Treatment of a Landfill Leachate Containing Compounds of Pharmaceutical Origin

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Abstract Paper reports the results of landfill leachate treatment with membrane bioreactor, nanofiltration and ozonation. Investigated leachate encompasses a number of specific compounds of pharmaceutical origin, including a suite of by-products deriving from the production of vