Since no external source of carbon such as methanol is needed in the ANR process and given that sludge production is negligible, cost estimations for the removal of nitrogen by ANR only took into account aeration costs. The oxygen requirements for ANR are 1.71 kg O_2/kg N (Gao et al., 2015a). In view of an oxygen efficiency of 1.8 kg O_2/kWh and an electricity cost of 0.1 €/kWh, leachate flow rate of 150 m^3/d and nitrogen loading rate of 60 kg N/d the aeration cost are 0.04 €/m^3 hence a total operating cost of 2,190 €/year. Aeration costs of the ANR process are much lower than the costs incurred in the N-dN process. Furthermore, up to 29,565 €/year can be saved by using the ANR for nitrogen removal instead of N-dN. Operational problems such as long start up periods prohibit the operation of ANR (Van Hulle et al., 2010). Therefore, only a combination of N-dN and ANR is preferred. Employing ANR to remove only a percentage (for example 40%), of nitrogen was found to be still cheaper than using solely the N-dN process. For instance, if only a limited amount of nitrogen (40%) is removed by ANR part of the removal should be attributed to N-dN (in this case 60%) in order to achieve the Flemish discharge limits for ammonium (Gao et al., 2015a). The additional costs for methanol addition and aeration are 0.6 * 0.58 €/m^3 = 0.348 €/m^3. Therefore, the total operational costs for the combined use of ANR and N-dN amount (0.4*0.04) + 0.348 = 0.36 €/m^3 (19,929 €/year). From the yearly costs, combined ANR and N-dN shows to be 38% cheaper than the full N-dN process. ANR (as the only process) and the combined ANR and N-dN process in this study were respectively 97 and 79% cheaper than full N-dN in returned activated sludge (RAS) system reported by Kochany and Lipczynska-Kochany (2009). The high costs for leachate treatment using a RAS system are due to the high energy (0.51 €/m^3), chemical (0.48 €/m^3)

and sludge disposal (0.75 €/m^3) costs. Assuming that GAC treatment costs are similar (1.32 €/m^3) for both the ANR, N-dN and the combined ANR & N-dN process, the total operating costs for leachate treatment using ANR only and GAC (further denoted as A1) is 1.36 €/m^3 (74,460 €/year). On the other hand, the total operating costs for sequence A2 which consists of 40% ANR + 60% N-dN + GAC is estimated to be 1.68 €/m^3.

7.3.2 Scenario 2: Incorporation of additional techniques into the existing treatment process (between biological treatment and adsorption)

Post-treatment of biologically treated landfill leachate before final polishing with GAC is a viable option for achieving the set limits for discharge of treated landfill leachate, and to improve the adsorption capacity of the activated carbon.

Using data presented in Chapter 3, ozonation of landfill leachate result into an increased COD removal as the ozone dosage increases. At a maximum dosage of 1.51 g O_3/g influent COD (COD_o), 44% COD removal can be achieved. Taking into account electricity costs of 0.1 €/kWh; 12 kWh are used to generate 1 kg O_3. Pure oxygen used to produce ozone costs 0.12 €/Nm^3 O_2, at an efficiency of 7 Nm^3 O_2/ kg O_3 (Chys et al., 2015a). Therefore, at a flow rate of 150 m^3 of leachate generated per day, the total operating costs for treating leachate (112 mg/L COD_o) at the maximum dose amount to 0.24 €/m^3 (energy) + 0.14 €/m^3 (oxygen) = 0.38 €/m^3 (21,111 €/year). On the contrary, treating undiluted leachate (724 mg/L COD_o) at a more economically feasible ozone dose of 0.14 g O_3/g COD_o (Chys et al., 2015a) resulted in up to 10% COD removal with 0.14 €/m^3 and 0.08 €/m^3 spent on energy and oxygen for ozone generation, respectively. Modeled data for COD removal from ozonated effluent by GAC adsorption show a fourfold improvement in adsorption capacity and breakthrough time of the activated carbon column (Chapter 6). Consequently, the effluent COD from GAC adsorption of ozonated effluent exceeded the specific Flemish discharge limit for IMOG (250 mg/L) after 3.5 BV. In comparison, GAC treatment of biologically treated leachate (N – dN) exceeded the required standards after 2.5 BV. Such improvements offer great benefits since the operating costs for GAC treatment of ozonated leachate are reduced to 0.95 €/m^3 compared to 1.32 €/m^3 when no ozone would have been applied. These GAC saving costs are in the range reported in Chapter 5. Thus the total operating costs for treatment of leachate using N – dN, ozonation and GAC adsorption (further denoted as A3) can be estimated as 0.58 + 0.23 + 0.95 = 1.76 €/m^3 (96,360 €/year). Addition of ozonation to the A0 treatment train thus reduces the operational costs by 7%. The values reported in this study for N – dN followed by ozonation are much lower than those reported in Cassano et al. (2011) and Di Iaconi et al. (2011). This is due to the high leachate COD$_o$ concentration and the high ozone doses (400-800 mg/L) applied to the biologically treated leachate in order to reach the set discharge limits.

Fenton oxidation is another AOP which has been investigated as a potential alternative to ozonation. It has been shown to be capable of removing a wide variety of compounds from landfill leachate (Barbusi and Pieczykolan, 2010). Experiments by Chys et al. (2015a) show that dosage of 1117 mg Fe^{2+}/L and 1020 mg H_2O_2 /L at pH 6 gives the best removal of organic matter from landfill leachate. At these conditions, up to 67% UV absorbance at 254 nm and 63% COD reduction could be achieved. Taking into account the chemical doses and costs of $FeSO_4.7H_2O$ as the Fe^{2+} source (0.33 €/kg) and H_2O_2 (0.385 €/kg), the operating costs incurred include 0.37 €/m^3 for $FeSO_4.7H_2O$ and 0.79 €/m^3 for H_2O_2. Next, at least 0.13 €/m^3 was needed for lowering the pH with HCl. With these costs - 0.37 + 0.79 + 0.13 = 1.29 €/m^3 - fenton oxidation is found to be 82% more expensive than ozonation. During GAC treatment of effluent from the fenton step, the effluent COD from the GAC column did not exceed the environmental discharge limit (250 mg/L) even after 36 BV. For this reason, the operating cost related to GAC adsorption of the fenton oxidation effluent is estimated to be low (0.09 €/m^3). In total, treatment of landfill leachate using N-dN, fenton oxidation and GAC (further denoted as A4) is calculated to be 0.58 + 1.29 + 0.09 = 1.96 €/m^3 (107,310 €/year). Incorporating fenton oxidation into A0 increases the costs by 3%. Due to differences in leachate characteristics and performance of the preceeding N-dN; the increase in total operating costs as a result of fenton addition is not high in comparison to 78% calculated from the study of Kochany and Lipczynska-Kochany (2009)

Depending on pH, coagulation-flocculation is one of mechanism of action in fenton oxidation. At pH higher than 3, the mechanism of action tends towards coagulation-flocculation. Moreover, the neutralization step favours the formation of iron hydroxide precipitates which further assist in the removal of pollutants from leachate. Therefore, to investigate the role of only coagulation-flocculation during fenton oxidation ferric chloride ($FeCl_3$) and polyaluminium chloride (PACl) were used to treat landfill leachate. Experiments without pH reduction were carried out to determine the best coagulant between the two. Generally, an increase in coagulant concentration promoted higher reductions in leachate COD and α_{254} absorbance as seen in Chapter 6. At initial COD concentration of 1378 mg/L and α_{254} absorbance of 8.24 cm^{-1}, better COD (66%) and α_{254} absorbance (88%) reductions were obtained with 1 g $FeCl_3$/g COD_o, compared with 44% COD and 72% UV_{254} absorbance removal at 1 g PACl /g COD_o. Additionally, the sludge produced during $FeCl_3$ treatment had better settling properties as shown by the low sludge volume index (154 versus 250 mL/g for PACl). As such, further coagulation-flocculation experiments were conducted using $FeCl_3$. To create conditions similar to those in fenton, pH of leachate was lowered to 6. At a dose of 1.3 g $FeCl_3$/g COD_o and pH 6, the influent COD concentration (2226 mg/L) was reduced by 59% (Chys et al., 2015a). This removal efficiency is comparable to the 63% obtained during fenton oxidation. Equally, it can be anticipated that GAC column will treat more than 36 BV of leachate coagulated at pH 6 before the effluent COD exceeds 250 mg/L. Therefore, GAC operating costs for coagulated effluent will be comparable to those of GAC treatment of fenton oxidation effluent (0.09 €/m^3). Considering a $FeCl_3$ cost of 0.625 €/kg, the operating cost for using coagulation-flocculation is 0.81 €/m^3. The total costs for sequence A5 with N-dN, coagulation-flocculation and GAC adsorption of landfill leachate is estimated to be 1.48 €/m^3. Treatment of 150 $m^3$of leachate per day for 365 days costs 81,030 €/year. Evaluation of the operating costs shows that addition of coagulation-flocculation to A0 reduces the total treatment costs by 21%.

7.3.3 Scenario 3: Alternative treatment configurations

Use of a completely different process other than A0 to treat leachate is another viable option to meet the effluent discharge standards. In the aforementioned studies, ANR and ozonation gave good nitrogen and COD removal in addition to lowering the leachate treatment costs. As such, the applicability of ANR, ozonation and GAC (A6) in reducing the pollutant load of the IMOG landfill leachate was investigated.

Ozonation of ANR effluent at ozone concentrations between 0.13 and 0.48 g $O_3/L_{leachate}$ resulted in 32% COD reduction at low initial COD concentration (426 mg/L) and only 19% removal at high initial COD concentration (869 mg/L) Furthermore, up to 24% of total nitrogen in the ANR effluent was removed by ozonation before GAC adsorption as already mentioned in Chapter 5. Taking into account aforementioned electricity costs and oxygen prices, the corresponding operating costs for ozonation of ANR effluent range between 0.19 and 0.69 €/m^3. Recirculation of ozonated ANR effluent to the ANR set up at a ratio of 1:9 (ozonated ANR leachate:raw leachate) improved the COD removal efficiency of the ANR from approximately 5 to 12%. This confirms the ability of ozonation to break complex recalcitrant compounds in leachate to simple compounds which can be removed by a biological step. Subsequent GAC treatment of ozonated leachate improved the time taken before the final effluent COD exceeded the standard discharge limits. These improvements were taken into account when calculating the operating costs of GAC treatment. Economic analysis of GAC adsorption of the ozonated effluent shows that the operating costs are significantly reduced to a range between 0.88 and 1.02 €/m^3 (compared to 1.32 €/m^3) as a result of enhanced GAC adsorption properties. On average, the total operating cost related to leachate treatment with ANR, ozonation and GAC is about 0.04 + 0.44 + 0.95 = 1.43 €/m^3 (78,292 €/year). Comparing the operating costs between A0 and A6, the results indicate that A6 is 24% cheaper.

According to Anfruns et al. (2013), ANR systems can be coupled successfully to photo- fenton and other chemical processes such as coagulation-flocculation to remove high concentrations of ammonium and recalcitrant organic matter. However, Anfruns et al. (2013) used a two-step approach (partial nitritation and anaerobic ammonium oxidation separate reactors) to accomplish leachate treatment by ANR. A two-step ANR process can have a significant impact on the capital costs, which is however out of scope of this study. The operational costs incurred by the treatment of landfill leachate by ANR followed by either fenton oxidation or coagulation-flocculation and finally GAC adsorption are presented in sequence A7 and A8, respectively. Considering an individual operating cost of 0.04 €/m^3 for ANR, 0.81 €/m^3 for coagulation-flocculation, 1.29 €/m^3 for the fenton oxidation, and 0.09 €/m^3 for GAC adsorption taking into account the COD discharge standards of 250 mg/L and assuming the GAC improvements achieved in A4 and A5 also apply; the total cost for the treatment of landfill leachate using sequence A7 and A8 amounts to 1.42 €/m^3 (77,745 €/year) and 0.94 €/m^3 (51,465 €/year), respectively. This indicates a cost saving of up to 52,560 €/year when sequence A8 should be used instead of A0. Moreover, the incorporation of a coagulation-flocculation step between ANR and GAC could increase the operation time of the GAC column, hence reducing the activated carbon cost by 93%. Though sequence A7 proves to be 33% more expensive than A8, it is still 25% cheaper than A0. Interestingly, the operating costs of sequence A5 and A7 are comparable. However, taking into account other hidden costs such as sludge disposal, sequence A5 could be a cheaper option.

7.4 Conclusions

This work provides interesting insights in the cost implications of the choice that landfilling facilities can make among different scenarios for adapting their leachate treatment systems. The operating cost of these scenario's (expressed as €/m^3) is summarized in Figure 7.3.

From Figure 7.3, the first scenario shows that, changing the working mechanism of the biological step from N-dN to ANR and making use of a combined ANR and N-dN process can significantly reduce the operating costs mainly because no or less methanol is needed as external carbon source. However, this strategy has no impact on the adsorption costs. In the second scenario with treatment sequence A3, A4 and A5 – all incorporating an intermediate step between N-dN and GAC – a significant decrease in GAC operating cost is observed in A4 and A5. However, this does not translate into operating cost savings for the sequence A4 because of the high costs incurred in the fenton step. Among the different possibilities considered in scenario 2, sequence A5 showed to be the cheapest option, being 22% cheaper than A0. Scenario 3 explored the possibility of changing the mechanism of the biological step as well as including an intermediate step. On average, the 3 sequences A6, A7 and A8 are 33% more cost effective than A0. As expected, use of fenton in A7 and coagulation-flocculation in A8 led to lower operating GAC costs. Among the three intermediate techniques between ANR and GAC ozonation was the cheapest. In conclusion, sequence A8 with ANR, coagulation-flocculation and GAC indicates to be the cheapest (0.94 €/m^3) option among the different scenarios investigated.

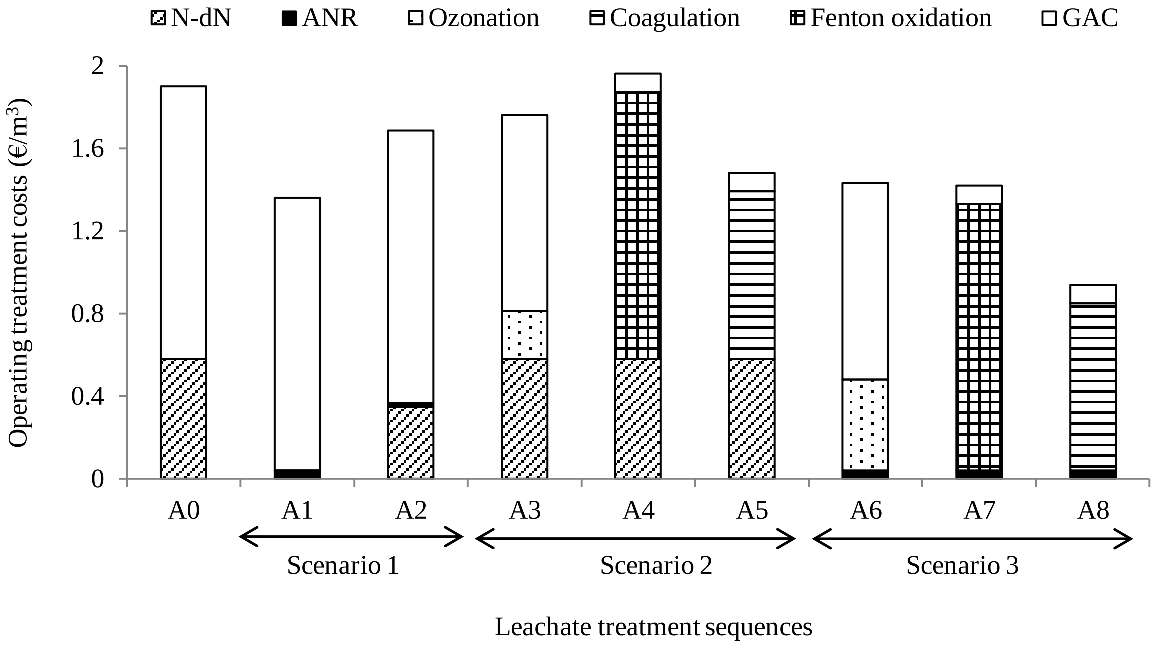


Table 7.3: Overview of the calculated operational costs related to the proposed alternative processes for the treatment of landfill leachate in comparison with that of the existing treatment process A0.

Though at such a dose of 1.3 mg $FeCl_3$/mg COD_o coagulation-flocculation proved expensive than ozonation at dose between 0.14 – 0.48 mg O_3/ mg COD_o, the savings achieved in the GAC step by coagulation-flocculation far outweigh those obtained by ozonation. Therefore, the total operating costs by coagulation-flocculation and GAC regardless of the biological technique are lower than those with ozonation and GAC. As such choice of coagulation-flocculation in combination with GAC is desirable more so given its potential to reach the specific COD discharge limit for IMOG (Chapter 6 Table6.1. Therefore, the next chapters will focus on the use of coagulation-flocculation and GAC in treatment of raw and biologically treated landfill leachate.

Chapter 8

Coagulation-flocculation and granular activated carbon as post-treatment techniques for the removal of fluorescence EEM - PARAFAC components in biologically treated landfill leachate

Redrafted after:

Violet Oloibiri, Kristof Demeestere, Robbin Vandewalle, Stijn W. H. Van Hulle (2018) Coagulation-flocculation and granular activated carbon as post-treatment techniques for the removal of fluorescence EEM - PARAFAC components in biologically treated landfill leachate. In preparation.

Contribution of Violet Oloibiri: Designing the experiments and writing the manusript

Abstract

Using fluorescence excitation emission matrices coupled with parallel factor analysis, two DOM (dissolved organic matter) components were identified in biologically treated landfill leachate, i.e. C1 representing humic/fulvic-like compounds and C2 representing humic-like compounds. Protein-like compounds that were observed in raw leachate were clearly removed during the biological treatment. Coagulation-flocculation with ferric chloride and granular activated carbon adsorption (GAC) were investigated as single and combined post-treatment techniques for the removal of the biorecalcitrant DOM components. A higher coagulant dose (0.1 – 2.2 mg $FeCl_3$/mg initial COD (COD_o)) resulted in an increased reduction of the maximum fluorescence intensity (F_{max}), up to 32.6% for C1 and 8.2% for C2. The COD and UV-VIS absorbance at 254 nm (α_{254}) could be reduced by 31.4% and 48.8%, respectively. Batch adsorption experiments revealed an optimum GAC dose of 150 g/L and a minimum contact time of 30 min for adsorption of both non-coagulated and coagulated biologically treated leachate. In contrast to coagulation-flocculation, GAC adsorption mainly reduces C2 fluorescence. With 0.8 mg $FeCl_3$/mg COD_o as the optimal coagulant dose, GAC columns operated in a continuous mode showed a longer lag-phase (up to 4.3 BV) and a slightly better F_{max} reduction of C1 (86% versus 79% at 10.7-12.8 BV) and C2 (92% versus 89% at 10.7-12.8 BV) when the biologically treated leachate was first coagulated prior to GAC adsorption. With regards to reduction of water quality parameters, 12.8 BV GAC treatment reduced the COD of biologically treated landfill leachate from 338 to 120 mg/L (65% removal) whereas the COD was reduced to 82 mg/L (76% removal) with 0.8 mg $FeCl_3$/mg COD_o + 12.8 BV GAC.

8.1 Introduction

Because of the limitations of biological methods in the treatment of landfill leachate, physical-chemical post-treatment is required to meet the stringent environmental discharge limits (Chapters 2, 4 – 6). Coagulation-flocculation with ferric chloride followed by granular activated carbon (GAC) adsorption already showed potential in reducing the dissolved organic matter (DOM) in biologically treated leachate; and proved to be more economical than other investigated techniques such as ozonation (Chapters 6 and 7). Therefore, in this chapter, coagulation-flocculation with ferric chloride coupled with GAC will be used in post treatment of biologically treated landfill leachate. Furthermore, combined optimization of the coagulation-flocculation and GAC adsorption steps will be investigated, which is new compared to the common approach involving a separated optimization of post-treatment techniques. This approach took into account the lessons learnt in Chapter 6 where by coagulation-flocculation did have an impact on GAC step. As such, it can be presumed that there is an optimum coagulant dose that when coupled with optimum GAC dose will provide both technical and economic benefits. It is important to note at this point that the GAC set up described in Chapter 3 and used in Chapter 5 and 6 are simulations of real life setups. However, in this chapter, the optimum GAC dose for treatment of leachate will be determined.

During post-treatment of biologically treated leachate, conventional parameters for dissolved organic matter (DOM) such as COD and UV-VIS absorbance are systematically monitored. However, these parameters give no indication of the changing character of the DOM constituents. Also, biological processes such as nitrification-denitrification have shown to transform DOM components in (waste)waters (Liu et al., 2015; Yang et al., 2013). For instance, an increase in certain humic compounds is observed as a result of microbial humification of protein- and fulvic-like DOM components. The knowledge of this changing character after biological treatment is of utmost importance as it can influence the choice of appropriate post-treatment techniques like coagulation-flocculation and GAC adsorption since these particularly target DOM of different nature.

Coagulation-flocculation is particularly efficient in removal of high molecular weight (HMW) humic-like organic matter, while GAC unselectively removes protein- and humic-like low molecular weight (LMW) compounds (Henderson et al., 2009). Given that several landfilling facilities employ biological processes as the initial treatment step, identifying and monitoring the distinct DOM components in biologically treated leachate before and during post-treatment will help to optimise their landfill leachate treatment strategies. In previous chapters, UV-VIS absorbance at 254 nm and 436 nm have been used to monitor DOM removal. In this chapter, a more in depth investigation is done on the specific identity of DOM components.

Fluorescence spectroscopy is a sensitive and highly robust method which has been used to provide important information on the identity and nature of organic matter present in natural and engineered water systems (Lee and Hur, 2016). It essentially takes advantage of the fluorescent nature of DOM such as humic substances and amino acids commonly found in water. Through the absorption of light energy, a loosely held electron in a molecule or atom is excited to a higher energy level. Through collisions, the electron loses some of its energy hereby emitting light. These compounds which absorb and re-emit light are referred to as fluorophores. The wavelength at which energy is absorbed and emitted is specific for a molecule (Hudson et al., 2007). The use of single excitation and emission wavelength pairs play an important role in determining the presence or absence of a particular compound in simple matrices. However, given that wastewaters and especially landfill leachate have a complex matrix, techniques generating a more complete fluorescence excitation emission matrix (EEM) are useful in providing detailed information of the fluorophores present in the complex matrix. Fluorescence EEM involves simultaneously collecting the fluorescence intensity of a sample at various emission and excitation wavelengths in order to develop an elaborate matrix when fluorescence intensity, emission and excitation wavelengths are plotted in a single chart. With such a matrix, a combination of excitation and emission wavelengths at which maximum fluorescence intensity (F_{max}) of a component occurs can be obtained (Coble, 1996). Given the wealth of information available in the EEMs, multivariate tools such as self-organizing maps (SOM) and parallel factor analysis (PARAFAC) can be used to obtain both qualitative and quantitative information on DOM.

SOM is an unsupervised algorithm and finds important use in clustering and visualizing samples with similar DOM composition. However, its use in landfill leachate studies is scarce. On the other hand, PARAFAC is a supervised algorithm which decomposes fluorescence EEM signals into a set of tri-linear terms and a residual array. Therefore, individual DOM components such as humic-like, fulvic-like, tryptophan and tyrosine compounds can be identified. Fluorescence EEM - PARAFAC has been applied in several landfill leachate studies to identify multi peak DOM fluorophores (Lu et al., 2009) and to describe how heavy metals and DOM bind to each other (Wu et al., 2011). However, these two tools - SOM and PARAFAC are rarely combined in analysing fluorescence EEM data from landfill leachate

In view of the wide application of biological processes for treatment of landfill leachate (Alvarez-Vazquez et al., 2004), fluorescence EEM and PARAFAC studies focusing on the identification of DOM components present before and produced during biological treatment and on the monitoring of behavioural changes during post-treatment are limited. Therefore, this chapter will mainly focus on the DOM characterization of biologically treated landfill leachate and the effect of physical-chemical post-treatment (coagulation-flocculation and GAC adsorption) on identified PARAFAC EEM components, as additional more in-depth information compared to COD and $\alpha_{254.}$ In particular, the performance of coagulation-flocculation and GAC adsorption will be compared alongside that of post-treatment with GAC only. The use of self-organizing maps to visualize the changes in DOM composition based on the (i) inclusion (or not) of the coagulation-flocculation step and (ii) changes in time during GAC treatment will also be described.

8.2 Materials and methods

8.2.1 Landfill leachate

Biologically treated leachate was sampled from IMOG (Moen, Belgium) between October 2016 and January 2017. The characteristics are found in Table 3.1

8.2.1 Physical-chemical treatment

8.2.1.1 Coagulation-flocculation

In Chapter 6, ferric salts showed to be more efficient and economical in organic matter removal from landfill leachate than aluminium based coagulants. Therefore, ferric chloride ($FeCl_3$) (Brenntag, Belgium) was employed during coagulation-flocculation of biologically treated landfill leachate. To optimise the coagulation-flocculation step, a wide range (0.1 - 2.2 mg coagulant /mg COD_o) of coagulant doses – relative to the initial leachate COD (COD_o) – was studied. This was done according to the procedure outlined in Chapter 3. After settling, the supernatant was withdrawn for further GAC studies and analysis of COD, UV-VIS absorbance, and fluorescence EEM.

8.2.1.2 GAC adsorption

Since the biologically treated leachate (without coagulation-flocculation) as well as the coagulated leachate at all doses have to be further treated by GAC, a fast simple method of GAC adsorption was required. Therefore, GAC adsorption of biologically treated (non-coagulated) and coagulated landfill leachate was investigated in different phases using batch adsorption experiments.

In a first phase, the optimum amount of GAC is determined in batch equilibrium experiments. Erlenmeyer flasks containing 0.2 L of biologically treated leachate and different amounts of GAC (25 – 250 g GAC/L leachate) are shaken for 240 minutes to allow the attainment of equilibrium conditions. Next, adsorption kinetics (stirring time of 5 – 240 min) are studied also in batch using 0.2 L of biologically treated leachate and the optimum amount of GAC (150 g/L see section 8.3.1.1).

This is done to determine the minimum treatment time that gives the highest removals. As a final batch test, the optimum coagulant dose to be applied in a coagulation-flocculation + GAC treatment train was determined by GAC adsorption (at optimum amount of GAC and at a minimum treatment time) of leachate coagulated at different ferric chloride doses, in order to find the technical-economical optimum.

In a second phase, biologically treated leachate coagulated at the optimum dose (0.8 mg $FeCl_3$/mg COD_o, see section 8.3.1.2) was passed through a GAC column to study the behavioural changes of DOM in a dynamic system (Figure 8.1). The performance of coagulation-flocculation + GAC adsorption post-treatment was compared to that of GAC only. Therefore, post treatment with GAC only was used as the benchmark. The continuous adsorption experiments were conducted in a glass column with the operational conditions outlined in Chapter 3. The samples were collected at the column exit at different time points for analysis of COD, UV-VIS absorbance and fluorescence excitation emission. Analysis of COD, UV-VIS absorbance (all leachate samples), pH, conductivity, ammonium (for biologically treated leachate only) were carried out according to the procedures in Chapter 3. Breakthrough from the GAC column was defined as the point where the effluent concentration is equal to 50% of the influent concentration. This definition of breakthrough was chosen because 100% exhaustion of the column is not possible during the experimental period due to the experimental design.

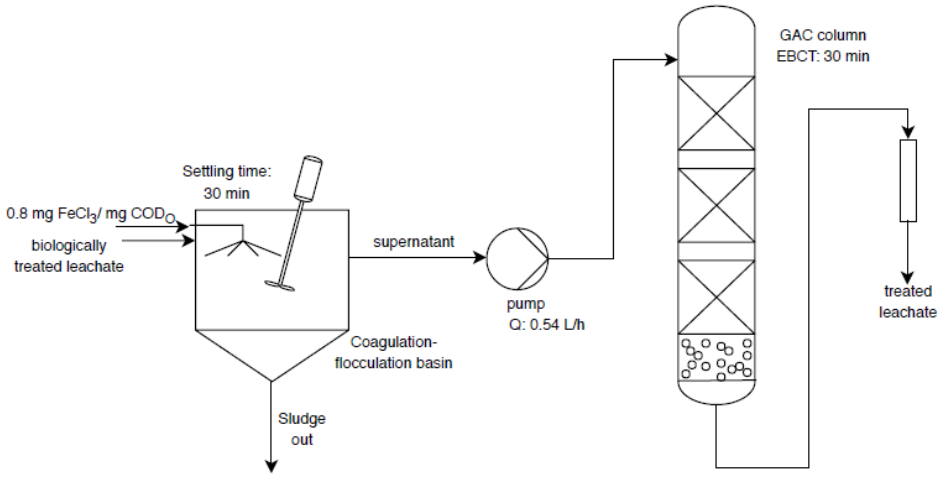


Figure 8.1: Flow diagram for the post-treatment of biologically treated landfill leachate with coagulation-flocculation and GAC adsorption

8.2.1.3 Fluorescence EEM, PARAFAC and SOM

Fluorescence EEM measurements were done according to the procedure outlined in Chapter 3. The analysis of available fluorescence EEM data was conducted in MATLAB R2012b and 2015a using the drEEM toolbox downloaded from www.model.life.ku.dk and the tutorial of Murphy et al. (2013a). The fluorescence EEM data used for PARAFAC modelling consisted of 259 samples. To improve PARAFAC modelling and the fluorescence EEM display, the Rayleigh-Tyndell and Raman scatter lines were removed in the data pre-processing step (Shutova et al., 2014). A two to four component PARAFAC model was fitted to the data, and all models were run on non-negativity restrictions to ensure that only chemically relevant results were used. PARAFAC decomposes fluorescence signals into F tri-linear components (Figure 8.2) and a residual array, according to equation 8.1 (Murphy et al., 2013b; Stedmon and Bro, 2008).

$$X_{ijk} = \sum_{f=1}^{F} a_{if}\, b_{jf} c_{kf} + e_{ijk} \quad (where\ i = 1, \dots I;\ j = 1, \dots J; k = 1, \dots K) \qquad equation\ 8.1$$

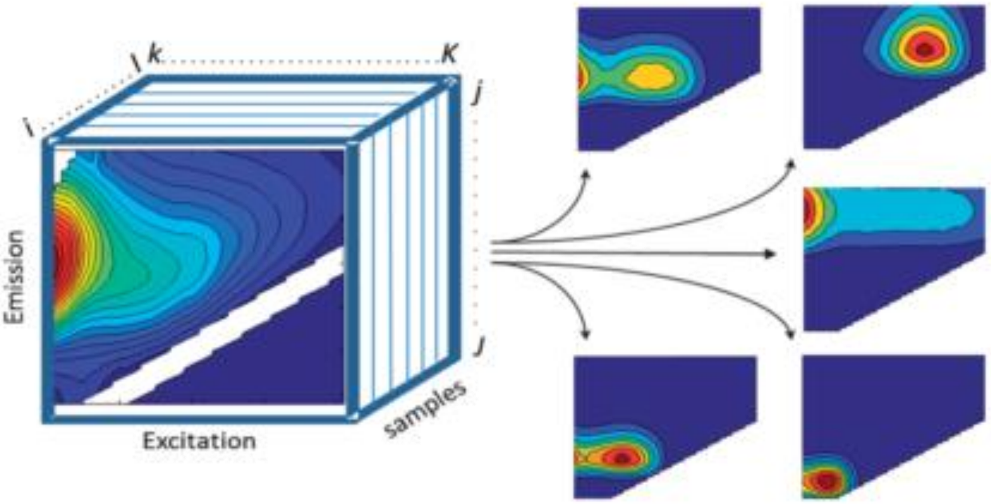


Figure 8.2: Fluorescence EEM data decomposed into five components using PARAFAC (Murphy et al., 2013b).

From equation 8.1 and Figure 8.2, *X* is the fluorescence intensity of sample *i* measured at emission wavelength *j* and excitation wavelength *k*. e_{ijk} represents variability unexplained by the model. *a, b, c* are outcomes of the PARAFAC model where *a* is directly proportional to the concentration of fluorophore /component *f* in sample *i*. *b* and *c* represent the emission and excitation spectra of the fluorophore/component *f* in sample *i*.

During PARAFAC modelling, six outlier samples with high leverages were eliminated. The optimum number of components was validated using split half analysis and core consistency. Core consistency (expressed in percentages) is an indicator of the model "appropriateness" (Murphy et al., 2013b). Higher core consistencies are associated with lower number of components and conversely, more components will often have lower or negative core consistencies (Murphy et al., 2013b). In this respect, core consistency alone is a weak validation tool since one would be prompted to dismiss a model with lower core consistency even when other indicators e.g. visual inspection indicate otherwise. Due to the aforementioned reasons, core consistency is combined with split half analysis. In split half validation, the EEM data is divided into two and a PARAFAC model is applied to both halves. If the number of components chosen is suitable, then the same excitation and emission loading will be obtained in both halves. The influence of the treatment techniques on the PARAFAC components was tracked using their maximum fluorescence intensity (F_{max}).

SOM modelling is an iterative process whereby each input is connected to a neuron in the output layer with a corresponding reference vector containing weights (Figure 8.3) (Bieroza et al., 2011; Carstea et al., 2010). Each reference vector from the input layer is associated with one neuron in the output layer. Once the best reference vector has been identified, its weight and the weights of the closest neurons are modified and moved towards the input vector according to equation 8.2:

$$w_i(k+1) = w_i(k) + \varepsilon(k)h_p(i,k)\{x_j(k) - w_i(k)\} \qquad equation\ 8.2$$

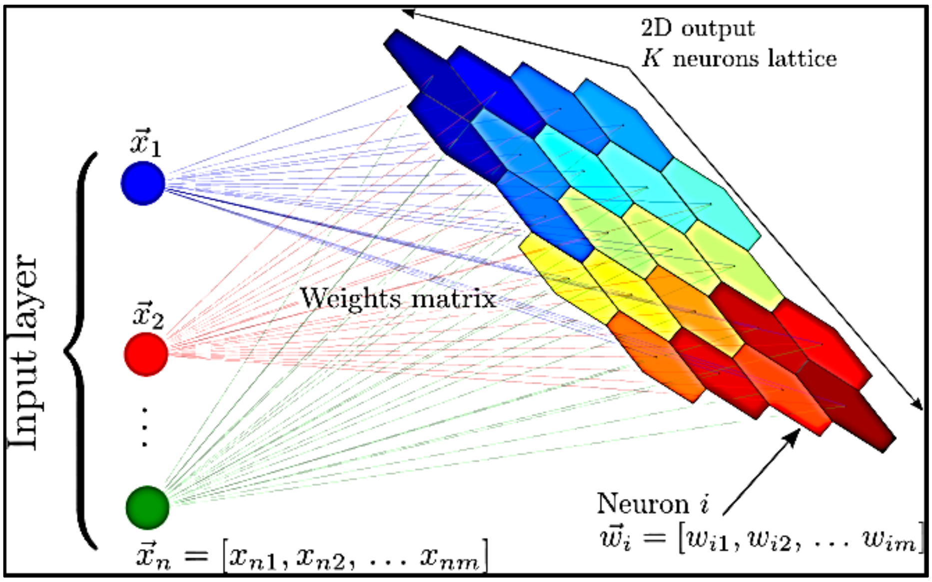


Figure 8.3: Self organizing map showing the relationship between the input and output layers (Mattias, 2018)

where $w_i(k)$ is the previous weight of the neuron, $w_i(k+1)$ is the new weight of neuron, $\varepsilon(k)$ is the learning rate, and $h_p(i,k)$ the neighbourhood size of the winning neuron p at iterations k.

To visualize the relationships between the samples based on the DOM components, SOM analysis was done using the results obtained from PARAFAC components (F_{max} values) with MATLAB R2012b and 2015a following the tutorial of Cuss and Gueguen (Cuss and Gueguen, 2016) and using the Fluor_SOmap and SOM toolboxes downloaded from http://people.trentu.ca/~celinegueguen/Fluor_SOmap.html and http://www.cis.hut.fi/projects/somtoolbox/download/, respectively. The use of SOM on results extracted from EEM analysis is motivated by the fact that (i) SOM analysis of whole EEMs cannot lead to the identification of specific fluorophores, (ii) a clearer interpretation of EEM data can be obtained, and (iii) it consumes less time (Cuss et al., 2014; Cuss and Guéguen, 2015). The SOM analysis involved the fluorescence composition (percentage contribution of the F_{max} value of each component to the total fluorescence) of the PARAFAC derived components excluding the outlier samples eliminated during PARAFAC analysis. Transforming the PARAFAC values to fluorescence composition provides a holistic picture of the way the composition of DOM in a sample changes due to e.g. treatment (Cuss and Guéguen, 2015). Finally, a unified distance matrix and best matching unit were obtained for clustering of samples.

8.3 Results and discussion

8.3.1 Optimisation of COD and α_{254} removal with coagulation-flocculation and GAC treatment

8.3.1.1 Optimal GAC dose for single post-treatment

Post-treatment of biologically treated leachate with 150 g/L GAC in a batch system for 240 minutes led to a decrease of the initial leachate COD from 573 mg/L to 120 mg/L (79% reduction). No further COD removal was observed upon an increment of the GAC dose to 250 g/L (final COD = 122 mg/L). This shows that 150 g GAC/L was sufficient to reduce the GAC amenable compounds in leachate. Use of the highest GAC dose (250 g/L) would not be economic since higher GAC costs would be incurred with no significant removals are achieved Therefore, further GAC batch studies considered 150 g/L. Regarding the contact time, 30 min proved to be sufficient in reducing the bulk organic matter (72%

COD removal) with a GAC dose of 150 g/L, compared to the aforementioned 79% reduction obtained after 240 minutes. Longer contact times thus lead to better removals, however, a minimum treatment time of 30 minutes was chosen for further GAC studies since very little gains in percentage COD removals are obtained at longer treatment periods. Additionally, 30 minutes is in line with the contact time that is used in the GAC column as indicated in Chapter 3, Section 3.2.2.

8.3.1.2 Optimal coagulant dose in the combined coagulation-flocculation + GAC post-treatment

A gradual increase of the $FeCl_3$ dose from 0.1 to 2.2 mg $FeCl_3$/mg COD_o led to an improved reduction of COD (up to 31 %) and α_{254} (up to 49 %) in the biologically treated leachate (Figure 8.4). The better performance at higher coagulant dosages is as a result of mechanisms such as sweep coagulation. Nevertheless, higher amounts of coagulant induce higher treatment costs which can outweigh the technological performance benefits. For instance, doubling of the coagulant dose from 0.5 to 1.0 mg $FeCl_3$/mg COD_o yields only an additional 4% COD removal but would increase the cost considerably given the high coagulant use at 1.0 mg $FeCl_3$/mg COD_o (Figure 8.4). These removal efficiencies are however, lower than those reported in Chapter 6 (Figure 6.5). This is because the leachate used for the studies in this chapter had lower concentrations of organic matter (as indicated by COD 315 - 573 mg/L compared to 612 – 1846 mg/L in Chapter 6) that can be removed by coagulation-flocculation. This difference in leachate characteristics was brought about by differences in sampling period.

The effect of GAC post-treatment on coagulated leachate with respect to COD and α_{254} removal is also shown in Figure 8.4. Improved COD and α_{254} removals are obtained when coagulation-flocculation with $FeCl_3$ is combined with GAC adsorption. When leachate was coagulated at a dose of 0.1 mg $FeCl_3$/mg COD_o and further treated with 150 g/L GAC for 30 minutes, a total removal of 53% COD and 70% α_{254} is realised. This increases up to 74% COD and 78% α_{254} at an 8 times higher coagulant dose (0.8 mg $FeCl_3$/mg COD_o). Further increasing the coagulant dose does not yield important improvements (only an increase of 4% COD up, to 78% and 12% in α_{254}, up to 90%) (Figure

8.4). However, increasing the coagulant dose does increase the costs since more coagulant is being used. When coagulation-flocculation is applied at very high doses, e.g. 2.2 mg $FeCl_3$ /mg COD_o, GAC amenable hydrophobic compounds have already been significantly removed from the leachate, decreasing the added value of an additional GAC step in the total removal. Hence, from both a technical (as seen in Figure 8.4) and economic perspective, the recommended optimum coagulant dose for biologically treated leachate before GAC adsorption is 0.8 mg $FeCl_3$/mg COD_o which is therefore also used in further column experiments (Section 8.3.1.3).

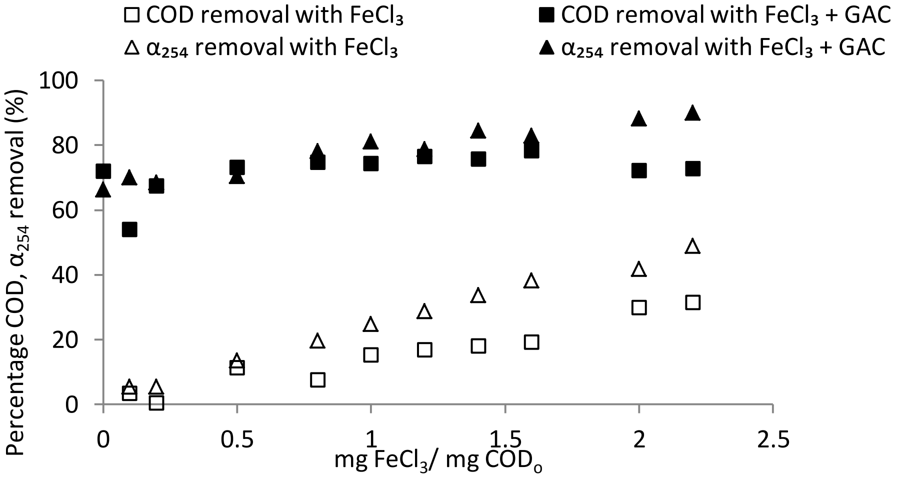


Figure 8.4: Removal of COD and α_{254} during coagulation-flocculation and coagulation-flocculation + GAC as a function of coagulant dosage. Initial values of COD and α_{254} are 356 mg/L and 3.86 cm^{-1}, respectively. GAC dose: 150 g/L; GAC treatment time: 30 minutes.

8.3.1.3 GAC column tests

Though the batch tests showed that the optimum GAC dose was 150 g/L, the GAC dose used in the column tests is still that described in Chapter 3. This was important since using the same set up would allow comparison of results. Dynamic system (fixed bed GAC column) experiments show that up to 65% COD and α_{254} removal is achieved when biologically treated leachate is treated with only 12.8 BV GAC. Breakthrough of COD from the GAC column is noticed approximately around 51 BV (24 hours). The total COD removal at this point was 47%.

Pre-treatment of biologically treated leachate with coagulation-flocculation (0.8 mg $FeCl_3$/mg COD_o) before GAC column adsorption (12.8 BV) resulted in better total removal efficiencies, up to 76% for both COD and α_{254} and no breakthrough during the experimental period of 12.8 BV. Through mechanisms such as charge neutralization and sweep coagulation, coagulation-flocculation acts on high molecular weight hydrophobic compounds (Zhu et al., 2016), which would otherwise reduce the number of GAC adsorption sites because of blockages. This further demonstrates the added value of coagulation-flocculation as a pre-treatment before GAC adsorption, so as in Chapters 6. Also in comparison with the COD removal efficiencies presented in Chapter 6 (53% COD removal, Table 6.1) for post-treatment of biologically treated leachate with coagulation-flocculation + GAC, the COD reductions presented in Chapter 8 are higher (76%). This is because of the low organic matter content of the landfill leachate (COD_o 337 mg/L) used in these column studies meaning less substances which can block the GAC adsorption sites in comparison to that used in the column studies in Chapter 6 (612 mg/L).

8.3.2 PARAFAC EEM components in biologically treated landfill leachate

Using core consistency and split half validation, 2 PARAFAC EEM components were identified in biologically treated landfill leachate (Figure 8.5). Component 1 (C1) with a maximum fluorescence intensity (F_{max}) at Ex/Em wavelengths of 270-320/420 nm is associated with humic-like substances with both hydrophobic and hydrophilic fractions (Lee and Hur, 2016; Wu et al., 2012). Though already found in several studies on landfill leachate, the identity of Component 2 (C2) – characterised by a single maximum peak at Ex/Em wavelengths of 250/450 nm and minor peaks at Ex/Em wavelengths of 300/450 and 360/450 nm – is uncertain. Wu et al. (2011) suggested that C2 may be associated with xenobiotic organic compounds in leachate, particularly those from the pyrene family. However, according to the classification of Chen et al. (2003), fluorescence at Ex wavelengths larger than 280 nm and Em wavelengths larger than 380 nm are related to humic-like compounds. The biologically treated leachate samples do not contain any protein-like substances, which is an indication of the biological stabilization of this leachate and further justifies the use of physical-chemical post-treatment (Lee and Hur, 2016). Quantitative information from PARAFAC analysis shows that F_{max} of C1 and C2 is 85 ± 8 RU and 140 ± 14 RU, respectively. These contribute respectively for 38 ± 1 % and 62 ± 1% to the biologically treated leachate's total fluorescence. Biological processes for wastewater treatment, e.g. nitrification – denitrification, are known to be effective in reduction or complete removal of protein-like fluorescence due to the decomposition of protein-like substances by bacteria (Huo et al., 2009; Liu et al., 2015; Yang et al., 2013). Interestingly, this leads to the relative accumulation of humic-like materials and thus an increase in humic-like fluorescence (Stedmon and Cory, 2014).

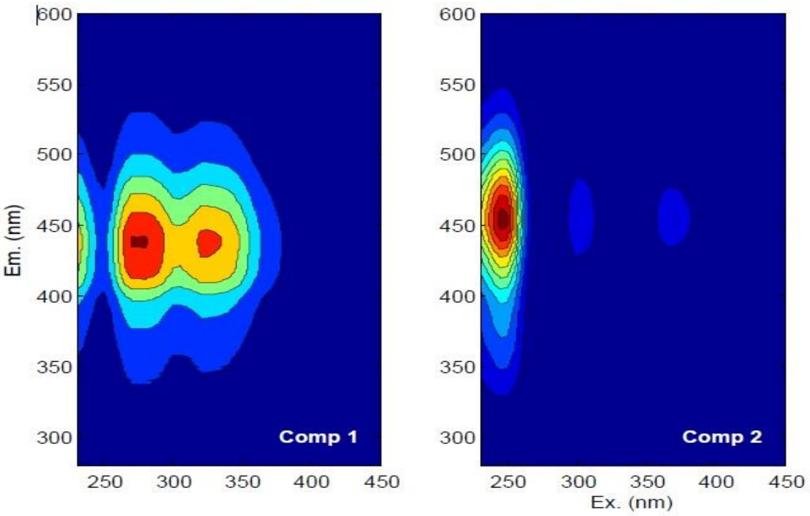


Figure 8.5: Contour plots of the PARAFAC EEM components C1 and C2 in biologically treated landfill leachate.

8.3.3 Fate of PARAFAC EEM components during coagulation-flocculation and GAC adsorption

8.3.3.1 Coagulation-flocculation: effect of coagulant dosage

Coagulation-flocculation is a treatment technique that reduces fluorescence intensity of DOM without breaking or changing the structure of DOM (Baghoth et al., 2011). Though common physical-chemical parameters have been used to determine the optimum coagulant concentration for further column studies, it is important to understand how the different components which make up the leachate DOM are removed during $FeCl_3$ coagulation-flocculation at varying doses. Similar to COD and α_{254}, an increase in percentage removal of the two DOM components is observed as the coagulant dose increases from 0.1 to 2.2 mg $FeCl_3$/mg COD_o (Figure 8.6). However, the susceptibility of the two components differed from each other. C1 is preferentially removed with an efficiency of 32.6% at a coagulant dose of 2.2 mg $FeCl_3$/mg COD_o, whereas only 8.2% C2 removal is obtained at the same dose. Lu et al. (2009) identified C1 as a component with higher molecular weight (3500 – 5000 Da) compared to C2 (2500 – 3000 Da). Therefore, these results are a further indication that coagulation-flocculation is the most effective in removing DOM of high molecular weight rather than low molecular weight DOM. Increase in coagulant dose also leads to changes in the dominance of the two components in coagulated effluent, because of their difference in removal. In biologically treated leachate, the F_{max} of C2 was found to be 1.6 times higher than that of C1. Upon coagulation-flocculation, the presence of low molecular weight humic-like compounds becomes more prominent (C2/C1 ratio equals 1.7 at 0.1 mg $FeCl_3$/mg COD_o and 2.2 at 2.2 mg $FeCl_3$/mg COD_o). This makes the fluorescence intensity of coagulated leachate going to GAC adsorption more dominated by C2.

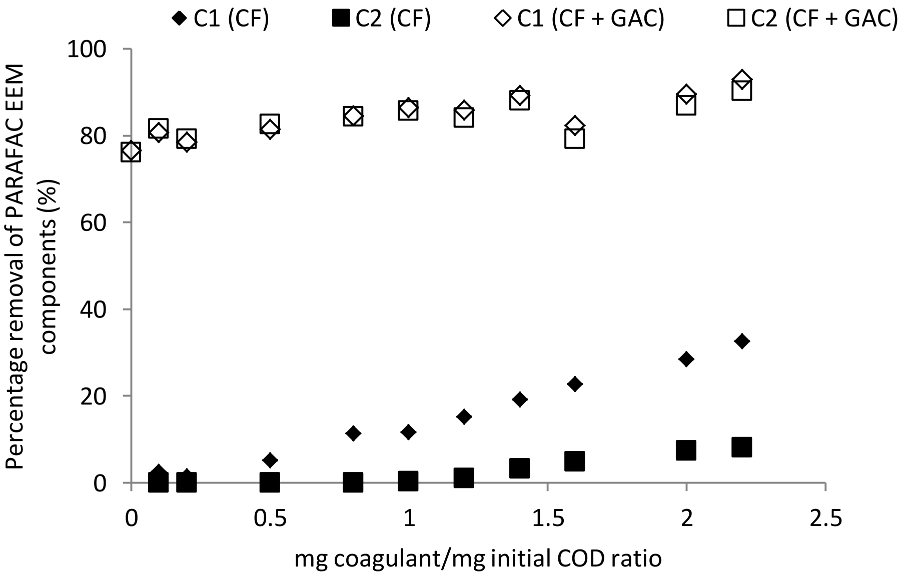
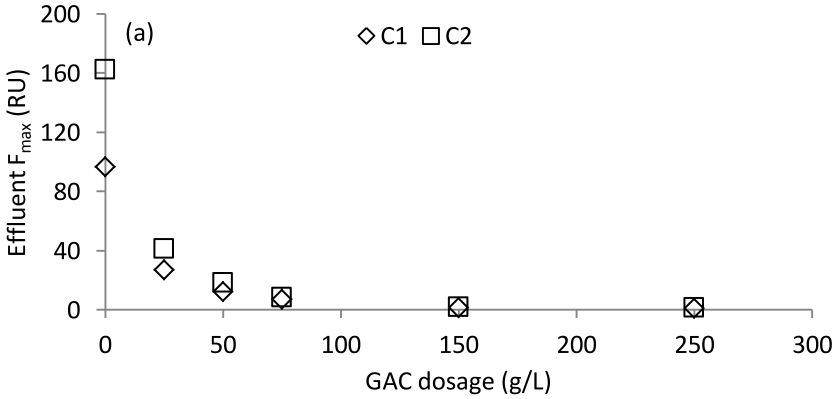


Figure 8.6: Removal of PARAFAC EEM components during coagulation-flocculation with ferric chloride followed by batch GAC adsorption of biologically treated landfill leachate. CF: coagulation-flocculation, GAC: granular activated carbon adsorption (GAC dose: 150 mg/L, 30 minutes treatment time). Influent values C1: 82 RU, C2: 129 RU.

8.3.3.2 GAC batch adsorption of PARAFAC EEM components

The impact of the adsorbent dosage and contact time on the two PARAFAC EEM components is illustrated in Figure 8.7a and 8.7b. Similar to the bulk organic matter (COD), the reduction in F_{max} of C1 and C2 in biologically treated landfill leachate (non-coagulated) increases at higher GAC dosages (Figure 8.7a), with a removal of 93-95 % at a GAC dosage of 75 g/L and a treatment time of 240 min. Further increase in the GAC dosage did not yield important reductions (99% at 250 g/L) in the F_{max} of the two components especially considering the high cost of GAC at high doses e.g. 250 g/L. Therefore, a dose of 75 g GAC/L is sufficient for reduction of DOM components. This is in contrast with the observation made during the removal of bulk organic matter (COD and α_{254}) where a double dosage 150 g/L was required (section 8.3.1). This can be attributed to the reduction of also non-fluorescent DOM (DOM with more aliphatic groups or simple in nature), which implies that the role of conventional water quality parameters such as COD cannot be ignored in determining optimum conditions for treatment of landfill leachate.

Regarding contact time, the F_{max} of C1 and C2 reduces at longer treatment times reaching a constant level from 120 min. At the minimum GAC treatment time of 30 min, chosen in section 8.3.1.1, a 76% F_{max} reduction of both C1 and C2 are obtained with 150 g GAC /L (Figure 8.7b).



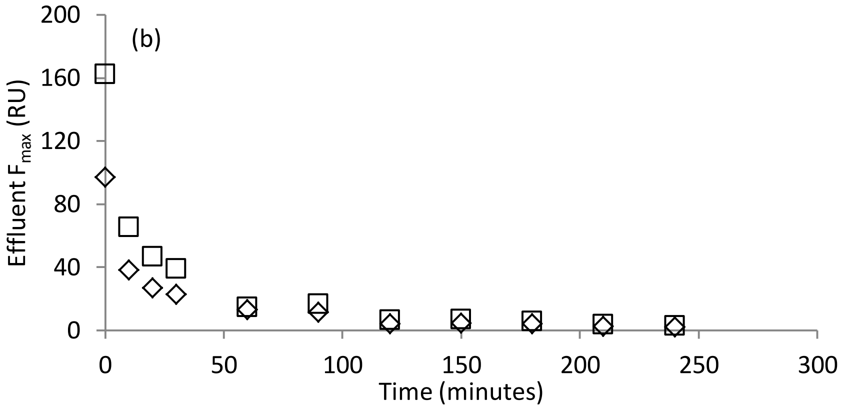


Figure 8.7: Effect of (a) GAC dosage at contact time of 240 minutes and (b) GAC contact time at a GAC dose of 150 g/L on the removal of F_{max} of C1 and C2 in biologically treated leachate. Initial F_{max} C1: 97 RU, C2: 162 RU.

To further describe the equilibrium interaction between the DOM components and GAC, the freundlich isotherm (equation 8.3) is used. A pseudo second-order kinetic model (equation 8.4) (Ho and Mckay, 1999; Simonin, 2016) is applied to study the adsorption kinetics.

$$q_e = \frac{V(C_O - C_{eqm})}{m} = K_f \, C_{eqm}^{1/n} \qquad equation\ 8.3$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad equation\ 8.4$$

where q_e is the removed F_{max} per gram adsorbent (RU/g) at equilibrium; $C_o$is the initial leachate F_{max} (RU/L); C_{eqm} is the equilibrium concentration (RU/L); V is the volume of leachate used (L); m is the mass of GAC (g); K_f is the freundlich constant related to adsorption capacity at unit concentration $(RU/g)(L/RU)^n$; and 1/n is the freundlich constant related to the adsorption intensity. q_t is the removed F_{max} per gram adsorbent at any time t (RU/g); k_2 is the kinetic constant (g/RU.hr); and t is time (hr). $k_2q_e^2$ = h (RU/g.hr) is also refered to as the initial adsorption rate.

Results in Table 8.1 show that the freundlich isotherm (R^2 > 0.97, n = 5) and the pseudo second-order kinetic model (R^2 = 0.99, n = 10) are suitable in describing the GAC adsorption of both C1 and C2. The 1/n values which are below 1 show that adsorption of the two components is favourable and similar for both components. K_f is found to be higher for C2 (0.63) than for C1 (0.46), showing that at a unit equilibrium concentration, C2 will be prefarably adsorbed by GAC than C1. One possible reason could be that, among the two humic-like components, C2 contributes in a higher extent to the fluorescence intensity than C1, making that the initial F_{max} of C2 plays a critical role in the high equilibrium adsorption capacity (Lee and Hur, 2016). Moreover, the low molecular weight of C2 acts as an advantage since it can easily penetrate into the GAC mesopores and micropores, favouring the adsorption. Table 8.1 also shows a good agreement between the experimental and the calculated q_e values. The rate constant k_2 indicates that more GAC is required to remove a unit F_{max} of C1 than C2 per time, which can be explained by the higher molecular weight compounds represented by C1.

Table 8.1: Freundlich isotherm and pseudo second-order kinetic model parameters describing the adsorption of PARAFAC EEM components from biologically treated leachate onto GAC.

PARAFAC EEM components	**$q_{e, exp}$ (RU/g)**	**Freudlich isotherm**			**Pseudo second-order kinetic model**			
		K_f (RU/g)(L/RU)^n	**1/n**	**R^2**	**$q_{e, calc}$ (RU/g)**	**k_2 (g/RU.hr)**	**h (RU/g.hr)**	**R^2**
C1	0.63	0.46	0.53	0.98	0.65	10.13	4.27	0.99
C2	1.06	0.63	0.55	0.97	1.09	6.45	7.66	0.99

exp: experimental; calc. calculated

When combining coagulation-flocculation with subsequent GAC in a batch system, 84% of the fluorescence intensity of C1 and C2 is removed when biologically treated leachate is first coagulated with 0.8 mg $FeCl_3$/mg COD_o and then treated with 150 g/L GAC for 30 minutes (Figure 8.6). Increasing the coagulant dose to 2.2 mg $FeCl_3$/mg COD_o translates into an increase in total removal up to 93 % C1 and 90 % C2. Comparing with the results obtained with only coagulation-flocculation, it becomes clear that GAC preferentially removes C2 from coagulated leachate, probably because of (i) its high fluorescence intensity in the influent (coagulated leachate) and thus a large driving force between the liquid and the solid phase, (ii) its low molecular weight, and (iii) its high initial adsorption rate (as shown by h).

8.3.3.3 Adsorption of PARAFAC EEM components in continuous-mode operated GAC columns

To study the behaviour of PARAFAC EEM components through a dynamic system (GAC column), the F_{max} of components C1 and C2 was monitored during treatment with GAC only and with 0.8 mg $FeCl_3$/mg COD_o + GAC . Breakthrough curves (Figure 8.8a) show that, at 3.2 BV GAC treatment, 97% of C1 and 98% of C2 are removed from the biologically treated leachate. Upon further GAC operation, the effluent F_{max} of C1 increases faster than C2 showing the preferential removal of C2 being in agreement with the batch results. However, unlike the equilibrium system where the ratio of C2/C1 decreases considerably (e.g from 1.7 to 1.4 after 4 hours treatment Figure 8.7b) with time, hence reducing the impact of the initial C2 F_{max}, fresh leachate flowing into the GAC column ensures that the initial C2/C1 ratio is maintained. Thus, in a GAC column, there is a great difference in the overall removal of C2 compared to C1 (Figure 8.8). No breakthrough of the two PARAFAC EEM components is observed during 12.8 BV treatment, even when the experimental period was extended to 51 BV, C1 and C2 removals were 58% and 63% respectively.

A different breakthrough profile is observed for the combined coagulation-flocculation + GAC treatment (Figure 8.8b). Unlike in the GAC only treatment showing an immediate increase in both C1 and C2 at the outlet of the GAC column, a prominent lag-phase lasting between 1 and 4.3 BV is observed with removal efficiencies higher than 99 % for both C1 and C2. This lag phase is 25% longer than that observed during treatment of biologically treated leachate with GAC only. Further GAC treatment of coagulated leachate to 10.7 – 12.8 BV results in a reduction of F_{max} of C1 and C2 by 86 % and 92%, respectively, which is slightly higher than the removal obtained with only GAC (79 % of C1 and 89 % of C2). It is important to note that the longer lag phase and slow increase in the effluent concentrations of C1 and C2 seen when GAC treats coagulated leachate (Figure 8.8b) is an indication that the GAC column will be used for a long time.

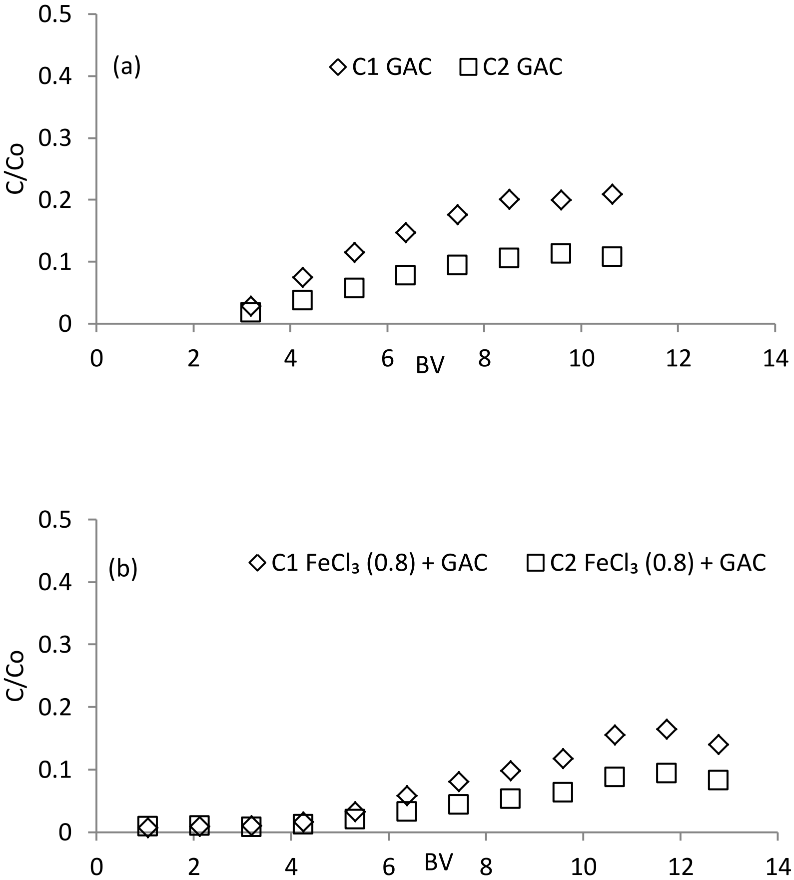


Figure 8. 8: GAC breakthrough curves for PARAFAC EEM components C1 and C2 in (a) biologically treated landfill leachate using GAC only and (b) with preceding coagulation-flocculation (0.8 mg $FeCl_3$/mg COD_0). Influent values (a) C1: 76 – 86 RU, C2: 129 – 141 RU; (b) C1: 69 RU, C2: 121 RU.

8.3.3.4 Structuring the results in self-organising maps

The influence of (i) coagulation-flocculation of leachate before GAC adsorption, (ii) the mode of GAC adsorption (batch or continuous mode), and (iii) treatment time during GAC adsorption are visualised in a self-organizing map. SOM analysis involved a data set with 61 samples. The unified distance matrix and best matching unit used in clustering of the different leachate samples are shown in Figure 8.9. The U-matrix is a coloured 2D structure that is used to visually demonstrate the similarity or difference between map units as a result of different variables in a bid to reveal potential clusters (Brereton, 2012). This visualization of samples with similar/different DOM composition in a 2D structure is not possible with PARAFAC. Moreover, the SOM analysis summarizes the PARAFAC analysis. Map units with similar fluorescence composition are clustered and characterized by lower colour differences (Figure 8.9a). However, areas with high colour differences correspond to map units having clearly different characteristics or areas of low data density. These areas can be used to mark the borders between clusters (Garća and González, 2004). A look at the upper centre of the best matching unit (Figure 8.9b) and the clusters (Figure 8.9c) shows that this area forms a clear border between cluster I and II and III

Cluster I is characterized by samples of biologically treated leachate which are treated in a continuous GAC system with and without preceding coagulation-flocculation. During coagulation-flocculation (0.8 mg $FeCl_3$/mg COD_o) of biologically treated leachate, the DOM composition does not change considerably (the C2/C1 ratio changes from 1.7 to 1.8), resulting in similar DOM composition in coagulated and non-coagulated biologically treated leachate. According to the codebook vectors (i.e. percentage fluorescence composition associated with a given map unit) these samples have a DOM composition which is slightly rich in C1 compared to C2. For instance, map unit 1 with biologically treated leachate samples post-treated with GAC only (denoted as RA) have a DOM composition which is 53% C1 and 47% C2. Whereas map unit 2 with biologically treated leachate post-treated with 0.8 mg $FeCl_3$/mg COD_o + GAC (denoted as FA) has a DOM composition which is 52% C1 and 48% C2. During GAC adsorption through a column, more C2 is removed however, due to the high C2 F_{max}, C2 still contributes a significant portion to the overall DOM composition.

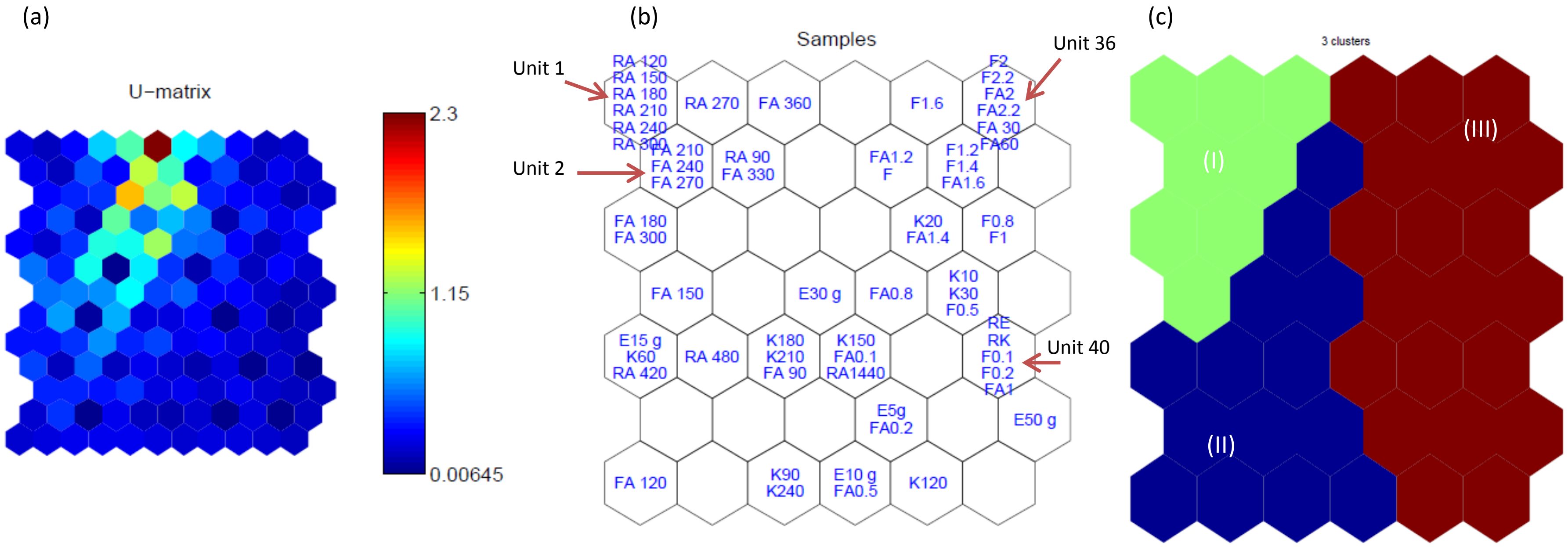


Figure 8.9: The unified distance matrix (U-matrix) (a), best matching unit (BMU) (b), and k means clusters (c) of biologically treated leachate samples based on SOM analysis of fluorescence composition. In (b) RA and FA represent leachate treated with GAC only and FeCl$_3$ + GAC, respectively. The numerical values 0.1 – 2.2 show the coagulant dose (mg FeCl$_3$/ mg COD$_o$), whereas the values 10-1440 show the treatment time (min). Samples indicated with E represent leachate treated in a batch system with different amounts of GAC, K represents leachate treated in a batch system with 150 g/L of GAC at different times. (c) The numerical values represent the clusters.

Cluster II (Figure 8.9 c) is dominated by biological treated leachate samples that are processed with only GAC in a batch system at contact times between 60 and 240 min. In a batch system, the same leachate sample is in contact with the same adsorbent for a long time, which results into a change (from 1.7 to 1.4) of the C2/C1 ratio. According to the codebook vectors, this gives a GAC treated leachate in which C2 (59%) contributes more than C1 (41%) to the fluorescence composition. Even though GAC preferentially removes C2, at the end of the treatment time, the F_{max} of C2 in the GAC treated leachate is still higher than that of C1.

Cluster III, on the other hand, comprises of biologically treated leachate (i) without any post-treatment, (ii) treated with GAC only in a batch system at treatment times up to 30 min, (iii) treated with different coagulant dosages, and (iv) treated with $FeCl_3$ + batch GAC adsorption (treatment time of 30 minutes). In this cluster, the DOM composition of the leachate samples are dominated by C2 instead of C1. In comparison to cluster II, the dominance of C2 in these leachate samples is much higher than that of C1. A closer look at this cluster shows that samples coagulated at higher dosages and also further treated by GAC are at the top of the best matching unit (BMU), e.g. in map unit 36 which contains biologically treated leachate post-treated with coagulation-flocculation (at 2 - 2.2 mg $FeCl_3$/mg COD_o) and batch GAC adsorption (Figure 8.9b). According to the codebook vectors, the use of higher coagulant dosages during coagulation-flocculation subsequently results into a GAC treated leachate which is dominated by C2 (68%) rather than by C1 (32%). Those coagulated at lower dosages (at 0.1 - 0.2 mg $FeCl_3$/mg COD_o) and biologically treated leachate without any post-treatment are located lower on the map, e.g. map unit 40.

Overall, this visual SOM analysis shows that landfill leachate with a low pollutant load and dominated by C2 is beneficial to maximise the removal of recalcitrant compounds such as C2 during GAC adsorption. This can be achieved by coagulation-flocculation, although doses higher than 0.2 mg $FeCl_3$/mg COD_o are needed to achieve F_{max} values which are different from that of biologically treated landfill leachate. On the other hand, coagulation-flocculation at higher dosages – 1.2 to 2.2

mg $FeCl_3$/mg COD_o – would be restricted by costs. As such, it seems that the optimum dosage for coagulation-flocculation of biologically treated landfill leachate before GAC adsorption lies between 0.8 and 1 mg $FeCl_3$/mg COD_o, which justifies the previously made choice of 0.8 mg $FeCl_3$/mg COD_o.

8.4 Conclusions

Characterization of biologically treated landfill leachate with fluorescence EEM coupled with PARAFAC led to the identification of two DOM components: C1 representing humic/fulvic-like compounds and C2 representing humic-like compounds. Coagulation-flocculation of biologically treated leachate with increasing amounts of $FeCl_3$ proved a more effective C1 removal compared to C2. From a technical and economic perspective, an optimum dose of 0.8 mg $FeCl_3$/mg COD_o was defined for a combined coagulation-flocculation and GAC adsorption post-treatment of biologically treated leachate. This is in contrast to the common practice applied in both a research and industrial context, whereby the highest coagulant concentration (e.g. 2.2 mg $FeCl_3$/mg COD_o) is most often preferred. Unlike coagulation-flocculation, GAC adsorption proved more effective in C2 removal, as a result of its high initial F_{max} and lower molecular weight. Continuous-mode GAC experiments showed that better F_{max} reductions of both C1 and C2 can be achieved when a preceding coagulation-flocculation step is included. For instance, F_{max} reductions of 86% C1 and 92%C2 are obtained with 0.8 mg $FeCl_3$/mg COD_o + GAC (at 10.7-12.8 BV) compared to 79% C1 and 89% C2 with 10.7-12.8 BV GAC treatment only. Moreover, use of coagulation-flocculation before GAC treatment increases the GAC lag phase by 25%. Such an improvement translates into a longer column life and hence less GAC treatment costs. Reducing the organic load of landfill leachate using biological and coagulation-flocculation means prior to GAC treatment is beneficial to reduce the recalcitrant character of C2 and thus improving its removal through a GAC column. In the coming Chapters (10) the identity of DOM components in raw landfill leachate and their behaviour through physical-chemical treatment will be investigated and compared with the findings in this Chapter 8

PART III: Raw landfill leachate

Chapter 9

COD removal and nitrogen recovery from raw landfill leachate using coagulation-flocculation, granular activated carbon and ion exchange: technological performance and operating cost estimations

Redrafted after:

Violet Oloibiri, Kristof Demeestere, Sam De Coninck, Stijn W. H. Van Hulle (2018). COD removal and nitrogen recovery from landfill leachate using coagulation-flocculation, granular activated carbon and ion exchange: technical performance and cost evaluation. In preparation.

Contribution of Violet Oloibiri: Designing and performing part of the experiments and writing the manusript

Abstract

The technical performance and cost implications for treatment of raw leachate with a combination of coagulation-flocculation, granular activated carbon (GAC) and/or ion exchange was investigated. Coagulation-flocculation with ferric chloride ($FeCl_3$) at a dose ratio of 2.2 mg $FeCl_3$/mg initial COD (COD_o) gave better removals (50% COD, 66% α_{254}, 79% nickel) and was 1.8 times cheaper than with polyaluminium chloride (PACl). Further treatment of raw leachate with $FeCl_3$ at a lower dose ratio, i.e. 1 mg $FeCl_3$ /mg COD_o, yields lower COD (28%), α_{254} (51%) and nickel (45%) removals, After 10.6 BV of GAC treatment of leachate coagulated at both 2.2 and 1 mg $FeCl_3$/mg COD_o, gave comparable total removals (79-80% COD, 82-91% α_{254}, 90-91% nickel) Moreover, leachate pre-treatment at 1 mg $FeCl_3$ /mg COD_o before GAC adsorption was capable of increasing the efficiency of GAC utilization by 19%, as opposed to 2.2 mg $FeCl_3$ /mg COD_o which lowered the GAC utilization efficiency by 26%. As such, pre-treatment of leachate at higher coagulant doses prior to GAC adsorption does not offer technical and economic benefits. Treatment of raw leachate by only GAC resulted into poor removals (42% COD, 23% α_{254}, 54% nickel) and was 40% more expensive than the $FeCl_3$ + GAC process. Ion exchange treatment of leachate (10.6 BV) that was pre-treated by GAC only or by a combination of $FeCl_3$ and GAC resulted in 100% ammonium removal and 70-76% regeneration of the ion exchange column, which can allow multiple reuse of the ion exchange resin. Compared to the performance of 10.6 BV GAC + 10.6 BV ion exchange, treatment of raw leachate with $FeCl_3$ (1 mg $FeCl_3$ /mg COD_o) + 10.6 BV GAC + 10.6 BV ion exchange gave better removals (84% COD, 83% α_{254}, 95% nickel) with similar costs.

9.1 Introduction

Traditional approaches to landfill leachate management include off-site treatment at publicly owned treatment works. Disposal of leachate at these facilities is marred by escalating transport costs and risks of the facility rejecting the leachate because of a high pollutant load which interferes with processes like UV disinfection (Arabi et al., 2014). In order to tackle these problems, highly efficient on-site leachate treatment facilities are needed. One such method is activated carbon adsorption. The acceptability of activated carbon in the reduction of organic matter and other pollutants in leachate is attributed to its large surface area and diversity in surface functional groups (Zanella et al., 2014). Additionally, its well-developed porous structure ensures proper distribution of compounds on its hydrophobic surface. According to Renou et al. (2008), activated carbon adsorption offers better COD removals irrespective of the initial COD concentration than, for instance, biological techniques. However, sole treatment of raw leachate by activated carbon adsorption is inefficient as fast breakthrough can occur, as already seen in Chapter 6. To improve the treatment efficiency of the activated carbon step, studies in literature – Chapter 2 in addition to our studies in Chapter 5 and 6 – show that it is essential to reduce the organic content, total suspended solids, and other leachate pollutants by techniques like coagulation-flocculation or ozonation. Results in Chapter 6 already showed that coagulation-flocculation of biologically pre-treated leachate before granular activated carbon (GAC) adsorption improved the total COD removal by a factor of 2.5, as compared to GAC treatment only. Treatment of similar biologically pre-treated leachate by coagulation-flocculation using $FeCl_3$ at a dose of 1.3 mg $FeCl_3$ /mg COD before GAC adsorption led to a decrease in GAC costs from 1.32 to 0.09 €/m^3 (Chapter 7) . In comparison, ozonation reduced GAC costs from 1.32 to 0.95 €/m^3. Based on these technical and economic aspects, this paper will focus on the use of coagulation-flocculation as a pre-treatment step for raw, i.e. non biologically pre-treated leachate, prior to GAC adsorption.

In Chapter 8, the importance of optimising the coagulant dose for enhancing GAC adsorption has been shown for biologically treated landfill leachate. However, such a study is still missing for raw landfill leachate but is important because the composition and concentration of pollutants in raw and biologically treated leachate differ (Chapter 3, Chapter 8 and to be discussed in Chapter 10).

Another important aspect that needs to be addressed when treating raw landfill leachate is the presence of nutrients such as ammonium. Ammonium is a significant component of stabilized raw landfill leachate with concentrations above 400 mg/L (see Chapter 2). Whilst biological methods offer a cheap solution for the reduction of ammonium below the recommended discharge limits, they do not allow for recovery as all the ammonium is converted into nitrogen gas. Furthermore, it is known that high ammonium concentrations inhibit proliferation of microorganisms in biological systems, with a poor performance as a result. Since ammonium is an important nutrient, there is need for processes capable of ammonium recovery and simultaneous reduction of other leachate pollutants below the discharge limit. In this context, ion exchange is a viable alternative for biological techniques. It is a simple, compact and highly selective method which is widely used in the treatment of municipal wastewater to remove not only nitrogen but also heavy metals like copper, chromium and nickel (Aiyuk et al., 2004; Zamri et al., 2015). Wastewaters with low biodegradability can be easily treated with ion exchange as opposed to biological methods where an extra source of carbon would be required. Moreover, combining ion exchange with coagulation-flocculation and GAC further offers a compact treatment train which is desirable in areas with scarcity of land. In leachate treatment, studies by Cabeza et al. (2007) and Primo et al. (2009) used anionic resins to eliminate nitrates from a synthetic solution at concentrations similar to that in landfill leachate treated by electro-oxidation. Still, its use as a final polishing step in the treatment of real landfill leachate to capture ammonium is limited because of the associated costs (Chapter 2). However, the possibility for regeneration of the used ion exchange medium offers potential to make this technique more cost effective (Primo et al., 2009). Chemical regeneration of exhausted resins requires large volumes of regenerating solution. Therefore, to minimize costs during regeneration, an optimal use of the solution is required.

This work will highlight the potential of cationic ion exchange in the capture and recovery of ammonium from landfill leachate, pre-treated with coagulation-flocculation and granular activated carbon to remove organic matter, ammonium and nickel. The latter is focused on since the raw leachate contains high nickel concentrations and the environmental regulations for discharge of heavy metals to the environment are very stringent. Specifically, the influence of the coagulant dose on the GAC adsorption, ammonium capture and chemical regeneration of the ion exchange step is investigated. The technical efficiency and costs of a coagulation-flocculation + GAC + ion exchange treatment train is compared with that of the GAC + ion exchange process.

9.2 Materials and methods

Leachate samples were collected from the Vanheede landfilling facility in Roeselare, Belgium (www.vanheede.com). The collection and storage procedure is outlined in Chapter 3, as well as the characteristics of the raw leachate (Table 3.1).

The procedure used to treat raw leachate is illustrated in Figure 9.1. To remove organic matter and other pollutants such as heavy metals, raw landfill leachate was first coagulated. Supernatant from the coagulation-flocculation step was then passed through a GAC column. To eliminate and recover ammonium from the treated landfill leachate, GAC effluent was passed through an ion exchange column. Four key physical-chemical parameters were used to monitor the treatment train. COD and α_{254} were chosen as indicators for respectively the bulk organic matter and the organic matter with aromatic and carbon-to-carbon double bonds. Nickel was chosen as an example of heavy metals which are abundant in landfill leachate. Ammonium was monitored since it is one of the major pollutants in old raw landfill leachate.

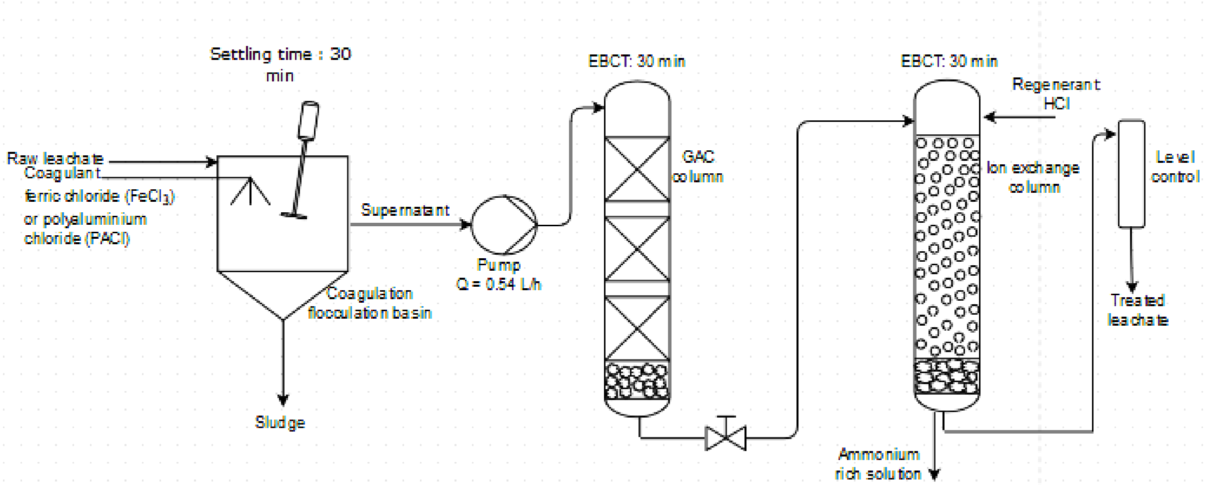


Figure 9.1: Flow diagram for the treatment of raw landfill leachate using coagulation-flocculation, GAC and ion exchange.

Although ferric chloride performed better than polyaluminium chloride during coagulation-flocculation of biologically treated landfill leachate (Chapter 2 and 6), it was still important to include both coagulants in this optimisation study for comparison reasons. Similar to the optimization approach used in Chapter 8, this study sought to optimize the coagulant use by focusing on the initial leachate characteristics. In particular the initial leachate COD concentration is considered, because it is representative for most of the organic pollutants present in the landfill leachate. As already mentioned in Chapter 8, the advantage of this method is that the coagulant concentration is increased relatively to the parameter of interest, e.g. COD_o, as opposed to increasing the coagulant concentration arbitrarily. As such, two different coagulant doses were studied, i.e. 1.0 and 2.2 mg coagulant/mg COD_o (1/1 and 2.2/1). These two doses were chosen because of the following reasons: Chapter 8 showed that the optimum coagulant concentration is around 0.8 – 1 mg coagulant/mg COD_o for biologically treated leachate, whereas the dose of 2.2 mg coagulant/mg COD_o is the highest dose that can be used as much higher doses can lead to restabilization and subsequent reduction in efficiency occurs.

The coagulation-flocculation, GAC adsorption and ion exchange experiments as well as the analysis of COD, UV-VIS absorbance, ammonium and nickel were performed as outlined in Chapter 3.

9.3 Results and discussion

Based on its characteristics, the leachate from Vanheede landfills can be classified as mature leachate. The low BOD_5, and consequently poor BOD_5/COD ratio of 0.01, evidently shows that the leachate is full of bio-recalcitrant organic matter. As such, biological methods for COD removal would be inefficient. The high concentrations of ammonium are known to be the principal cause of acute toxicity (Vedrenne et al., 2012).

9.3.1 Coagulation-flocculation

At a ratio of 2.2/1, $FeCl_3$ (50% removal) performed better than PACl (29% removal) for the reduction of COD in raw leachate. The percentage removal of α_{254} was better than that of COD with 66% and 49% removal obtained with $FeCl_3$ and PACl, respectively. The difference in performance between the two coagulants is also observed in Chapter 6 and other studies in literature (Ntampou et al., 2006; Zhang and Wang, 2009). Furthermore, at a ratio of 2.2/1, coagulation-flocculation was more effective in reducing the concentration of nickel in the raw leachate compared to COD and α_{254}. This is owed to the fact that nickel readily forms insoluble hydroxides whose removal from leachate is enhanced by sweep coagulation. Additionally, nickel removal from leachate is further improved by the removal of organic matter with nickel in its matrix (Peters and Shem, 1993). Nickel removal efficiencies of 79% and 71% were obtained with $FeCl_3$ and PACl, respectively (2.2/1 ratio).

Generally, ferric salts are more effective in coagulation-flocculation of leachate than aluminium salts. Pre-hydrolysed salts of aluminium are known to form several hydrolysis species, of which $\mathrm{Al_{13}O_4(OH)_{24}^{7+}}$, commonly known as Al_{13}, easily depolymerizes in the presence of natural organic matter (Ntampou et al., 2006) explaining its lower performance in COD and α_{254} removal than $FeCl_3$. Although coagulation-flocculation is effective in the removal of COD and α_{254} because it works on particulate matter, it is inefficient in the removal of ammonium which occurs in the dissolved state and does not form any insoluble hydroxides. This is exemplified by the poor removal (< 3%) of ammonium by both coagulants (Figure 9.2). Though certain studies have reported a reduction in ammonium during coagulation-flocculation, this might be attributed to the removal of colloidal matter existing as albuminoid-type nitrogen (Vedrenne et al., 2012).

Based on the good performance of $FeCl_3$ in the reduction of COD, α_{254} and nickel, the use of $FeCl_3$ was further investigated at a lower coagulant/COD_o ratio of 1/1. Lower reductions of COD (28%), α_{254} (45%) and nickel (51%) and no significant ammonium removal were observed (Figure 9.2).

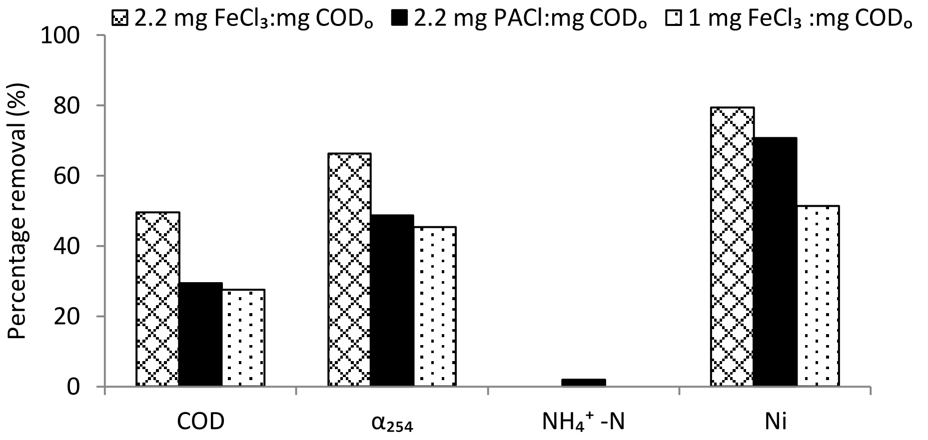


Figure 9.2: Percentage reduction in the physical-chemical parameters of the raw leachate after treatment with coagulants at a ratio of 2.2 and 1.0 mg coagulant/mg initial COD. Initial leachate characteristics: COD 3152 – 3205 mg/L, α_{254} 15.4 - 18.4 cm^{-1}, NH_4^+-N 1060 - 1885 mg/L, nickel 2.1 - 3.7 mg/L

9.3.2 GAC adsorption

Given that the leachate concentrations after coagulation-flocculation with $FeCl_3$ were still above the Flemish discharge limits (COD: 450 mg/L), GAC adsorption was used as a next step in the treatment train. Similar to the optimization process in Chapter 8, raw leachate coagulated at both 1/1 and 2.2/1 $FeCl_3$/COD_o ratios was treated by subsequent GAC adsorption, albeit in a fixed bed operated in the continuous mode, to determine the effect on (i) the removal of the main water quality parameters and (ii) breakthrough and utilization efficiency of the GAC. For comparison purposes, raw landfill leachate without previous coagulation-flocculation treatment was also sent through the GAC column.

Results show that GAC treatment of non-coagulated raw leachate results in a fast decrease in removal performance (Figure 9.3a). In freshly loaded activated carbon (1 BV of treatment), up to almost 100% removal is obtained for all measured parameters, but this decreases to 23% (α_{254}), 42% (COD) and 54% (nickel) at the end of the treatment period (10.6 BV). The GAC performance is thus the highest for nickel, where several sorption mechanisms are involved: (i) ion exchange with H^+ on the GAC surface, (ii) formation of complexes with negatively charged adsorption sites, and (iii) sorption together with organic matter (Modin et al., 2011). The observed decrease in performance is probably because high molecular weight humic and fulvic DOM (dissolved organic matter) components rapidly adsorb and block the surface sites. The influence of high molecular weight DOM on GAC adsorption will be discussed intensively in Chapter 10.

At higher BV, clearly better results are obtained for organic matter and nickel removal when raw leachate is coagulated prior to GAC adsorption (Figure 9.3b and 9.3c). At 10.6 BV and at a coagulant dose ratio of 2.2/1, COD was removed for 79%, while 91% reduction was obtained for α_{254} and nickel. Comparable results are observed at a coagulant dose ratio of 1/1, being an indication that coagulation-flocculation at the lowest investigated dose could already be sufficient in lowering the pollutant load to the GAC and possibly incurring less treatment costs. Furthermore, Figure 9.3b and 9.3c show that α_{254}, COD and nickel do not reach the column breakthrough (effluent concentration = half of the influent concentration) during the 10.6 BV GAC treatment of $FeCl_3$ pre-treated leachate. Comparison with the breakthrough times of α_{254} (4.26 BV), COD (6.39 BV) and nickel (8.53 BV) during GAC treatment of raw leachate indicates that $FeCl_3$ pre-treatment of raw leachate can prolong the breakthrough time of α_{254}, COD and nickel by more than 60%, 40% and 20%, respectively. Apart from breakthrough, also the utilization efficiency of GAC is affected by coagulation-flocculation pre-treatment. After 10.6 BV of raw leachate GAC treatment, an average bed capacity of 31.3 mg COD removed/g carbon can be calculated from the experimental data. When prior coagulation-flocculation with $FeCl_3$ is applied at a dose of 1/1, the utilization efficiency of the GAC improves by 19%, exemplified by an average capacity of 37.1 mg COD removed/g carbon. A further increase in

$FeCl_3$ dose to 2.2/1, however, led to a 26% less efficient utilization of the activated carbon in the column: 23.1 mg COD removed/g carbon at 10.6 BV. An explanation can be found in the fact that both coagulation-flocculation and activated carbon adsorption are known to work mainly on hydrophobic compounds. During coagulation-flocculation at a dose ratio of 2.2/1, a higher percentage of GAC adsorbable compounds are already removed, leaving a coagulated effluent which is lower in hydrophobic compounds (see further in Chapter 10) and thus decreasing the driving force for adsorption; hence a lower utilization efficiency of the GAC is noticed. Considering both effects – pollutant removal efficiency and GAC utilization efficiency at high BV – a coagulant dose ratio of 1/1 is used for further ion exchange experiments. These are needed because no ammonium removal is observed from 4 BVs GAC treatment on, independent on the use of coagulation-flocculation as pre-treatment. GAC is known to have a highly hydrophobic surface which is favourable for the removal of many organic compounds (indicated by COD and α_{254}) but has a poor interaction with more polar substances such as ammonium.

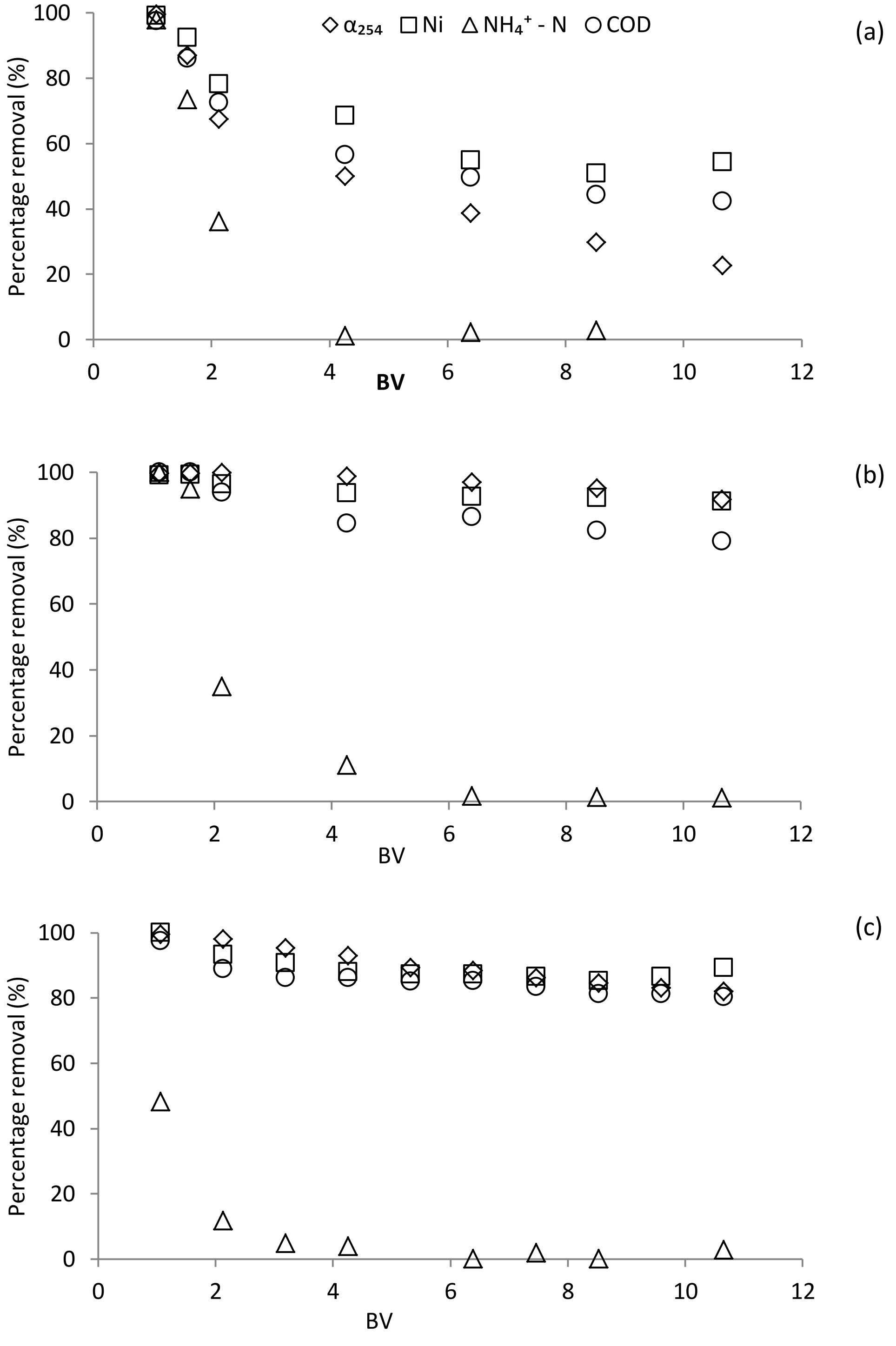


Figure 9.3: Percentage removal of α_{254}, nickel, ammonium and COD after treatment of raw leachate by (a) only GAC, (b) $FeCl_3$ (2.2 mg coagulant/mg COD_o) dose ratio + GAC, and (c) $FeCl_3$ (1 mg coagulant/mg COD_o) dose ratio + GAC. GAC influent concentrations: (a) α_{254} 16.5 cm^{-1}, nickel 2.6 mg/L, ammonium 1487 mg/L, COD 2759 mg/L; (b) α_{254} 6.2 cm^{-1}, nickel 0.76 mg/L, ammonium 1950 mg/L, COD 1589 mg/L; (c) α_{254} 8.4 cm^{-1}, nickel 1.0 mg/L, ammonium 1075 mg/L, COD 2321 mg/L.

9.3.3 Ion exchange

9.3.3.1 Pollutant removal

Discharge of (coagulated) GAC-treated leachate, containing high ammonium concentrations (1060 – 1090 mg/L), could lead to intense eutrophication of surface waters. Ion exchange provides a robust and regenerating process which is not affected by variations in ammonium as a result of leachate age. A very high removal efficiency (100%) of ammonium, stable in time, is obtained when both non-coagulated (Figure 9.4a) and coagulated (Figure 9.4b) GAC effluent is passed through the ion exchange. When comparing with Figure 9.3a and 9.3c, it is clear that ammonium is solely removed by the ion exchange step, particularly at higher BV. Moreover, ammonium does not show breakthrough in the ion exchange column during the entire treatment period (Figure 9.4a and 9.4b). According to Bashir et al. (2011) and Malovanyy et al. (2013), natural and commercial ion exchange resins have a higher affinity for ammonium than for organic matter. Therefore, the exchangeable ions contained in the cationic resin are easily replaced by the ammonium in the landfill leachate. Additionally, the high concentration of ammonium in the leachate creates a large driving force for its removal by ion exchange, compared to the other parameters (organic matter and nickel) since these are already largely removed via the preceding treatment processes. The total removal of COD, α_{254} and nickel obtained after 10.6 BV of GAC and ion exchange amounts 51-62% for non-coagulated leachate and 83-95% for coagulated leachate. However, in absolute amounts, it is mainly ammonium (549 – 1110 mg NH_4^+-N removed/L) that is removed during the ion exchange step compared to e.g. COD (10 – 232 mg COD removed/L) .

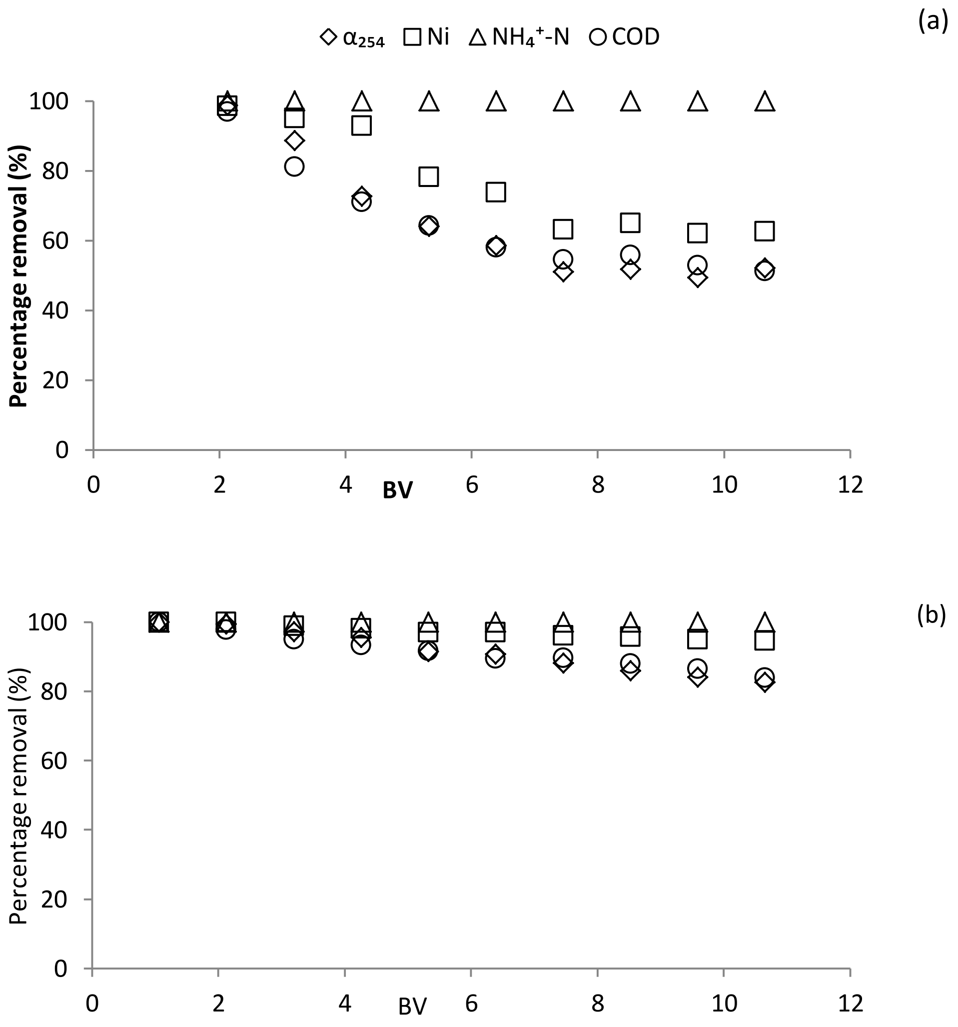


Figure 9.4: Overall percentage removal of α_{254}, nickel, ammonium and COD percentage removal after treatment of raw leachate by (a) GAC + ion exchange (b) $FeCl_3$ (1 mg coagulant/mg COD_o) dose ratio) + GAC + ion exchange treatment. GAC influent concentrations: (a) α_{254} 14.5 cm^{-1}, nickel 1.46 mg/L, ammonium 1090 mg/L, COD 2365 mg/L; (b) α_{254} 8.42 cm^{-1}, nickel 1.0 mg/L, ammonium 1075 mg/L, COD 2321 mg/L.

During the entire experimental period (10.6 BV), a total amount of 2208 and 2097 mg NH_4^+-N is captured by the ion exchange resin for leachate treated with GAC + ion exchange and with $FeCl_3$ + GAC + ion exchange, respectively. This corresponds to an ion exchange resin utilization efficiency of 12.2 (GAC + ion exchange) and 11.6 ($FeCl_3$ + GAC + ion exchange) mg NH_4^+-N retained/g resin. Though it could be expected that the other pollutants would greatly inhibit the removal of ammonium, the ion exchange efficiency for the treatment of the two types of effluent was comparable. This is most probably because the high ammonium concentration induces a strong concentration gradient between the leachate and the resin, hence overcoming other factors such as interference from competing but less abundant species. The slight differences in resin efficiency are expected to be a result of the difference in initial ammonium concentration in landfill leachate depending on the type of pre-treatment. Preliminary batch studies with a pure ammonium solution showed that the experimental resin capacity is 25.7 mg NH_4^+-N removed/g resin. This implies that only half of the capacity of the resin is used after 10.6 BV. For further research, it might be interesting to investigate the effect of coagulation-flocculation on the utilization efficiency of the ion exchange resin in terms of ammonium removal after longer treatment periods (BV ≥ 10.6), approaching saturation of the resin with ammonium and organic matter. Especially since literature shows that longer usage of the ion exchange resin can be obtained with leachate containing lower concentrations of suspended solids, organic matter, e.t.c. (see Chapter 2).

9.3.3.2 Ion exchange regeneration

Regeneration of the used ion exchange is an important economic aspect in the treatment of landfill leachate by ion exchange. According to Goel et al. (2005), the main aim of the regeneration step is to produce (i) a resin which can be reused several times by spending the least amount of regenerating solution, and (ii) a concentrated solution which can be further safely treated or used as a resource in the recovery of important nutrients.

In this study, HCl was used as the regenerating solution since the ammonium that would be recovered as NH_4Cl can find its use as a fertilizer (Aiyuk et al., 2004). Though Lewatit monoplus S108 has a higher affinity for ammonium than for H^+, the high concentration of hydrogen ions in the regenerating solution outweighs this affinity, hence replacing the ammonium captured in the resin's matrix. Results show that a maximum of 2.4 BV of HCl solution (2.74 M) is sufficient to reduce the effluent ammonium concentration in the regenerant below the detection limit. Therefore, when considering the 10.6 BV (it's possible that this can be longer) treated by the ion exchange resin when capturing ammonium, the ammonium in landfill leachate can be concentrated by a factor of 4.4, regardless of the step(s) preceding ion exchange. Ammonium solutions with a maximum concentration of 6500 and 9460 mg/L were obtained from the GAC + ion exchange and $FeCl_3$ + GAC + ion exchange treatment trains, respectively. Taking into account the ammonium concentration and the volumes of the collected regenerant, a resin regeneration efficiency of 76% (GAC + ion exchange) and 70% ($FeCl_3$ + GAC + ion exchange) was achieved. Though complete regeneration of ion exchange resin would be ideal, these would certainly require counter current flows or more regenerating solution which could lead to higher operating costs for the ion exchange process (Aiyuk et al., 2004).

9.3.4 Economic evaluation

Evaluating the economic as well as the technical feasibility of a leachate treatment process is important since its implementation will be largely determined by the associated operating costs (Chapter 7), (Gupta and Singh, 2007; Van Hulle et al., 2010). Whereas economic assessments involve several aspects – capital, labour, consumables, maintenance costs – this study will only focus on providing the operational costs associated with reagents, adsorbent and ion exchange resin, in a bid to provide a simple basis on which these processes can be compared with others. A leachate production volume of 150 m^3/day is used for the operating cost calculations.

Coagulation-flocculation of landfill leachate with PACl using a dose ratio of 2.2/1 (mg coagulant/mg COD_o , COD_o 3152 mg/L) proved to be more expensive than $FeCl_3$ at the same dose (Table 9.1). Given also its better technical performance, $FeCl_3$ is clearly the preferred coagulant for landfill leachate. When reducing the dose to 1 mg $FeCl_3$ /mg COD_o (COD_o 3146.7 mg/L), the operating cost lowers to 1.9 €/m^3. Comparing these costs with those obtained in Chapter 7 (0.81 €/m^3, COD_o 2226 mg/L, initial pH 6) during coagulation-flocculation of biologically treated landfill leachate, coagulation-flocculation of raw leachate is more expensive. This is because more coagulant is used to meet the desired ratio with COD_O.

Table 9.1: Operating costs (€/m^3 associated with the treatment of raw landfill leachate with coagulation-flocculation, 10.6 BV GAC and 10.6 BV ion exchange.

Treatment	**Raw leachate**	**Coagulated leachate (2.2 mg PACl/mg COD$_o$)**	**Coagulated leachate (2.2 mg FeCl$_3$/mg COD$_o$)**	**Coagulated leachate (1 mg FeCl$_3$/mg COD$_o$)**
Coagulation-flocculation	-	8.1	4.4	1.9
GAC	4.5	-	2.7	2.7
Ion exchange (treatment + regeneration)	23.3	-	-	23.3
Total operating costs	27.8	-	-	27.8
Effluent concentration (mg/L) after 10.6 BV ion exchange				
COD	1155	-	-	512
Ni	0.55	-	-	0.11
NH_4^+ - N	0.019	-	-	0

Since in this study GAC adsorption is mainly used to further reduce the COD content, operating costs will be estimated based on COD removal. The GAC operating costs needed to reduce the COD content of non-coagulated raw leachate to 1591 mg/L (at 10.6 BV) is calculated to be 4.5 €/m^3, which is 40% more expensive than the adsorption costs incurred when leachate is first pre-treated with coagulation-flocculation using FeCl$_3$ (2.7 €/m^3), with no significant differences between the two coagulant doses. A higher dose ratio (2.2 mg FeCl$_3$ /mg COD$_o$) does consequently not offer technical neither economic advantages than the preferred 1/1 FeCl$_3$ dose. In Chapter 7 it was already observed that GAC costs can be significantly reduced when biologically treated leachate is first coagulated before GAC adsorption, which is in agreement with this study on raw leachate. However, the total operating costs for both coagulation-flocculation + GAC adsorption – 4.6 €/m^3 when using a FeCl$_3$ dose ratio of 1/1 – is comparable to the GAC costs for non-coagulated leachate with a combination of FeCl$_3$ (2.2/1) + GAC largely increases the operating costs. This shows that, though coagulation-flocculation has the potential to reduce the GAC costs, the total cost can only be kept similar to that of a single GAC treatment if the coagulant dose is limited. However, from a technological point of view, it is important to note that the effluent COD concentration of FeCl$_3$ + GAC (631 - 659 mg/L at both doses) is at least 2.5 times lower than that in the GAC effluent when used as a single treatment (1591 mg/L). Moreover, better heavy metal removals are achieved with

$FeCl_3$ + GAC than with GAC only. Therefore, to reach the effluent concentrations achieved by $FeCl_3$ + GAC, more GAC and thus higher costs will be needed, making a single GAC treatment an expensive option.

Considering a resin cost of 1.14 €/kg, a HCl cost of 0.07 €/kg, the amount of resin used 180 g, (for the first time only) and assuming a leachate production of 150 m^3/day and resin capacity of 11.6 - 2.2 mg NH_4^+ - N retained/mg resin, the operating costs of removing ammonium (initial concentration of 1075 - 1095 mg/L) with ion exchange proved to be more expensive than the preceding steps (Table 9.1). These operating costs are similar for both the $FeCl_3$ (1/1) + GAC + ion exchange and the GAC + ion exchange process. However, it is important to note that the ion exchange column with influent treated with GAC only receives leachate with higher organic matter and nickel concentrations. It can thus be expected that saturation will occur earlier necessitating a faster replacement or regeneration. Therefore, in view of long term operation, $FeCl_3$ (1/1) + GAC + ion exchange is a cheaper option. Relative to the operating cost of ammonium removal using nitrification denitrification (0.58 €/m^3) and autotrophic nitrogen removal (0.04 €/m^3) as reported in Chapter 7, ion exchange is very expensive. These biological processes encounter, however, other limitations including operational problems, land requirements and scarcity, and emission of greenhouse gases. However, if the compact nature and the possibilities for cost reduction through resin regeneration and reuse are considered, ion exchange might become a competitive alternative for other methods of ammonium removal from landfill leachate.

The total operating costs for the treatment of raw leachate by $FeCl_3$ (1/1) + GAC + ion exchange is estimated to be 27.9 €/m^3, being similar to that for the GAC + ion exchange treatment. However, again, the effluent concentrations of the GAC + ion exchange process are clearly higher at 10.6 BV than those of the $FeCl_3$ (1/1) + GAC + ion exchange process. To reach similar effluent concentrations as achieved by the $FeCl_3$ (1/1) + GAC + ion exchange, the GAC + ion exchange process will incur higher GAC costs. To further reduce the total operating costs of the entire 3-step treatment train, strategies such as optimizing the pH during the coagulation-flocculation process could lead to the use of less coagulant and to an increase in the amount of humic substances removed. This could lower the organic matter to the subsequent steps and, therefore, lower related adsorption and ion exchange costs. The total operating costs for treatment of raw leachate with coagulation-flocculation ($FeCl_3$) + GAC + ion exchange is certainly more expensive (27.9 €/m^3) than those generally incurred in coagulation-flocculation ($FeCl_3$) + GAC (0.90 €/m^3) treatment of biologically treated landfill leachate. This is because of the high costs incurred during the coagulation-flocculation ($FeCl_3$) and GAC, and especially during the ion exchange process.

9.4 Conclusions

An in-depth optimization of the coagulation-flocculation process before GAC treatment of raw landfill leachate is important in order to achieve a better performance at lower operating costs. The use of $FeCl_3$ as a coagulant results in better COD, α_{254} and nickel removal and is more cost-effective than PACl. With regards to GAC adsorption of coagulated leachate, higher doses of coagulant (e.g. 2.2 mg $FeCl_3$ /mg COD_o) reduce the efficiency of GAC utilization during the adsorption step. Moreover, high doses neither improve the overall performance of the $FeCl_3$ + GAC treatment process, nor offers economic benefits. As such, coagulation-flocculation of raw leachate at a lower coagulant dose ratio (1 mg $FeCl_3$ /mg COD_o) prior to GAC adsorption is recommended instead of using higher coagulant doses or direct GAC treatment. Results further show that up to 10.6 BV ion exchange treatment, ammonium removal at the ion exchange step is not influenced by the pre-treatment steps. Up to 100% ammonium removal was achieved from single GAC and $FeCl_3$ (1 mg $FeCl_3$ /mg COD_o) + GAC effluents, with a similar operating cost of 17.7 €/m^3. In both cases, regeneration of the ion exchange resin resulted in 70-76% recovery, and an additional regeneration cost of 5.6 €/m^3. Overall, from a technological and economic point of view, treatment of raw leachate with $FeCl_3$ (1 mg $FeCl_3$ /mg COD_o) + 10.6 BV GAC + 10.6 BV ion exchange is the recommended strategy especially when space for implementation of biological treatment is limited .

Chapter 10

Characterisation of landfill leachate by EEM-PARAFAC-SOM during physical-chemical treatment by coagulation-flocculation, activated carbon adsorption and ion exchange

Redrafted after:

Violet Oloibiri, Sam DeConinck, Michael Chys, Kristof Demeestere, Stijn W. H. Van Hulle (2017) Characterisation of landfill leachate by EEM-PARAFAC-SOM during physical-chemical treatment by coagulation-flocculation, activated carbon adsorption and ion exchange. Chemosphere, 186, 873 – 883.

Contribution of Violet Oloibiri: Designing the experiments and writing the manusript

Abstract

The combination of fluorescence excitation-emission matrices (EEM), parallel factor analysis (PARAFAC) and self-organizing maps (SOM) is shown to be a powerful tool in the follow up of dissolved organic matter (DOM) removal from landfill leachate by physical-chemical treatment consisting of - coagulation-flocculation, granular activated carbon (GAC) and ion exchange. Using PARAFAC, three DOM components were identified: C1 representing humic/fulvic-like compounds; C2 representing tryptophan-like compounds; and C3 representing humic-like compounds. Coagulation-flocculation with ferric chloride ($FeCl_3$) at a dose of 7 g/L reduced maximum fluorescence of C1, C2 and C3 by 52%, 17% and 15% respectively, while polyaluminium chloride (PACl) reduced C1 only by 7% at the same dose. DOM removal during GAC and ion exchange treatment of raw and coagulated leachate exhibited different profiles. At less than 2 BV of treatment the humic components C1 and C3 were rapidly removed, whereas at BV ≥ 2 the tryptophan-like component C2 was preferentially removed. Overall, leachate treated with coagulation-flocculation + 10.6 BV GAC + 10.6 BV ion exchange showed the highest removal of C1 (39% - $FeCl_3$, 8% - PACl), C2 (74% - $FeCl_3$, 68% - PACl) and no C3 removal; whereas only 52% C2 and no C1 and C3 removal was observed in raw leachate treated with 10.6 BV GAC + 10.6 BV ion exchange only. Analysis of PARAFAC-derived components with SOM revealed that coagulation-flocculation, GAC and ion exchange can treat leachate at least 50% longer than only GAC and ion exchange before the fluorescence composition of leachate remains unchanged.

10.1 Introduction

The treatment of raw landfill leachate with coagulation-flocculation, GAC adsorption and ion exchange has been demonstrated in Chapter 9. The efficiency of the three physical-chemical processes was monitored using percentage removals of COD, α_{254}, ammonium and nickel. Water quality parameters such as COD, ammonium and nickel provide very little information on the nature of DOM which is an important constituent of the organic matter in landfill leachate. On the other hand, α_{254} offers a glimpse into the heterogeneous nature of DOM, by only reflecting the presence of carbon-to-carbon double bonds and aromaticity of the leachate. Therefore, a more profound knowledge on the specific DOM components is important since different components respond in a different way to various treatment processes, as exemplified in Chapter 8. Therefore, this chapter will focus on the characterization of DOM in raw landfill leachate (i.e. without prior biological treatment). According to literature, the DOM composition of raw wastewater can be different from that of biologically treated wastewater (Yang et al., 2015). This is because during biological treatment of wastewaters, certain fractions (mostly proteinaceous material) are degraded by micro-organisms (Yang et al., 2015). Hence, it is importantto characterize DOM also in raw landfill leachate.

Due to the aforementioned advantages of fluorescence EEM (Chapter 8), it is the preferred technique for the characterization of leachate DOM. Moreover, the combination of fluorescence EEM and peak identification has been used in monitoring the efficiency of treatment techniques. Cui et al. (2015) employed fluorescence EEM to various leachate fractions to study the effectiveness of a sequencing batch reactor (SBR) for treating landfill leachate, and to obtain insights in the nature of DOM components. The results show that the fluorescence intensity of hydrophobic acids and neutral organic fractions at Ex/Em wavelengths 300-370/400-500 (humic-like region) significantly decreased. Analysis of the hydrophilic leachate fraction after a combined physical-chemical and biological treatment resulted in a complete removal of high excitation wavelength tryptophan substances (Ex/Em=280/345), humic-like (Ex/Em=295/400) and fulvic-like (Ex/Em=235/400) compounds (Liu et al., 2015). These studies (Cui et al., 2015; Liu et al., 2015) involved resin fractionation of DOM in leachate; however, resin fractionation is time consuming and depending on the resin used, the amount of NOM components recovered differ (Baghoth et al., 2011; Peuravuori et al., 2002), Moreover, peak identification was used in the analysis of EEM data. Peak identification is, however, limited by the possibility of peak shifting as a result of sample dilution and overlapping of peaks (Yang et al., 2015). While peak identification has been useful for the identification of DOM components, more comprehensive information can be extracted from the massive EEM dataset using robust chemometric techniques such as PARAFAC and self-organizing maps SOM (Chapter 8) (Henderson et al., 2009). Moreover, components identified during PARAFAC modelling have proved to be highly sensitive surrogates for traditional measurements such as COD (Yang et al., 2015).

Therefore, similar to the study in Chapter 8, the goal of this chapter is to use the combined power of both PARAFAC and SOM analysis of fluorescence EEM measurements to identify and monitor DOM components changes during physical-chemical treatment of raw landfill leachate through coagulation-flocculation followed by GAC adsorption and ion exchange. This study will focus on comparing the performance of the lab scale 3-step treatment scheme (coagulation-flocculation + GAC + ion exchange) to remove DOM from raw landfill leachate relative to a treatment scheme using only GAC + ion exchange. Especially with the view of highlighting the importance of coagulation-flocculation as a pre-treatment efficient in removing high molecular weight compounds which can block the GAC pores.

10.2 Materials and methods

Raw landfill leachate samples were collected from the Vanheede municipal landfill in Roeselare (Belgium). The characteristics are provided in Table 3.1.

Raw landfill leachate was first treated with coagulation-flocculation to remove high molecular weight organic matter. The coagulated effluent was further passed through a GAC column for polishing and finally through an ion exchange column to remove the high concentrations of ammonium which were still present in the GAC effluent. Figure 9.1 is a flow diagram of the leachate treatment process.

For this specific study, coagulation-flocculation was done using Ferric chloride ($FeCl_3$) and polyaluminium chloride (PACl) without any pH adjustments and at a coagulant dose of 2.22 mg coagulant/mg COD_o (corresponding to 7 g/L) was applied. Raw leachate and effluent from each step were taken for both physical-chemical (COD, ammonium, nickel, UV-VIS absorbance) and fluorescence EEM analysis. The analyses were done according to the descriptions found in Chapter 3. The effluent from both the GAC and ion exchange columns were sampled at different time intervals. The lab set-up and conditions for the coagulation-flocculation, GAC and ion exchange treatment are as outlined in the methodology Chapter 3.

Analysis of fluorescence EEM with PARAFAC and subsequently with SOM was done following the procedure in Chapter 8. The fluorescence EEM data available for PARAFAC modelling consisted of 49 samples. A two to five component PARAFAC model was fitted to the data to ensure that the optimum number of components is chosen. During PARAFAC modelling, four outlier samples with high leverages were eliminated. SOM analysis was done on the PARAFAC output according to the description in Chapter 8

10.3 Results and Discussion

10.3.1 Common physical-chemical characteristics of the raw and treated leachate

From the COD and NH_4^+-N concentrations shown in Table 3.1, the raw leachate can be classified as old (Table 1.1, Chapter 1).The performance of the whole treatment chain in the removal of common physical-chemical parameters is already described in much more detail in Chapter 9. Briefly, coagulation-flocculation with 2.22 mg $FeCl_3$/mg COD_o was more effective (≥ 50% removal) than PACl at the same dose in the reduction of COD, α_{254} and nickel, but no ammonium decrease was obtained during coagulation-flocculation. Subsequent 10.6 BV (300 minutes) GAC and ion exchange treatment of coagulated leachate led to higher removals of the four key parameters, with ammonium being primarily removed by the ion exchange column. However, these parameters - COD, α_{254}, nickel and ammonium give no indication of the DOM components (humic-, fulvic-, and protein-like compounds) present in the raw leachate or removed during treatment, similar to the study in Chapter 8 with biologically treated landfill leachate

10.3.2 EEM spectra of the raw and treated leachate

Visual inspection of pre-processed EEMs (data corrected for inner filter effects and scatter signals removed) indicate the presence of 3 peaks in raw landfill leachate (Figure 9.1, 1A). Peak *a* with a maximum fluorescence intensity at an Ex/Em wavelength of 250/450 nm is attributed to humic and fulvic-like compounds which are abundant in raw landfill leachate (Cui et al., 2015; Hudson et al., 2007; Wang et al., 2016). Intense fluorescence is also observed at an Ex/Em wavelength of 230/350, which in this chapter is referred to as peak *b*. According to Coble (1996), Liu et al. (2015) and Yan et al. (2000), this fluorescence is characteristic of tryptophan-like substances such as amino acids, although Baker and Curry (2004) attributed fluorescence in this region to xenobiotic organic compounds like naphthalene. Landfill leachate is rich in amino acids due to the hydrolysis of organic matter (Renou et al., 2008) but is also a significant source of xenobiotic organic compounds. Peaks *a* and *b* seem to be important characteristic peaks of raw landfill leachate as they have been identified in several studies (Baker and Curry, 2004; Huo et al., 2008; Liu et al., 2015; Wang et al., 2016). According to the fluorophore naming technique in Chen et al. (2003) the minor peak *c,* present at an Ex/Em wavelength of 290/440, falls under Region V and indicates the presence of humic-like substances in landfill leachate.

The fluorescence intensities of the peaks reduced considerably during coagulation-flocculation, GAC and ion exchange treatment. By visual inspection, the most significant reduction in fluorescence at peak *a* and *b* were observed during coagulation-flocculation and GAC treatment with very little changes in fluorescence intensity after ion exchange. Fluorescence intensity of peak *a* was reduced by approximately 40% and 30% after treatment with $FeCl_3$ and PACl (Figure 10.1, 1B and 1C) respectively and 88%, 70% after GAC treatment of $FeCl_3$ and PACl effluent (Figure 10.1, 2B and 2C). In contrast, the fluorescence intensity of peak *b* remained unchanged after coagulation-flocculation.

However, it decreased by approximately 75% and 90% after GAC treatment of raw leachate and PACl effluent respectively and disappeared during GAC adsorption of $FeCl_3$ effluent. This is an indication that coagulation-flocculation preferentially removes humic-like components as opposed to protein-like or xenobiotic substances (Yang et al., 2015) whereas GAC adsorption is able to remove both types of compounds hence a clear advantage for combining the two treatment steps. Due to the aforementioned limitations of peak picking method, the reduction of DOM components during leachate treatment can be tracked clearly using maximum fluorescence intensity (F_{max}) values obtained from PARAFAC analysis.

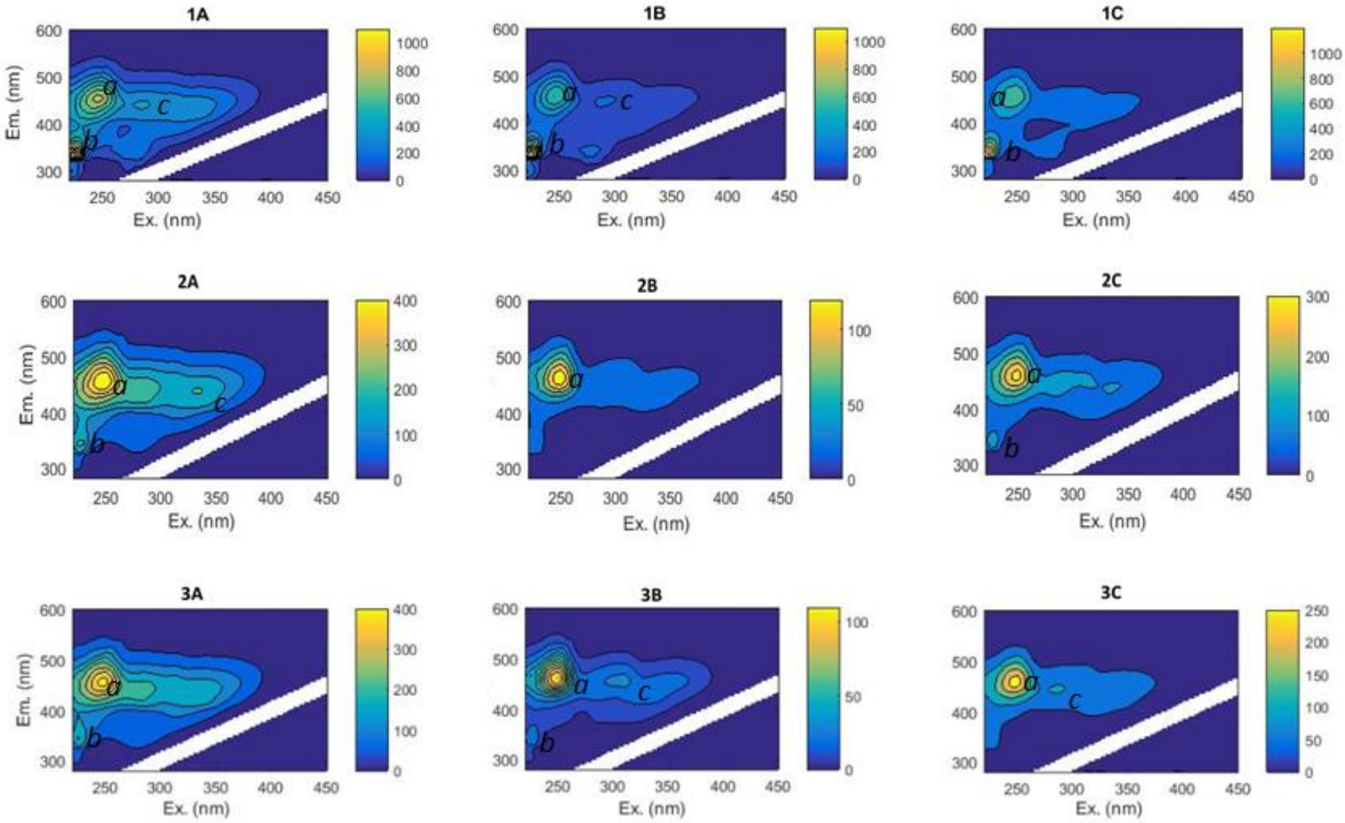


Figure 10.1: EEM spectra of raw landfill leachate (1A) and effluent of different treatment stages. Coagulation-flocculation with $FeCl_3$ (1B) and PACl (1C); 10.6 BV GAC adsorption of raw leachate (2A), $FeCl_3$ effluent (2B), and PACl effluent (2C); and 10.6 BV ion exchange treatment of raw leachate treated by GAC (3A), $FeCl_3$ + GAC (3B), and PACl + GAC (3C).

10.3.3 PARAFAC analysis of the raw and treated leachate EEM spectra

10.3.3.1 Identification of EEM components

PARAFAC modelling of EEM spectra led to the identification and split half validation of three components at a core consistency of 96%. Figure 10.2 shows the contour plot of the three components. Component C1 has two maximum peaks: the peak at Ex/Em 250/425 nm is associated with humic-like substances (Lee and Hur, 2016), whereas the peak at Ex/Em 320/425 nm is associated with the aromatic and aliphatic compounds in DOM cumulatively referred to as fulvic-like compounds (Baker and Curry, 2004). In comparison with a visual inspection (Figure 10.1), PARAFAC modelling enabled the identification of the peak at Ex/Em 320/425 nm; hence acknowledging the presence of highly conjugated molecules in leachate samples (Hua et al., 2007). Component C1 is similar to the C1 identified in Chapter 8. Fluorescence of component C2 occurred at shorter wavelengths (Ex/Em 270/340 nm) and is associated with protein-like tryptophan compounds (Ye et al., 2016), existing as 'free molecules' or bound in peptides or humic structures (Gone et al., 2009). Their presence in landfill leachate is attributed to microbial activity or wastes introduced in to the landfill (Gone et al., 2009). Component C3, with a maximum fluorescence intensity (F_{max}) at Ex/Em wavelengths of 250/460 nm, is also associated with humic-like compounds. Secondary peaks in C3, with very low intensity at Ex 310 nm and 370 nm, are also attributed to humic-like compounds. However, Lu et al. (2009) and Wu et al. (2011) attributed this type of fluorescence to compounds from the pyrene family. Component C3 is similar to component C2 described in Chapter 8. Though C1 and C3 are both associated with humic-like substances, they come from different sources. For instance, according to Lee and Hur (2016) and Stedmon et al. (2003); C1 could be from microbial origins since it resembles microbial humic like fluorescence and C3 from terrestrial sources. This is based on the differences between the ratios of fluorescence at 500nm and 450nm at excitation 370 nm. These fulvic-, humic- and tryptophan-like components offer important information on the nature of DOM in leachate. The fulvic- and humic-like components are linked to the stability of the leachate, whereas the tryptophan component reflects the bioavailable substrate and microbial products of a given bacterial community (Hudson et al., 2007). Tryptophan compounds are related to amino acids and other protein like substances which can be removed easily by microbial processes (Yang et al., 2013). This forms an important criteria in determining the biodegradability of leachate. These three PARAFAC derived components are in agreement with data on PARAFAC modelling of landfill leachate EEM spectra in literature (Table 10.1). It should be noted that excitation wavelengths lower than 250 nm were excluded during PARAFAC modelling to improve the signal-to-noise ratio.

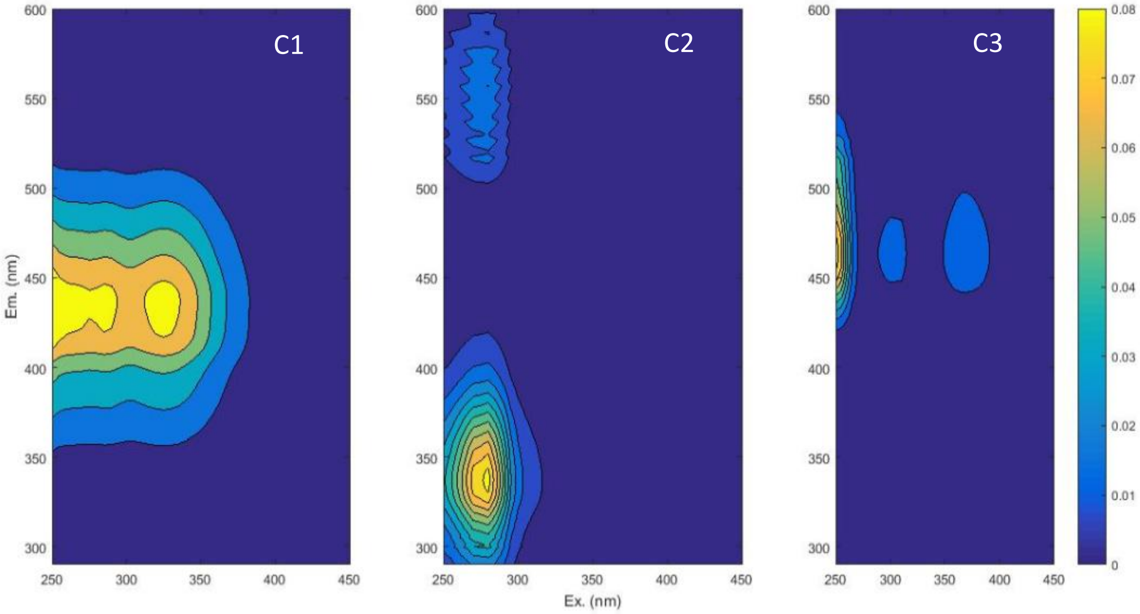


Figure 10. 2: Contour plot of the three PARAFAC derived components

Table 10. 1: PARAFAC derived components in this study compared with others identified in landfill leachate

Component	**Description**	**Hydrophilicity**	**Location Ex/Em (nm)**		**Reference**
			This study	**Literature**	
C1	Humic- and fulvic-like compounds	Hydrophobic acids [a,b]	250, 320/425	250,330/417	(Lee and Hur, 2016)
				241,330/410	(Ye et al., 2016)
				250,360/450	(Ye et al., 2016)
				240,320/400	(Wu et al., 2012)
				240,300/420	(Lu et al., 2009)
				230,325/410-430	(Hua et al., 2007)
				240,330/412	(Wu et al., 2011)
				242,352/452	(He et al., 2013)
				241,328/405	(He et al., 2013)
C2	Protein-like tryptophan compounds	Hydrophobic base fraction [a,b] Hydrophilic acids [a] Hydrophilic neutral fraction [a]	270/340	280/322	(Wu et al., 2012)
C3	Humic-like compounds	Hydrophobic acids [a,b]	250,310,370/460	250,310,390/458	(Wu et al., 2012)
				250,300,360	(Wu et al., 2011)
				250,310,360/464	(Lu et al., 2009)
				255/459	(Lee and Hur, 2016)

[a]: (Hudson et al., 2007)

[b]: (Lu et al., 2009)

10.3.3.2 Coagulation-flocculation treatment: effect of coagulant type on the EEM compounds

Quantitative information from PARAFAC analysis shows that the total maximum fluorescence intensity of the raw leachate is 5.4 RU. C1 (humic and fulvic -like compounds) and C3 (humic-like compounds) contribute each to about 40% of this fluorescence, while C2 (tryptophan-like compounds) is less dominant (20%) (Figure 10.3). The low fluorescence intensity of C2 is an indication that the leachate is tending towards biological stabilization (Hudson et al., 2007; Lee and Hur, 2016). The F_{max} values of raw leachate (Figure 10.3). are much lower than those measured in a biological leachate (C1 -85 RU, C2 – 140 RU) reported in Chapter 8. Coagulation-flocculation of raw landfill leachate by $FeCl_3$ at a dose of 7 g/L (2.22 mg $FeCl_3$/mg COD_o) led to a higher reduction (30%) of the total fluorescence intensity than the reduction obtained (7.5%) with the same dose of PACl. Specifically, $FeCl_3$ reduced the fluorescence intensities of C1, C2 and C3 by 52%, 17%, 15%, respectively. With regards to PACl, only C1 showed a decrease of 27%. A similar trend was observed in Chapter 8 whereby the F_{max} of a C1-similar component was greatly reduced by coagulation-flocculation of raw leachate, more than the F_{max} of C3. Though the coagulation efficiency of PACl is the collective action of various species (metal hydroxides, Al_{13}), The efficiency of PACl in the removal of the DOM components is primarily limited by the presence of Al_{13}. This species forms small Al_{13}-NOM flocs which are not easily removed by settling (Yan et al., 2008). Based on methods such as size exclusion chromatography, resin fractionation and fluorescence EEM, (Lu et al. (2009) was able to determine the molecular weights of components similar to C1 (Ex/Em 240, 300/420) and C3 (Ex/Em 250, 310, 360/464) in landfill leachate as about 3500 – 5000 Da and 2500 – 3000 Da, respectively. Coagulation-flocculation is known to preferentially remove higher molecular weight compounds explaining the poor reduction of fluorescence intensity of C3. It is possible that the tryptophan-like compounds C2 have less charges hence are not neutralised easily which explains the limited reduction of the fluorescence intensity of C2. On the contrary, humic-like compounds are more hydrophobic in nature and have an anionic charge which can be neutralised easily by the hydrolysis products of $FeCl_3$ and PACl.

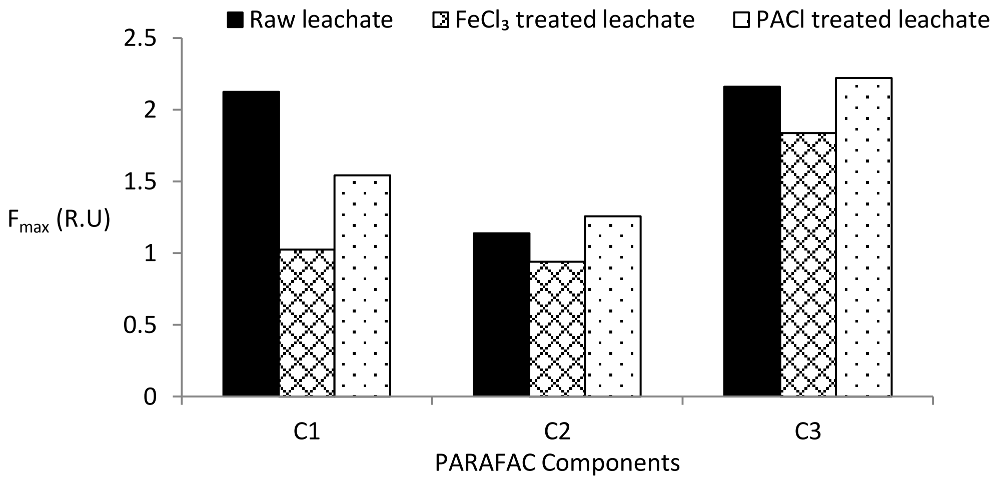


Figure 10.3: Maximum fluorescence intensity (F_{max}) of PARAFAC components in raw and coagulated leachate.

10.3.3.3 GAC Adsorption: effect on EEM compounds

Activated carbon adsorption is a technique widely used to remove DOM components that are not removed by coagulation-flocculation (Chapters 6 and 8). Therefore, the coagulated leachate was subjected to adsorption through a GAC column and breakthrough curves of the 3 EEM components were compared with that of raw leachate. Up to 80% of the humic- and fulvic-like compounds (C1 and C3) were removed in the first 2 BV (60 minutes) of treatment (Figure 10.4 a). However, further treatment led to a decrease in removal with almost no removal after 4 BV (120 minutes) treatment. Humic-like compounds are known to have a high adsorption rate (Lee et al., 2015); hence they are rapidly adsorbed onto GAC surface. However, their adsorption onto GAC is limited due to the inaccessibility of the mesopores and micropores of GAC as a result of their large molecular size. Removal of C2 by GAC exhibited a different profile. After 2 BV GAC treatment, only 20% of C2 was removed however, additional treatment resulted into a steady C2 removal which stabilised at an average of 64%.

Both $FeCl_3$ and PACl coagulated effluents going for GAC adsorption showed fluorescence intensity mainly at C3 (44 – 48% of the total fluorescence intensity) and a lower and almost equal contribution of both C1 and C2 (Figure 10.3). Better reduction in fluorescence intensity of C1 (95%) and C3 (91%)

was achieved by the combined treatment of leachate by $FeCl_3$ + 2 BV GAC compared to 83% C1 and 86% C3 removal obtained after PACl + 2 BV GAC (Figure 10.4 b and c). The slightly lower reduction of fluorescence intensity from PACl effluent can be attributed to the presence of more higher molecular weight compounds compared to the $FeCl_3$ effluent. Certainly, when compared to GAC treatment of raw leachate, better removals of humic- and fulvic- like compounds can be achieved when coagulation-flocculation is combined with GAC adsorption. Albeit at lower efficiencies, C1 removal was observed with further GAC treatment of coagulated leachate with an overall removal of 62% obtained after 12.8 BV treatment of $FeCl_3$ effluent. However, after 10.6 BV, GAC could not remove C1 from PACl effluent. Similar to GAC removal of C3 from uncoagulated leachate, C3 removal from PACl proved recalcitrant to GAC treatment after 4 BV. Conversely, the GAC column could treat $FeCl_3$ effluent for 6.4 BV (180 minutes) before no removal of C3 was observed. This gives a further advantage as to why it's better to pre-treat leachate with $FeCl_3$ than PACl before GAC adsorption. A component similar to C3 was also reported to be refractory to anoxic/aerobic treatments and age related processes taking place in a landfill (Lu et al., 2009). As such, biological treatment of GAC effluent would not be of added value in the removal of C3.

In comparison, GAC removal of a components similar to C1 and C3 from biologically treated landfill leachate exhibited a different profile. In fact, it was continuously removed at higher GAC BV (>2) and with high efficiencies The lag-phase observed in the GAC breakthrough curve for a component similar to C3 in the biological leachate (Figure 8.8b of Chapter 8) is twice longer than that in Figure 10.4 b. The difference in initial COD values going into the GAC column might be an important aspect explaining this different behaviour: the biologically treated leachate used in Chapter 8 had a CODo of 337 mg/L, and 287 mg/L after coagulation-flocculation with 0.8 mg $FeCl_3$/mg CODo, while in Chapter 10 the raw leachate had a COD_o of 2759 mg/L and 1589 mg/L after coagulation-flocculation with 2.2 mg FeCl3/mg CODo. Moreover, the raw leachate had high concentrations of ammonium (1885 mg/L) and nickel (3.7 mg/L). Pre-treatment by both biological and coagulation-flocculation processes clearly lowered the pollutant load (fluorescent and non-fluorescent) and/or change the DOM composition of leachate. This reduces the compounds that might compete with the two PARAFAC components for GAC adsorption sites. Overall, comparing the results in Chapter 8 with the findings here suggests that to improve the removal of recalcitrant compounds such as C3 from raw landfill leachate, the treatment facility benefits from a biological process as the initial treatment step prior to further physical-chemical treatment by coagulation-flocculation and GAC adsorption. Though in Chapters 1 and 2 it has been indicated that biological processes are inefficient in removing recalcitrant organic matter, their role in reducing both fluorescent and non-fluorescent biodegradable matter and ammonium is still important. As already mentioned, biological processes ensure that less organic matter goes to the subsequent steps, hence improving the chance of different types of DOM being removed efficiently.

In order to use biological treatment for leachate with very low biodegradability, a landfilling facility may choose more robust alternatives such as ANR or ANR + N-dN since these are more efficient and cheaper.

In contrast to C1 and C3 removal during GAC treatment, C2 removal was Lower at BV≤2 and higher or stable at longer GAC adsorption times. GAC treatment of $FeCl_3$ effluent resulted in a total removal of C2 by 71% after 2 BV (60 minutes) treatment, and slightly increased to an average removal of 79% at BV≥ 2. With regards to the PACl effluent, 64% C2 removal was observed at 2 BV, and an average removal of 60% at BV≥ 2. Linking to the high removal in organic matter at BV ≥ 2 (see Chapter 9 Figure 9.3 b for the COD removal at 10.6 BV GAC adsorption, up to 79%), it is clear that the high reductions in COD are mainly from a reduction in C2. With coagulation-flocculation as a pre-treatment step, the ability of GAC to remove C2 during the entire treatment period is significantly improved.

It seems during GAC adsorption of raw leachate, the major components which could account for differences in COD removal and breakthrough time between raw and coagulated leachate and $FeCl_3$ and PACl are C1 (humic- and fulvic- like compounds) and C2 (tryptophan compounds).

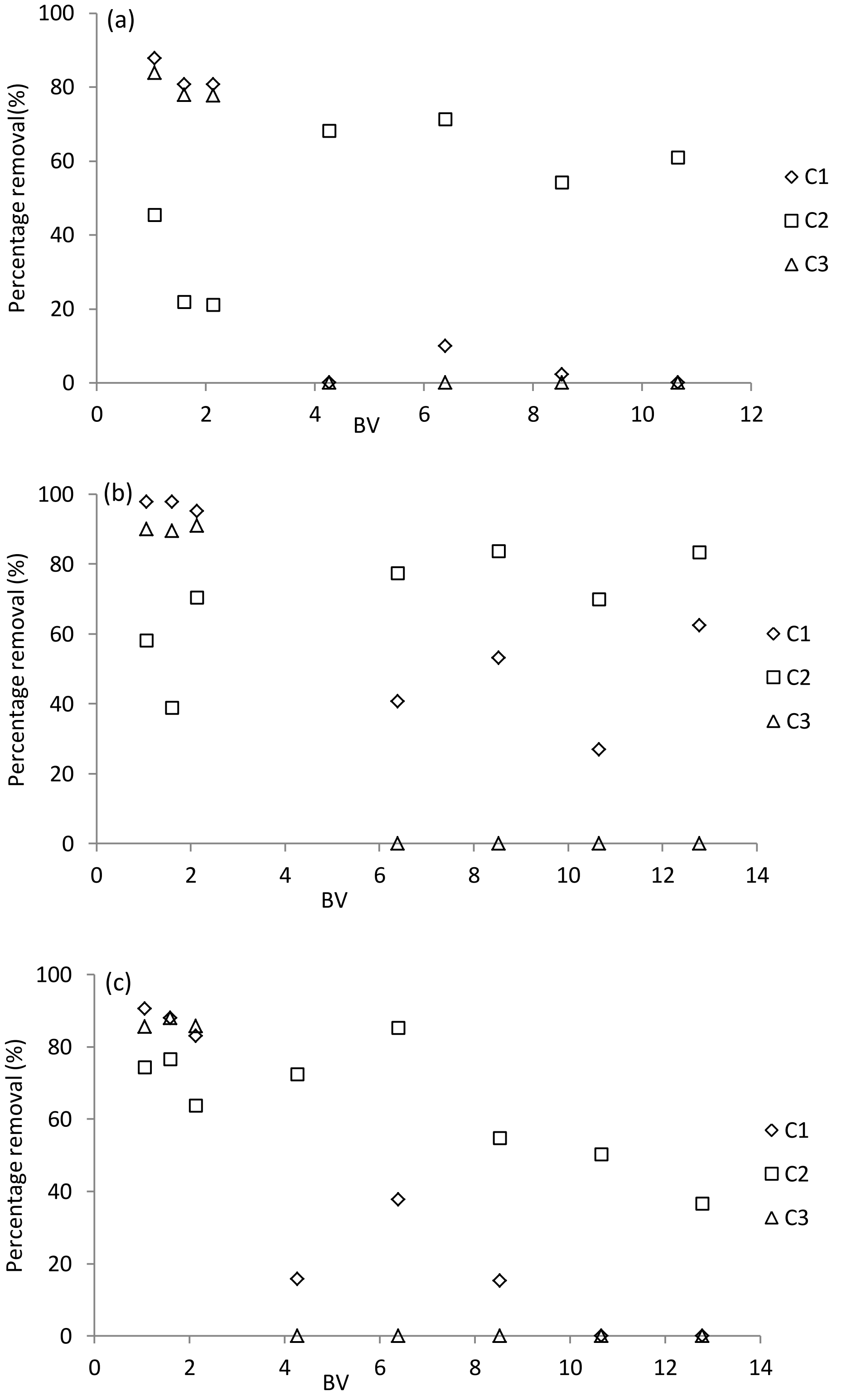


Figure 10.4: Percentage removal of PARAFAC components during GAC adsorption of (a) raw leachate, (b) $FeCl_3$-treated leachate, and (c) PACl-treated leachate.

10.3.3.4 Ion exchange: effect on EEM compounds

Considering the F_{max} values of C1, C2 and C3 in raw leachate (Figure 10.5) and in the ion exchange effluent after GAC treatment, up to 83%, 23% and 91% of C1, C2 and C3 respectively was removed after 2 BV (Figure 10.5 a). At BV = 10.6, C2 was better removed (53%) but C1 and C3 were raised again up to their initial values. This shows that the COD reduction at 10.6 BV reflected in Figure 9.4a in Chapter 9 (51% in case GAC + ion exchange is used) is the result of the removal of tryptophan-like compounds.

Also for coagulated leachate, a clear difference can be seen when considering the reduction in fluorescence intensities by ion exchange as a function of the number of treated BV. After 2 BV ion exchange treatment of $FeCl_3$ + GAC (Figure 10.5 b) and PACl + GAC (Figure 10.5 c) effluent, the intensity of the EEM compounds were reduced by 87 – 90% (C1), 38 – 75% (C2) and 82 – 91% (C3), showing again the preferential removal of humic- and fulvic-like compounds in the first phase of the treatment process. Whereas the removal of these C1 and C3 compounds decreases at higher BV, e.g. C1 removal after coagulation-flocculation and 10.6 BV GAC and ion exchange treatment dropped to 39% and 8% for $FeCl_3$ and PACl respectively, the removal of C2 increased or remained stable at about 68 – 74%. Overall, $FeCl_3$ coagulated leachate shows – mainly for the C1 compound – better reduction in fluorescence intensities after more than 6.4 BV GAC and ion exchange treatment, compared to non-coagulated raw leachate.

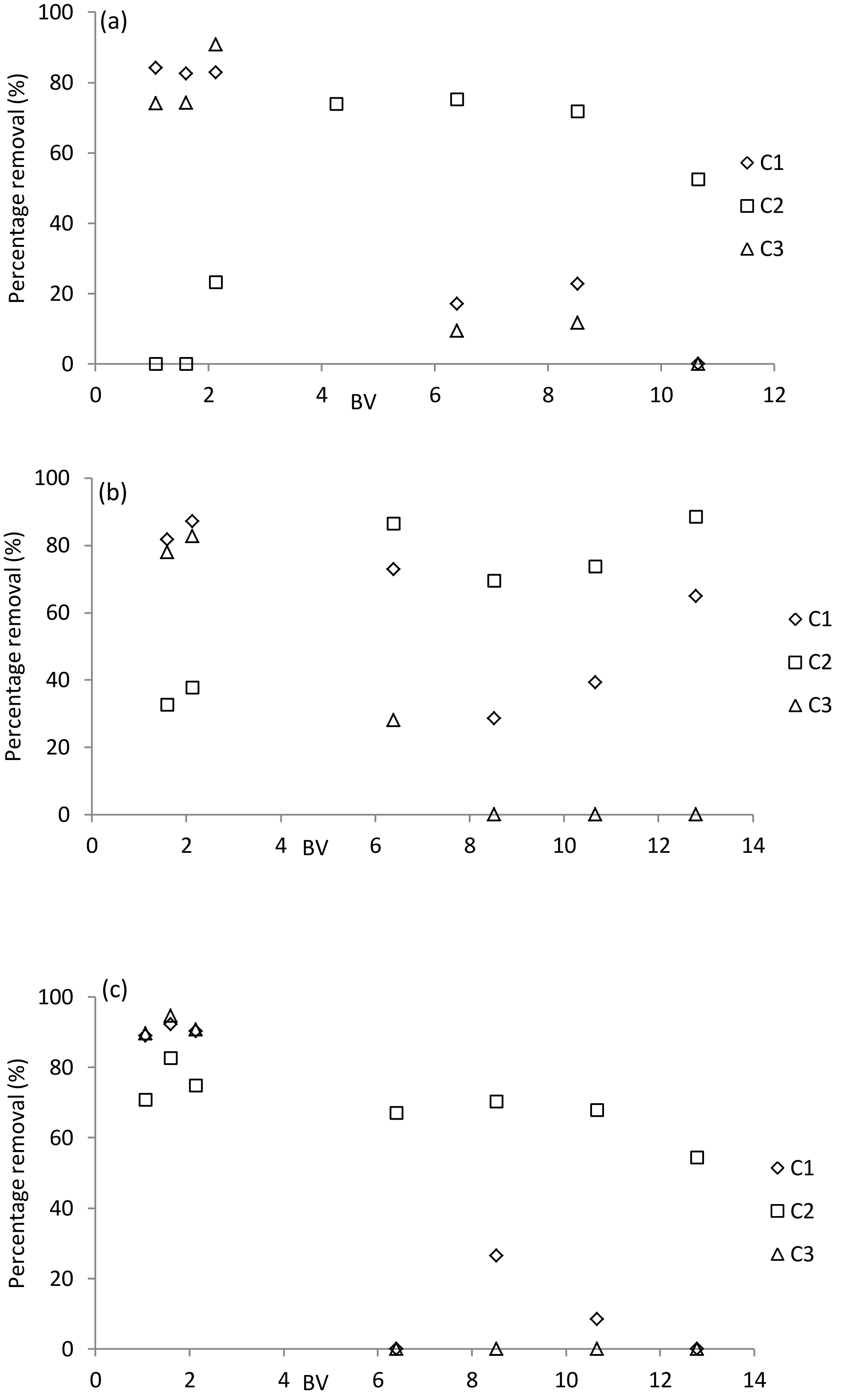


Figure 10.5: Percentage removal of PARAFAC components after ion exchange treatment of the GAC effluent of (a) raw leachate, (b) $FeCl_3$-treated leachate, and (c) PACl-treated leachate. (Raw leachate values in R.U: C1-2.13, C2-1.14, C3-2.16)

10.3.3.5 EEM compounds as surrogate measurements

PARAFAC components have been linked to the removal of physical-chemical parameters such as COD, $\alpha_{254,}$ BOD_5, ammonium and heavy metals with the aim of establishing a quick, sensitive method for monitoring the aforementioned parameters in landfill leachate (Henderson et al., 2009). In Chapter 6, the use of UV-VIS absorbance as a surrogate measurement for COD was explored. In this chapter, the use of fluorescence EEM coupled with PARAFAC is demonstrated. Depending on the treatment step, the ratios of tryptophan-like and humic-like substances (C2:C1) are correlated with COD, α_{254}, ammonium and nickel, instead of establishing direct correlations between single PARAFAC components and physical-chemical parameters. The reason is that correlation of single PARAFAC compounds does not account for changes in other PARAFAC components or can give poor correlations (Appendix 4) (Henderson et al., 2009). For instance, a decrease in concentration of tryptophan-like compounds during treatment can affect the correlation between humic-like compounds and COD, because COD considers both tryptophan-like and humic-like compounds next to other fluorescent and non-fluorescent substances in the leachate (Baker and Curry, 2004; Henderson et al., 2009).

In GAC treatment of raw leachate, the results show that there is a strong negative correlation between the C2:C1 ratio and the effluent COD, α_{254}, and nickel values with R^2 all higher than 0.81 (n=7, Table 10.2). At lower bed volumes (BV ≤ 2), the C2:C1 ratio is high since the treated leachate contains more protein-like compared to humic-like substances since the latter are preferentially removed at the start-up of the GAC treatment. As the GAC column tends towards breakthrough and the values of the physical-chemical parameters increase, the C2:C1 ratio decreases since the removal of protein-like compounds is favoured compared to that of humic-like compounds (see Section 10.3.3.3). This trend is also observed during GAC adsorption of PACl-treated and $FeCl_3$-treated leachate. The strong correlations between C2:C1 on the one hand and COD and nickel on the other hand show the great potential of fluorescence EEM measurements combined with PARAFAC analysis to be used as a surrogate for monitoring of COD and heavy metal removal from landfill leachate by coagulation-flocculation and GAC adsorption. The relationship with nickel is supported by the fact that DOM plays an important role in the availability of heavy metals in natural and engineered systems (Wu et al., 2011).

Table 10. 2: R^2 values for the correlation between the C2:C1 ratio and the physical-chemical parameters in raw, $FeCl_3$- and PACl-treated leachate after GAC and ion exchange treatment (n=7).

Leachate Stream	**COD**	**α_{254}**	**Ni**
GAC			
GAC only	0.86	0.84	0.81
$FeCl_3$ + GAC	0.81	0.66	0.86
PACl + GAC	0.88	0.84	0.92
Ion Exchange	**COD**	**NH_4^+-N**	**Ni**
GAC + ion exchange	0.91	0.13	0.87
$FeCl_3$ + GAC + ion exchange	0.83	0.12	0.10
PACl + GAC + ion exchange	0.86	0.11	0.33

The C2:C1 ratios of the effluent from the ion exchange step were also correlated with COD, ammonium, and nickel since ion exchange reduced their concentration in landfill leachate compared to α_{254}. A strong negative correlation with COD ($R^2 \geq 0.83$) is noticed, independent if coagulation-flocculation is used or not as a pretreatment step. Ammonium and nickel correlated poorly with C2:C1 (Table 10.2), most probably because of other removal mechanisms in the ion exchange column. It is likely that the bulk organic matter (~ COD), is removed through adsorption; whereas ammonium and nickel are primarily removed through ion exchange processes that do not largely affect EEM-derived DOM compounds.

10.3.3.6 SOM analysis of PARAFAC components

SOM analysis of PARAFAC components as opposed to full EEMs was chosen as a simpler and easier method to visually explore the differences/similarities in fluorescence composition of the samples during the entire treatment train (Cuss and Guéguen, 2015). Often, SOM is used as an alternative to

PARAFAC modelling of EEM (Bieroza et al., 2011); but this chapter (similar to Chapter 8) investigates to what extent SOM can be used complimentarily with PARAFAC to obtain valuable information which can be used in decision making regarding the removal of DOM from raw landfill leachate. The studies in Chapter 8 and in this chapter are one of the first instances where fluorescence EEM is coupled with PARAFAC and SOM in unravelling the heterogeneity of landfill leachate.

The unified distance matrix (U-matrix) is one of the useful outputs of SOM analysis, showing the degree of similarity/difference among samples. Higher values indicate larger distances between adjoining units; hence larger differences in fluorescence composition or location of fluorescence peaks (Bieroza et al., 2012). The yellow units located in the middle of the U-matrix thus indicate samples with a fluorescence composition that is different from other samples (Figure 10.6 a). A closer look at the best matching unit (BMU) (Figure 10.6 b) identifies these samples as raw leachate, $FeCl_3$- and PACl-coagulated leachate. The low geometric distances as represented by the blue colours dominate in the upper and lower parts of the U-matrix, and denote samples with similar characteristics. For instance, according to the BMU, samples on the lower part are those collected at higher BV (> 4 BV, corresponding to > 120 minutes of treatment) during GAC and ion exchange treatment, all have higher fluorescence composition of humic-like compounds. Conversely, the upper part of the BMU consists of samples that are dominated with tryptophan-like substances. Those were collected at lower BV < 2 (less than 60 minutes of treatment). Therefore, dividing the map horizontally reflects the increase in humic- like and decrease in tryptophan- like components in leachate effluent and level of saturation of the GAC and ion exchange column.

In an SOM, the important units are those with the highest hits since they reveal typical fluorescence properties of leachate observed during treatment (Carstea et al., 2010; Zhang et al., 2015). As such, units 9, 27 and 35 with 8, 7 and 7 hits respectively are important map units (Figure 10.6 b). Unit 9 consists of raw (non-coagulated) leachate samples treated during 4 – 10.6 BV (120 – 300 minutes) with GAC and GAC + ion exchange; whereas units 27 and 35 contain PACl- and $FeCl_3$-coagulated leachate sampled after 6.4 – 12.8 BV (180 – 360 minutes) GAC and GAC + ion exchange treatment.

Therefore, vertically, the SOM can be divided into leachate treated with only GAC and ion exchange to the left, and leachate treated by coagulation-flocculation prior to GAC and ion exchange to the right. Hence, SOM highlights a clear difference in fluorescence composition of leachate when coagulation-flocculation is used as treatment before GAC and ion exchange. Moreover, these SOM results show that a treatment chain with coagulation-flocculation + GAC + ion exchange columns can treat raw landfill leachate 2.4 BV longer (50% longer) than GAC + ion exchange before the fluorescence composition remains unchanged.

SOM further groups samples into different clusters such that samples in the same cluster are ‘more similar’ to each other (Garća and González, 2004). Using the k means algorithm (Cuss and Guéguen, 2015), the effective number of clusters was 6 (Figure 10.6 c). Cluster I and II and III represent respectively non-coagulated, $FeCl_3$-coagulated and PACl-coagulated samples collected at the effluent of the GAC and ion exchange unit at BV ≤ 2 (less than 60 minutes treatment). These three clusters are characterised by a higher fluorescence composition of tryptophan-like compounds (C2) than of humic/fulvic-like and humic- like compounds (C1 and C3), with C1 and C3 being preferentially removed at lower BV. Cluster IV represents the coagulated (both by $FeCl_3$ and PACl) leachates. These samples, not treated by GAC and ion exchange have a higher composition of humic/fulvic-like and humic- like components; in comparison with cluster I, II, III.

Cluster V consists of raw untreated leachate and non-coagulated effluent samples collected after more than 4 BV (≥ 120 minutes) GAC and ion exchange treatment. The fluorescence composition of this cluster is rich in C1 and C3 but deficient in C2 components when compared to the first four clusters. In comparison with cluster V, the fluorescence composition of cluster VI, which contains leachate samples that are collected after more than 6.4 BV treatment with coagulation-flocculation (both $FeCl_3$ and PACl) + GAC + ion exchange, is poor in C1 and C2 which are primarily removed during coagulation-flocculation and GAC adsorption.

In this chapter, a clear distinction (clustering) is seen between GAC-treated non-coagulated and coagulated leachate samples compared to the clustering of leachate samples in Chapter 8,. The humic like/humic and fulvic-like ratio (C3/C1) might be an important factor explaining the different clustering in this chapter and Chapter 8. During coagulation-flocculation (0.8 mg $FeCl_3$/mg COD_o) of biologically treated leachate (Chapter 8), the DOM composition does not change considerably (the C3/C1 ratio changes from 1.7 to 1.8), resulting in similar DOM characteristics in coagulated and non-coagulated biologically treated leachate. Hence grouping of coagulated and non coagulated samples in the same cluster. On the other hand, in this chapter, coagulation-flocculation of raw leachate at 2.2 mg $FeCl_3$/mg COD_o changes the DOM composition significantly (C3/C1 ratio shifts from 1.0 to 1.8, which results in a significant difference in DOM composition and clustering.

Whereas PARAFAC provides the quantitative information on the fluorescence intensity of the three components, SOM gives a simple yet powerful visual representation of the similarities or differences in fluorescence characteristics among leachate samples, resulting from a different treatment technique or different treatment conditions (e.g. coagulant type in coagulation-flocculation or operation time in GAC adsorption and ion exchange). Moreover, by studying the removal of PARAFAC components through the treatment sequence, a clear understanding of the way leachate treatment techniques should be arranged is obtained. The limited removal of the DOM components by GAC as a first step clearly highlights the need for leachate pre-treatment before GAC adsorption. The high removal of C1 humic- and fulvic-like compounds by coagulation-flocculation and subsequent improved performance of GAC step in removal of the three components shows that coagulation-flocculation is a suitable technique prior to adsorption. Furthermore, it contributes towards a better overall pollutant removal when ion exchange is added as a final step. During leachate treatment, C3 (humic compounds) proved recalcitrant to the three leachate treatment techniques. Therefore, future work should focus on the addition of an extra technique after ion exchange e.g. advanced oxidation process to remove also the C3 fraction. Although the results in

Chapter 8 show that addition of a biological step prior to coagulation-flocculation results in improved removal of C3 by the treatment steps downstream.

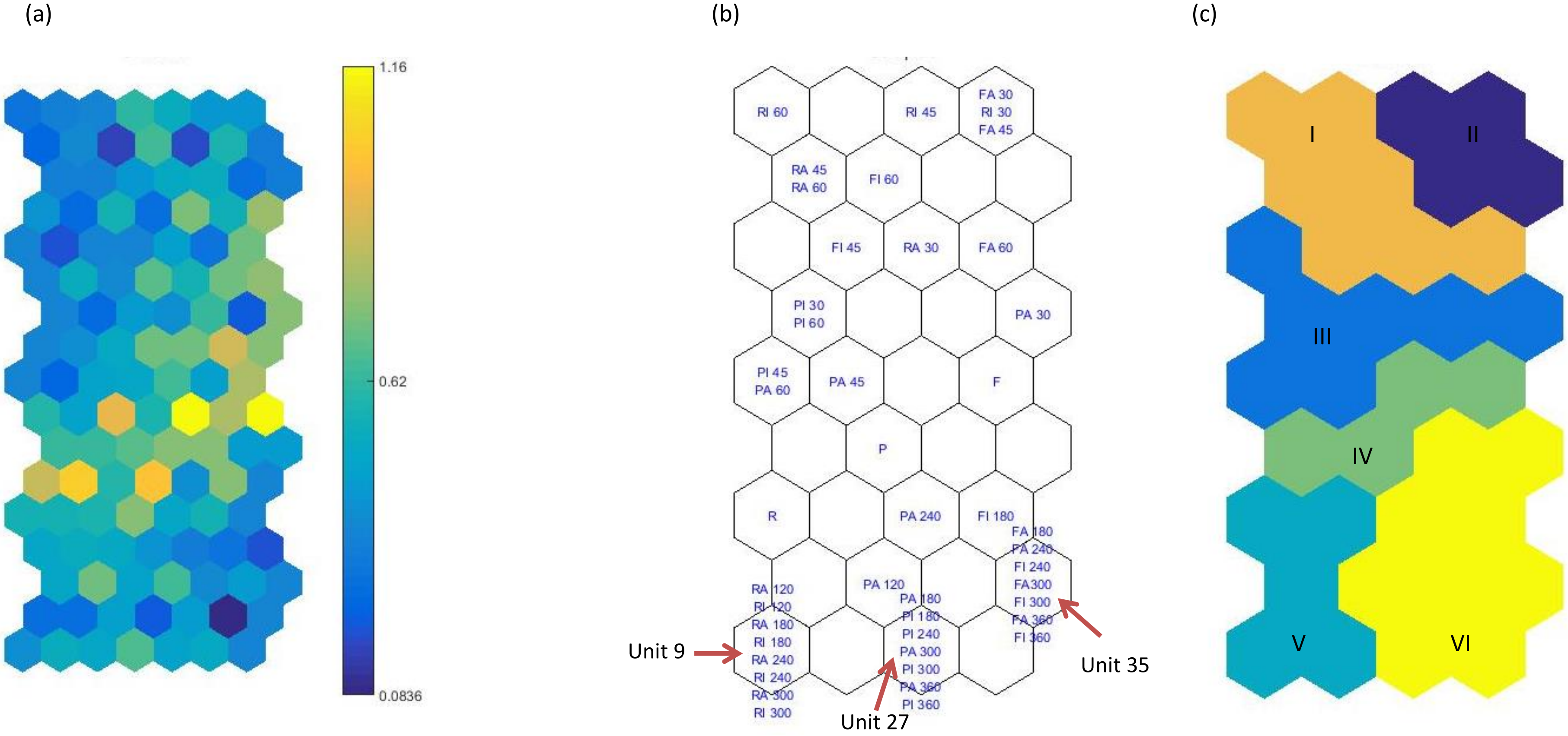


Figure 10. 6: The unified distance matrix (U-matrix) (a), best matching unit (BMU) (b) and k means clusters (c) of the samples based on SOM analysis of fluorescence composition. In (b) R, F and P represent raw leachate, $FeCl_3$ –coagulated and PACl-coagulated leachate, respectively. A and I denote GAC and ion exchange effluent samples; and the numerical values show the time of sampling in minutes. In (c) the numerical values represent the clusters.

10.4 Conclusions

Monitoring the coagulation-flocculation, GAC and ion exchange treatment of landfill leachate with fluorescence EEM and PARAFAC analysis revealed valuable information on the presence and behaviour of DOM components and characteristics during removal. Using PARAFAC, three components were identified in landfill leachate: C1 which is associated with humic/fulvic-like compounds; C2 associated with tryptophan-like protein compounds; and C3 representing humic-like compounds. C1 and C3 were similar to DOM components identified in biologically treated landfill leachate. Coagulation-flocculation was the most effective in removing the C1 humic/fulvic-like compounds. During subsequent GAC and ion exchange treatment, the operational time proved to be an important factor regarding the removal characteristics of the three components, with clearly different patterns at BV ≤ 2 on the one hand and BV > 2 on the other hand. C1 and C3 were rapidly removed at lower BV but tend to breakthrough at prolonged operation, while C2 removal remained stable or even increased at higher BV, up to 12.8. Use of SOM as a complimentary technique to PARAFAC enabled the clustering of similar samples. This yields a simple visual representation of the time at which the GAC and ion exchange columns are exhausted. Such results offer valuable information which can be used to optimise the removal of DOM without incurring extra treatment costs.

PART IV: General discussion and future perspectives

Chapter 11

11.1 Towards an optimized integrated leachate treatment train

Landfill leachate, a hazardous waste from landfills, is a significant source of pollution for ground and surface water. Strict environmental legislations such as the Landfill Directive and the European Water Framework Directive have necessitated efficient treatment of landfill leachate to minimize pollution of the aquatic environment. In this PhD thesis, several physical-chemical techniques were optimized and combined in a bid to obtain an efficient and cost effective strategy for (post-)treatment of raw and biologically treated landfill leachate. Based on the technologies studied and results obtained in this PhD thesis, some simple and practical guidelines are proposed that can be used by landfilling facilities to optimize an existing or develop a new leachate treatment. Three critical questions related to the objectives were put forward:

(i) what are the characteristics of the landfill leachate to be treated?

(ii) what are the factors affecting the performance of the technologies chosen?

(iii) how can the balance between achieving the discharge standards and treatment costs be created?

Following the schematic guideline provided in Figure 11.1, this chapter will critically discuss the answers to these questions and the take home messages from this PhD. It should be noted that technologies (e.g. membrane bioreactor, fenton oxidation or other advanced oxidation processes) that are not experimentally studied in this PhD are not included in (the discussion of) Figure 11.1.

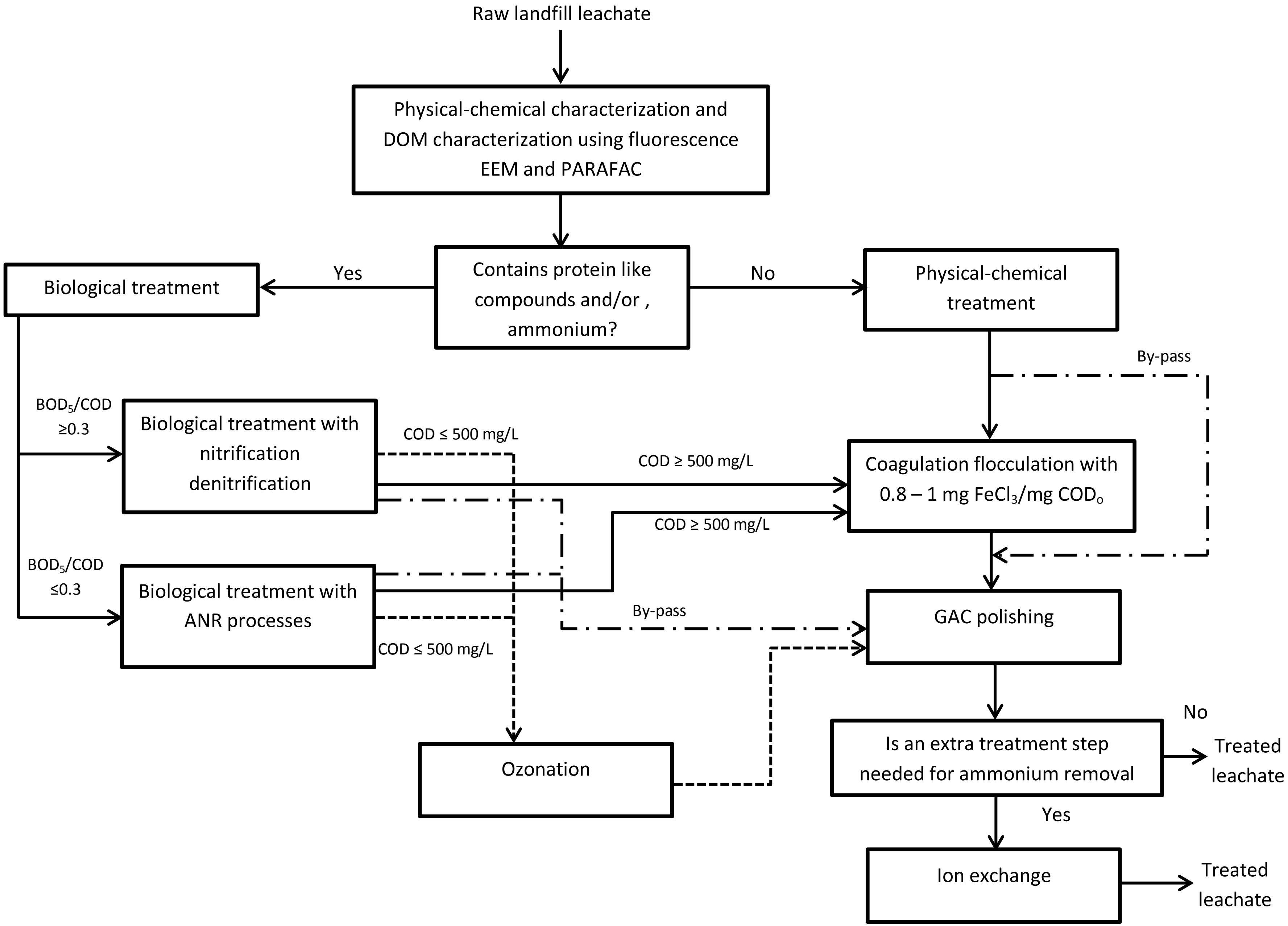


Figure 11.1: Schematic guideline for defining an optimized (post-)treatment train for raw and biologically treated landfill leachate.

11.1.1 What are the characteristics of the landfill leachate to be treated?

This question is related to the third objective in this thesis which was to characterize DOM present in the raw and biologically treated landfill leachate using rather simple and fast (e.g. UV-absorbance) as well as innovative techniques like fluorescence EEM coupled with PARAFAC.

Characterization of the landfill leachate is an important step in determining the appropriate technology to use for its treatment (Figure 11.1). As is the norm, water quality parameters such as COD, pH, BOD_5, are used. However, based on the results of this thesis, these are not sufficient as they do not provide a wholistic character of the landfill leachate. For instance, the physical-chemical characteristics of raw landfill leachate from Vanheede (Table 3.1) show a leachate which is high in COD, ammonium and low in biodegradability. As such, the tendency is to recommend a physical-chemical treatment. More advanced leachate characterization methods provide however more detailed information regarding e.g. the nature and identity of DOM, which can lead to other treatment options. Whereas UV-VIS absorbance gives an overall picture on the heterogeneous nature of leachate based on organic compounds containing carbon-to-carbon double bonds and aromatic rings, fluorescence EEM coupled with PARAFAC reveals more information on the identity of DOM in landfill leachate. Characterization of raw landfill leachate with fluorescence EEM and PARAFAC revealed the presence of three DOM components: (i) humic/fulvic-like compounds with F_{max} at Ex/Em 250, 320/425 nm; (ii) protein-like tryptophan compounds with F_{max} at Ex/Em 270/340 nm; and (iii) humic-like compounds with F_{max} at 250/460 nm and secondary peaks at Ex/Em 310, 370/460 nm. The presence of tryptophan compounds in this leachate indicates the availability of a biodegradable fraction indicating that an initial biological step would be beneficial. However, for such a leachate with low biodegradability and high ammonium concentrations, biological treatment with ANR processes is recommended since the need for an external carbon source is eliminated amongst other advantages (Chapter 7). However, in the event that the biodegradability is higher, i.e. $BOD_5/COD \geq 0.3$, then biological treatment with nitrification-denitrification can be used. The importance of such a biological step is seen during the follow up of the DOM components during GAC adsorption of raw and biologically treated leachate. The humic-like components had a fast breakthrough on the GAC column, i.e. after 4 BV with leachate treated with GAC only and PACl + GAC and after 6.4 BV for $FeCl_3$ + GAC treated leachate. In comparison, DOM characterisation of a biologically treated leachate revealed the presence of two DOM components, namely humic/fulvic-like and humic-like compounds. Combining this knowledge with the results from the physical-chemical characterization, e.g. low biodegradability and ammonium concentrations, would help a landfilling facility to realise that post-treatment with physical-chemical methods is preferred as opposed to a single biological step. This is because the biologically treated leachate is devoid of the easily biodegradable tryptophan-like organic matter, and it does not offer a solution for the humic-like components which are recalcitrant to biodegradation (Yang et al., 2015, 2013). (Post)-treatment of biologically treated leachate with GAC adsorption shows that humic-like compounds did not breakthrough the GAC column even after 10.6 BV unlike during GAC adsorption of raw leachate. Therefore, as shown in Figure 11.1, biological treatment is recommended when there is tryptophan compounds and high ammonium concentrations.

Undertaking physical-chemical bulk characterization and more detailed DOM characterization together is also beneficial. Due to their sensitivity to changes in leachate characteristics, fluorescence EEM coupled with PARAFAC and UV-VIS absorbance can act as surrogate measurements for the commonly used water quality parameters (Henderson et al., 2009). As such, they can be important tools for the online monitoring of quality parameters of leachate before and during treatment (Shutova et al., 2014). In comparison to other absorbance coefficients, α_{254} proved to be a reliable surrogate for COD concentrations in coagulated and ozonated leachate, as exemplified by the high correlation coefficient (R^2 = 0.89 - 0.96, n = 12 - 38).

For fluorescence EEM coupled with a developed PARAFAC model, correlating a ratio between tryptophan-like and humic-like substances with the water quality parameters is more accurate than a direct correlation with the individual components. In this PhD thesis, a strong relationship was found between the ratio of tryptophan-like : humic-like substances and COD (R^2 = 0.81 - 0.88, n = 7), nickel (R^2 = 0.81-0.92, n = 7) from GAC step. In the ion exchange step, a strong correlation was established with the COD only (R^2 = 0.83 – 0.91, n = 7). However, a poor relationship was established between the tryptophan-like : humic-like components ratio and ammonium and nickel in the ion exchange effluent. Whereas the use of fluorescence EEM with PARAFAC and UV-VIS as surrogate parameters is not limited to characterize leachate before treatment, the applicability of fluorescence EEM with PARAFAC as surrogate for the behaviour of certain pollutants during treatment can be limited by the respective mechanisms of removal, as in the case of ammonia and nickel. Landfilling facilities should keep this in mind.

In the chronology of experimental work within this PhD thesis, the characterization of landfill leachate with fluorescence EEM coupled with PARAFAC comes after the treatment and cost analysis. However, in retrospect and for practical use, this characterization step should come at the beginning - before treatment - just as illustrated in Figure 11.1.

11.1.2 What are the factors affecting the performance of the technologies chosen?

This question is related to the first objective which was to investigate the factors (leachate characteristics and operational parameters) affecting the technological performance of the different techniques in a bid to obtain an optimized and integrated treatment train for both raw and biologically treated landfill leachate.

Leachate which is efficiently treated by biological processes (N-dN or ANR) is often stabilized with ammonium concentrations below the discharge standards. This is true for instance for biologically treated leachate from IMOG (Table 3.1). Based on the DOM characterization, it was advised that such a leachate would benefit from a physical-chemical post-treatment to remove the recalcitrant organic matter which is still present in the leachate (Section 11.1.1). Also raw leachate with no biodegradable fraction can be treated with physical-chemical methods. Four physical-chemical technologies, i.e. ozonation, coagulation-flocculation, GAC adsorption, and ion exchange, were investigated for the (post-)treatment of raw and biologically treated landfill leachate.

For leachate with high concentration of COD, e.g. COD_O of 500 mg/L, coagulation-flocculation is a suitable choice as a first/next step in the (post-)treatment of raw and biologically treated landfill leachate. The efficiency of coagulation-flocculation to remove recalcitrant high molecular weight humic compounds and other pollutants from leachate is affected by both the type and dose of the coagulant. Though hydrolysed coagulants are meant to have better performance than non-hydrolysed coagulants due to the presence of high charges associated with their hydrolysis species, e.g. Al_{13} (Duan and Gregory, 2003), in this PhD thesis $FeCl_3$ performed better than PACl. For instance, better COD (66%) and α_{254} (88%) were achieved at 1 mg $FeCl_3$/mg COD_o compared to 44% COD and 75% α_{254} removals with PACl at the same dose. Therefore, for landfilling facilities seeking to employ coagulation-flocculation in treatment of landfill leachate, $FeCl_3$ is recommended based on the present research. With regards to coagulant dose, higher doses gave better organic matter removals as shown during coagulation-flocculation of raw landfill leachate. At a dose of 2.2 mg $FeCl_3$/mg COD_o, 50% COD removal was achieved compared to 28% at 1 $FeCl_3$ /mg COD_o. However, the optimization of coagulation-flocculation with a subsequent GAC step revealed that the optimum coagulant dose for (post-) treatment of raw and biologically treated leachate was in the range of 0.8 – 1.0 mg $FeCl_3$/mg COD_o. Leachate treatment at this range offered maximum technological and economic benefits. This is contrary to research norms where the coagulant dose with the highest improvement in water quality is commonly chosen for further GAC adsorption studies.

Ozonation is another chemical technique that can be used in post-treatment of biologically treated landfill leachate. Use of ozonation as an initial step in treatment of raw landfill leachate would be very expensive as very high doses are required to attain meaningful organic matter removal. Hence, its recommendation as a (post-)treatment step only after biological treatment (Figure 11.1). The efficiency of ozonation was found to depend on three important factors: (i) ozone dose, (ii) initial leachate pH, and (iii) initial leachate COD.

Higher transferred ozone doses as a result of longer treatment times result in better organic matter removal efficiency. For instance, the transferred ozone dose for ozonation of biologically treated leachate increased from 145 to 243 mg/L when the treatment time increased from 30 to 60 minutes, respectively. Subsequently an increase in COD (1 – 5%) and α_{254} (14 – 27%) removals was obtained. Nevertheless, it is important to note that there can be no unlimited increase in the transferred ozone dose. This is because higher ozone doses would attract higher energy and oxygen requirements and thus higher treatment costs (Chapter 7). Moreover, Amaral-Silva et al. (2016) showed that the use of very high ozone doses, i.e. 1800 mg/L (0.96 mg O_3/mg COD_o), gave similar COD removals (8%) as a lower and more economic ozone dose of 300 mg/L (0.16 mg O_3/mg COD_o). At a certain point, the organic matter remaining in the leachate is not longer amenable to ozonation giving rise to many side-reactions taking place.

With regards to COD_o, which is a practical parameter inherent to a certain type of leachate, it is recommended that ozonation is used for leachate with a lower COD_O, e.g. less than 500 mg/L, (this value may vary from one leachate to another) but still higher than the discharge limit. This is because better percentage removals of organic matter are obtained at lower COD_O: 20-30% at a COD_o between 426 and 502 mg/L compared to 5-18% at a COD_o in the range of 736 – 1846 mg/L. At such lower and economical doses of 0.3 - 0.4 mg O_3/mg COD_o, partial mineralization is sufficient to decrease the leachate COD so that subsequent GAC adsorption of the ozonated leachate would result in longer COD breakthrough times. To further improve the performance of ozonation, landfilling facilities can increase the pH of leachate to more alkaline levels, although costs and practical implications should be carefully considered. Better ozonation efficiency, i.e. 0.79 mg COD removed/mg O_3, was obtained when biologically treated leachate was ozonated at an pH 10 compared to 0.32 mg COD removed/mg O_3 at pH 7.0. This high performance of ozonation at alkaline conditions is attributed to the presence of hydroxyl radicals with high oxidation potential and non-selectivity towards organic matter and other pollutants (Amaral-Silva et al., 2016) (Chapter 2). Addition of chemicals such as H_2O_2 to facilitate the production of hydroxyl radicals is also an option to improve the ozonation efficiency. However, also here, a cost-benefit analysis should be done (Amaral-Silva et al., 2016) (Chapter 7).

As a polishing step following ozonation and coagulation-flocculation, GAC adsorption is proposed (Figure 11.1). In this PhD thesis the performance of GAC was influenced by the presence or absence of a pre-treatment step. Post-treatment of biologically treated leachate with ozonation and GAC led to improved COD removals, i.e. from a range of 10 – 33% after ozonation to 65 – 85% after 3 – 6 BV GAC adsorption of ozonated leachate (Chapters 5 and 6). Moreover, the α_{254} removals also increased from 71% to 90% with 6 BV of GAC treatment (Chapter 6). In comparison, post-treatment of biologically treated leachate with only GAC for 3 – 6 BV resulted in a lower performance, i.e. 20 - 80% COD (Chapter 5 and 6) and 8% α_{254} (Chapter 6) removal. Indeed, as also reported by Ramirez Zamora et al. (2000), treatment of leachate with coagulation-flocculation or an advanced oxidation process before GAC adsorption improves the adsorption capacity and breakthrough time on the GAC column. The experimental GAC breakthrough time of COD from ozonated leachate could be increased by 1.3 – 9 times. This high improvement is related to a low initial leachate COD (578 mg/L). A two-fold increase in breakthrough time of COD from the GAC column (and a 4% slight increase in the experimental adsorption capacity) was observed when biologically treated leachate was first coagulated with 1.96 mg $FeCl_3$ /mg COD_o compared to the same leachate treated with GAC only (Chapter 6). These improvements in COD breakthrough time (2 times) are in the same range as those obtained with GAC adsorption of ozonated leachate (1.3 – 9 times). This confirms that coagulation-flocculation can be used as an alternative for post-treatment of biologically treated leachate before GAC adsorption whenever ozonation is not available or when ozonation is available, coagulation-flocculation is a first option.

With regards to the adsorption of raw landfill leachate that has been treated with coagulation-flocculation (optimum dose: 1 mg $FeCl_3$/mg COD_o), reductions of 80% COD and 82% α_{254} were achieved after 10.6 BV of GAC treatment (Chapter 9). In comparison to that, 42% COD and 23% α_{254} removal was obtained with only 10.6 BV GAC. Additionally, an improvement in the COD breakthrough time by a factor of 1.6 was observed when raw leachate was first coagulated with 1 mg $FeCl_3$/mg COD_o. Though these removal efficiencies seem higher than those achieved during post-treatment of biologically treated leachate with coagulation-flocculation and GAC, it is important to note that the GAC effluent COD will be lower for the biologically treated leachate compared to the raw leachate. This is because of the different COD_o of the two leachates, amounting 337 mg/L for biologically treated leachate and 2759 mg/L for raw leachate. As already mentioned, raw landfill leachate is known to have a high concentration of high molecular weight organic matter which easily blocks the pores of GAC during adsorption. Thus, the effluent COD after GAC adsorption of coagulated raw leachate is higher.

Raw landfill leachate contains high amounts of ammonium as exemplified in the Vanheede leachate. Coagulation-flocculation and GAC adsorption are inefficient towards the removal of ammonium. On the other hand, ion exchange succeeded in removing 100% of ammonium from leachate treated with only GAC and with 1 mg $FeCl_3$/mg COD_o + GAC. Also better total removal of other leachate constituents such as organic matter and heavy metals are obtained with a further ion exchange treatment. This makes ion exchange a desirable alternative for ammonium removal, compared to air stripping where only a minimal COD removal is obtained. Like the GAC step, it is important to note that the efficiency of ion exchange to remove organic matter and heavy metals was influenced by the pre-treatment steps. Better COD, α_{254} and Ni removals (83-95%) were obtained after 10.6 BV of GAC and ion exchange treatment of coagulated leachate, compared to 51-62% removal of COD, α_{254} and nickel for non-coagulated leachate. Though expensive (23.3 €/m^3 treated leachate) (see section 11.1.3), the efficiency with which ion exchange achieves ammonium reduction and its high regeneration capacity is an indication that it is a viable alternative to biological means. According to

Halim et al. (2010), the efficiency of an ion exchange resin to remove ammonium from leachate is not affected by a single regeneration. However, the ability of the resin to remove organic matter will be affected. To ascertain this, this PhD thesis recommends reuse and follow-up of the reused resin.

11.1.3 How can the balance between achieving the discharge standards and treatment costs be created?

This question is related to the second objective which was to evaluate the operating costs related to the (post-)treatment of raw and biologically treated landfill leachate. Since costs have a large influence on the choice of techniques to be implemented in real practice, the goal was to come-up with a cost-effective treatment strategy for landfill operators.

With the treatment technologies optimized, the operating costs were taken into account. The costs involved only take into account the materials (reagents, adsorbent, ion exchange resin and regeneration) and energy used. Other cost contributions from e.g. labour or CAPEX were not considered in this work, since they are expected to be more contant (and thus less differentiating) among the different physical-chemical treatment options that were considered. Moreover, due to the improvement in technology, e.g. online monitoring, it is possible to manage several leachate treatment installations remotely. With these assumptions labour costs were excluded from the operating costs.

The operational cost of post-treatment of biologically treated landfill leachate with ozonation was found to increase with higher transferred ozone dose. This is because higher ozone doses have larger energy and oxygen requirements. For instance, ozonation of biologically treated leachate at a dose of 1.51 g O_3/g COD_o costs 0.38 €/m^3, whereas a lower dose of 0.14 g O_3/g COD_o is more economical at 0.23 € per m^3 of treated leachate (Chapter 7). With lower COD_o concentration, lower ozone dosages is sufficient for partial mineralisation, given the fact that the leachate will be further treated with GAC there is no need for complete mineralization. Overall, ozonation of biologically treated leachate (IMOG and ANR samples) was in the range of 0.19 to 0.69 €/m^3. The improved breakthrough times associated with GAC adsorption of ozonated leachate have potential to decrease the GAC operating costs. The latter decreased from 1.32 €/m^3, when biologically treated leachate is directly treated with GAC, to 0.88 – 1.02 €/m^3 when ozonation is combined with GAC. In total, the operating cost of post-treating biologically treated landfill leachate with ozonation and GAC was in the range of 1.07 – 1.71 €/m^3. Though in certain instances the GAC operating costs might seem high, the effluent COD concentrations are much lower than those incurred when biologically treated leachate is (post-)treated directly with GAC only.

Similar to ozonation, the operating cost of coagulation-flocculation of raw and biologically treated leachate increases with higher coagulant doses. Coagulation-flocculation of raw leachate at 2.2 mg $FeCl_3$/mg COD_o is more expensive (4.4 €/m^3) than at a lower dose (1.9 €/m^3 at 1 mg $FeCl_3$/mg COD_o). In comparison, coagulation-flocculation of biologically treated landfill leachate is 2 – 5 times cheaper (0.81 €/m^3) due to the low amounts of coagulant required to match the initial leachate COD. Future studies can also consider the contribution of sludge disposal to the coagulation-flocculation operating costs as sludge production is an important consequence of coagulation-flocculation. Like ozonation, GAC adsorption of leachate pre-treated with coagulation-flocculation incurs lower operating costs. For instance, only GAC treatment of raw leachate incurred 4.5 €/m^3 whereas GAC treatment of coagulated effluent costs 2.7 €/m^3. GAC adsorption of biologically treated leachate first treated with coagulation-flocculation cost 0.09 €/m^3 when the COD breakthrough time from the GAC column was prolonged for a very long time (>36 BV). On the contrary, a cost of 1.32 €/m^3 occurred when biologically treated leachate was post-treated with GAC only. Taking into account the total operating costs of coagulation-flocculation and GAC (during the experimental time periods), addition of coagulation-flocculation with $FeCl_3$ at pH 6 and a dose of 1.3 mg $FeCl_3$ /mg COD_o to a treatment train can reduce the total operating costs, e.g. from 1.32 to 0.90 €/m^3. However, landfilling facilities should take note that this is not always the case. For instance, the total costs of raw leachate treatment by coagulation-flocculation + GAC (4.6 €/m³) are comparable to those with GAC only (4.5 €/m³) because of the high coagulation-flocculation costs. Then again, the effluent quality of leachate treated with coagulation-flocculation + GAC are much better.

In certain cases, addition of ozonation or coagulation-flocculation to the treatment train may seem more expensive than treatment with only GAC. However, it is important to note that ozonation or coagulation-flocculation + GAC offers better organic matter, nitrogen and metal removals than GAC only (Table 5.3, Figure 9.3, Figure 10.5). Therefore, to achieve similar high removals with only GAC adsorption as obtained in ozonation/coagulation-flocculation + GAC, more adsorbent should be used which will ultimately increase the costs substantially. From a technological and economic perspective, it is advisable that landfilling facilities employ optimum chemical/oxidant doses during ozonation or coagulation-flocculation such that when the ozonated or coagulated effluents are treated with GAC adsorption, high pollutant removals will be achieved at lower costs. Therefore, based on technological performance and operating cost analysis, post-treatment of biologically treated leachate with coagulation-flocculation + GAC is efficient and offers economic benefits.

Removal of ammonium with ion exchange was shown to be expensive. Ion exchange treatment of raw leachate treated with GAC only and with 1 mg $FeCl_3$/mg COD_o + GAC required at least 23.3 €/m^3 to reduce the ammonium concentration to below the detection limit of the analytical method. Among the four techniques used for leachate treatment, ion exchange is the most expensive. Considering the technological and economic aspects, long-term use of the column receiving leachate treated with 1 mg $FeCl_3$/mg COD_o + GAC will be cheaper since it receives leachate with a low concentration of organic matter, hence less blockage of the ion exchange sites. Overall, the treatment cost of raw landfill leachate with 1 mg $FeCl_3$/mg COD_o + 10.6 BV GAC + 10.6 BV ion exchange is estimated at 27.9 €/m^3 which is comparable with the treatment costs incurred when raw leachate is treated with 10.6 BV GAC + 10.6 BV ion exchange. However, when raw leachate is first coagulated, the GAC and ion exchange steps can treat leachate up to 9.6 BV before the COD discharge limit of 450 mg/L is passed. Direct treatment of raw leachate with GAC and ion exchange allows treatment for only 3.2 BV, above which new adsorbent and resin would be required since the effluent COD (685 mg/L) is higher than its discharge limit.

Take home messages

- Physical-chemical characterization of landfill leachate should include more detailed DOM characterization. This will provide a wholesome picture of the leachate to be treated.
- The treatment of raw landfill leachate can be accomplished by a cost effective treatment train which includes a biological step followed by coagulation-flocculation (0.8 mg $FeCl_3$/mg COD_O) and final polishing with GAC. In case a compact treatment plant and/or ammonium recovery is required, coagulation-flocculation (1 mg $FeCl_3$/mg COD_O) followed by GAC and ion exchange can be used.
- Addition of a treatment step between the biological and GAC steps has the benefits of not only improved technological performance but also lower operating costs.

11.2 Future perspectives

11.2.1 Operational conditions

Coagulation-flocculation has proved to be an effective and cost efficient technique for the treatment of landfill leachate. To further optimise its performance, future studies should also consider the influence of leachate pH. Knowledge of the optimum pH could further reduce the required dose of coagulant. Additionally, the cost implications of adjusting the pH should be taken into account.

GAC batch studies showed that more adsorbent (150 g/L) is required for the removal of organic matter from biologically treated landfill leachate compared to the 42 g/L used in the column studies.

Therefore, future research can investigate how the size of the GAC fixed bed can be increased while ensuring that proper flow dynamics are adhered to.

While this PhD thesis highlighted the possibility of regenerating the ion exchange resin, reuse of the regenerated ion exchange resin was not studied. Future research should investigate how the efficiency of the ion exchange resin is affected after regeneration.

11.2.2 Detailed characterization of landfill leachate

Using fluorescence EEM coupled with PARAFAC, this thesis was able to identify the main dissolved organic matter components present in raw and biologically treated landfill leachate. To further gain insight in the characteristics of these DOM components and their behaviour during leachate treatment with coagulation-flocculation, GAC adsorption and ion exchange, aspects such as molecular weight distribution should be studied. Knowledge of the molecular weights of the DOM components will further help in differentiating similar DOM components.

This thesis only monitored the removal of DOM from raw and biologically treated landfill leachate during treatment with coagulation-flocculation, GAC adsorption and ion exchange. It would be interesting to monitor the conversions of DOM also during ozonation and subsequent treatments with fluorescence EEM and PARAFAC.

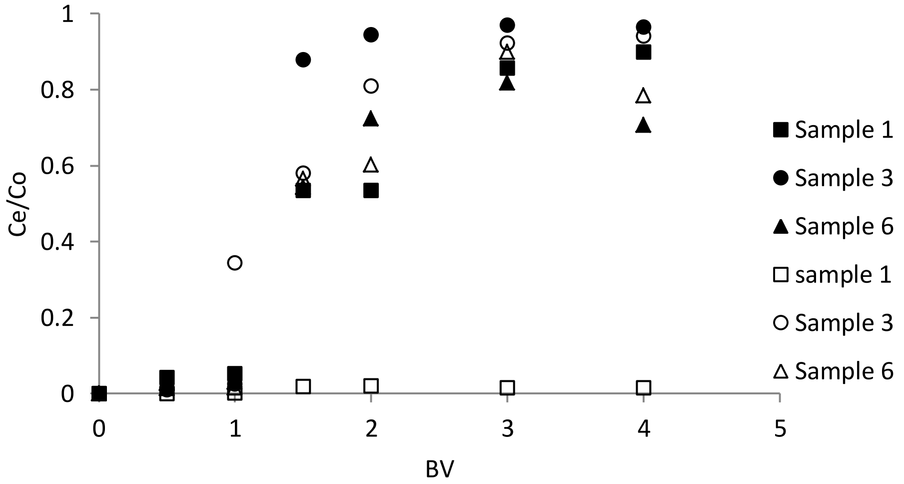
This thesis focused on organic matter removal during physical-chemical treatment. However, landfill leachate is a complex matrix containing a large diversity of other xenobiotic organic compounds (XOCs) which are of environmental significance. Therefore, future studies could also monitor the efficiency of the four studied techniques – or optimized treatment train – towards the removal of these XOCs. Among the four technologies considerd, ozonation is the only one which reduces the organic matter and XOCs content in leachate by oxidation. At lower and thus more economic ozone doses, partial oxidation occurs leading to the formation of intermediate products. Transformation products of XOCs still contribute to the landfill leachate properties (e.g. COD). As such, it would be of interest for future research to look into the identity and possible pathways through which these intermediate products are formed and degraded. Since there is a possibility that the by-products formed during leachate oxidation have a higher toxicity than the original compounds, future studies could also consider how the toxicity of leachate varies before and after oxidation and eventual polishing with GAC.

11.2.3 Landfill management

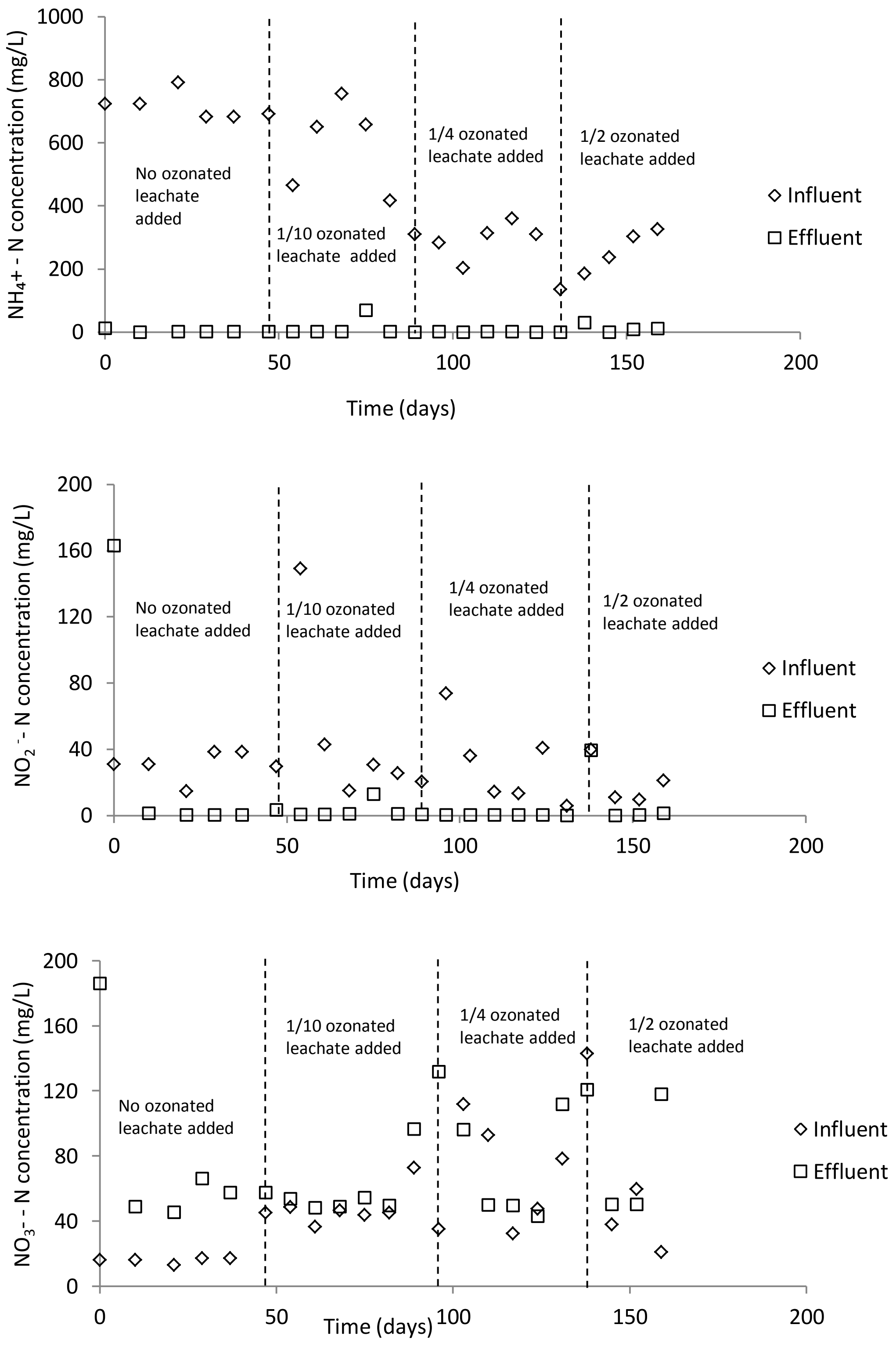
As the global call (e.g. the Paris agreement) to reduce greenhouse gas emissions as a result of poor waste management practices grows louder, developing countries are adapting more sustainable options such as recycling, reuse, composting, circular economy, co-sharing . However, these need to be encouraged through government facilitation and even embedded in legislation e.g. plastic bag ban in Kenya. However, there are still challenges with waste management and certain products (industrial waste) will end up in a dumpsite. Developing countries are also striving to move away from waste dumping to sanitary landfilling. The latter allows proper management of landfill leachate and landfill gas. Waste disposed in the 'closed' dumpsites and formed landfills are of a different composition (mostly organic) from that disposed in landfills in developed countries. Moreover, the 'closed' dumpsites need to be remediated and the leachate produced during after care period treated. As such, it would be interesting to characterize the DOM from the 'closed' dumpsites and yound landfills and further investigate how the four physical-chemical techniques used in this PhD thesis perform towards the treatment of young leachate with a different composition.

Appendix

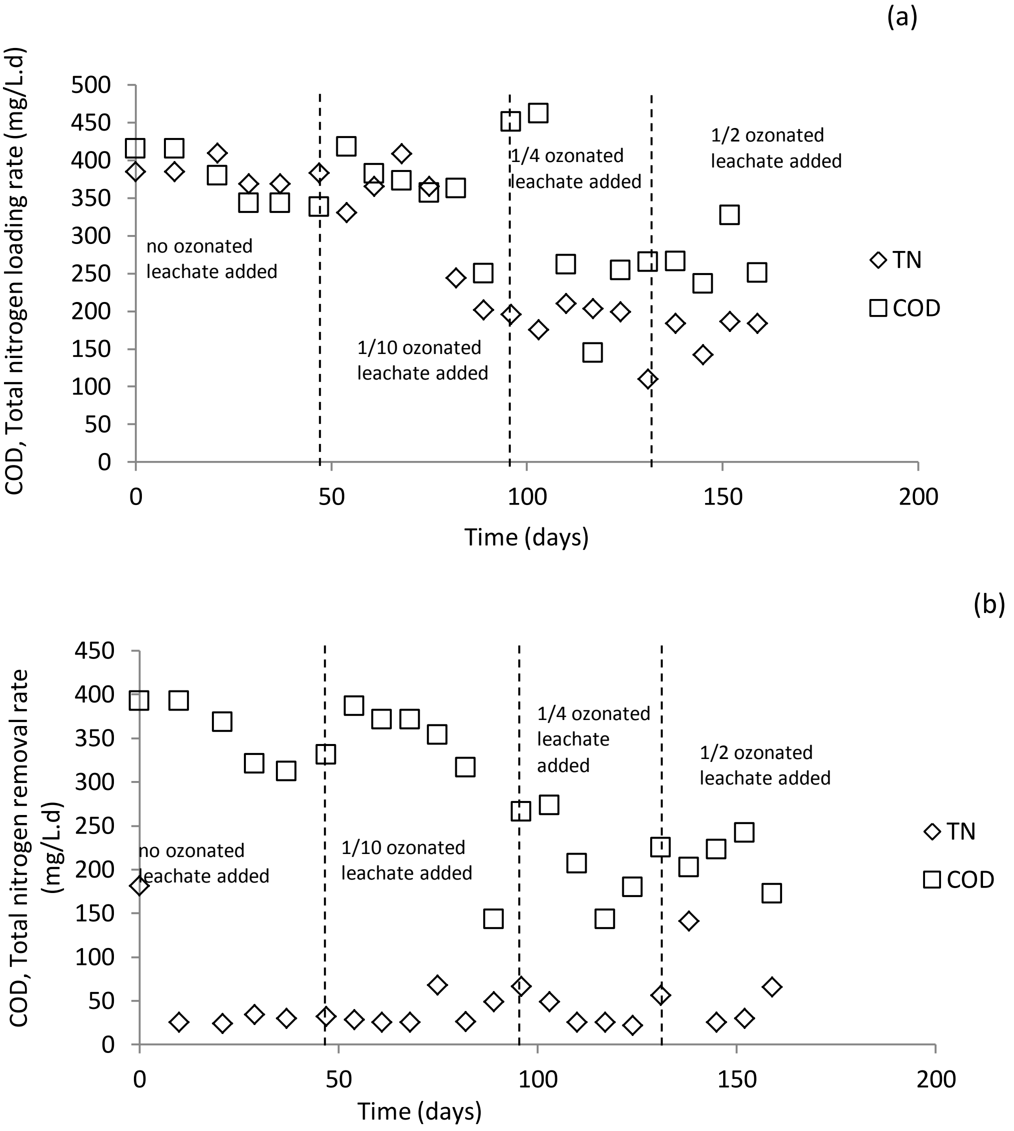
Chapter 5



Appendix 1: Nitrogen removal versus filtered bed volumes, (■, ● and ▲) represents GAC adsorption of biologically treated leachate; (□, ○ and △) represents GAC adsorption of ozonated leachate.



Appendix 2: Nitrogen compounds (NO_2^--N, NO_3^--N and NH_4^+-N) evolution due to recirculation of ozonated ANR effluent. Days 0 – 47 no ozonated effluent, 48 – 89 ozonated effluent at ratio 1/10, 90 – 131 ozonated effluent at ratio 1/4, 132 – 159 ozonated effluent at ratio ½



Appendix 3: The total nitrogen and COD loading rates during recirculation of ozonated landfill leachate to the biological step. Days 0 – 47 no ozonated effluent, 48 – 89 ozonated effluent at ratio 1/10, 90 – 131 ozonated effluent at ratio 1/4, 132 – 159 ozonated effluent at ratio

Chapter 10

Appendix 4: Correlations between the three PARAFAC components and COD, NH_4^+ - N, Ni, α_{254}

		Raw leachate			FeCl treated leachate			PACl treated leachate		
		C1	**C2**	**C3**	**C1**	**C2**	**C3**	**C1**	**C2**	**C3**
GAC	COD	0.80	0.44	0.84	0.78	0.65	0.77	0.94	0.47	0.95
	Ni	0.70	0.44	0.76	0.78	0.72	0.77	0.94	0.37	0.95
	α_{254}	0.77	0.44	0.81	0.64	0.39	0.66	0.89	0.47	0.92
IE	COD	0.67	0.88	0.64	0.38	0.87	0.45	0.85	0.87	0.85
	Ni	0.77	0.83	0.73	0.06	0.10	0.07	0.86	0.61	0.64
	NH_4^+ - N	0.24	0.07	0.26	0.00	0.24	0.00	0.23	0.62	0.22

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Curriculum Vitae

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Education

2011 - 2013	Master of Science in Environmental Sanitation – Magna cum Laude Centre Environmental Science and Technology, Ghent University, Belgium
2004 - 2007	Bachelor of science in Industrial Chemistry – Honours Makerere University Kampala, Kampala Uganda

Research experience

2013 - 2018	Doctoral Researcher, Laboratory of Industrial Water and Eco-technology (LIWET) and Environmental Organic Chemistry and Technology (ENVOC) research groups, Department of Green Chemistry and Technology, Ghent University Belgium
2008 - 2018	Research scientist Kenya Industrial Research and Development Institute, Nairobi Kenya
August 2012	Intern, Jimma University, Jimma Ethiopia
May 2011 – July 2011	Visiting researcher, The International centre of Insect Physiology and Ecology, Nairobi Kenya

Guiding masters theses

Ufomba Innocent C. (2014).Treatment chain for biologically stabilized landfill leachate:coagulation-flocculation versus ozonation prior to activated carbon adsorption. MSc Environmental Sanitation, Ghent University

Sam Deconink (2015). Fysicochemische behandeling van biologisch gestabiliseerd stortplaatspercolaat. Master in de Industriele Wetenschappen: Chemie, Ghent University.

Robbin Vandewalle (2017). Optimalisatie van het coagulatieproces bij het behandelen van percolaat als voorbehandeling op actief koolfiltratie. Master in de Industriele Wetenschappen: Milieukunde, Ghent University

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Scientific output

Publications in journals referenced in the Web of Science

Violet Oloibiri, Sam Deconinck, Michael Chys, Kristof Demeestere, Stijn W. H. Van Hulle (2017) Characterisation of landfill leachate by EEM-PARAFAC-SOM during physical-chemical treatment by coagulation-flocculation, activated carbon adsorption and ion exchange. Chemosphere, 186, 873-883

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Extended abstracts

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V. Oloibiri, I. Ufomba, M. Chys, W. Audenaert, K. Demeestere, S.W.H. Van Hulle (2015). Treatment of landfill leachate by coupling coagulation-flocculation or ozonation to granular activated carbon adsorption. *Communications in Agricultural and Applied Biological Sciences, 80(1), 57-62.*

Oral presentations

V. Oloibiri, S. DeConinck, M. Chys, K. Demeestere, S. W. H. Van Hulle (2017). Use of spectral and chemometric methods to understand dissolved organic matter removal during physical chemical treatment of landfill leachate. *International water Association – Young water professionals – BeNeLux,* Ghent, Belgium, July 2017.

V. Oloibiri, I. Ufomba, M. Chys, W. Audenaert, K. Demeestere, S.W.H. Van Hulle (2015). Treatment of landfill leachate by coupling coagulation-flocculation or ozonation to granular activated carbon adsorption. *20th National symposium of Applied Biological Sciences (NSABS 2015),* Louvain-La-Neuve, Belgium, 30th January 2015.

Poster presentations

V. Oloibiri, S. Deconinck, K. Demeestere, S. Van Hulle (2015). Organic matter and nitrogen recovery from landfill leachate using granular activated carbon and ion exchange. *In Proceedings of the International Solid Waste Association (ISWA) World Congress*, Antwerp, Belgium, 7 – 9 September 2015.

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Awards

2015 Audience prize, TEDxGhent PhD contest.

2012 Ghent University Masters grant for Msc IN Environmental sanitation.

2012 VLIR UOS North South allowance to undertake an internship in Jimma Ethiopia.

I shall be telling this with a sigh

Somewhere ages and ages hence:

Two roads diverged in a wood, and I –

I took the one less travelled by

And that has made all the diference

Robert Frost, The road not taken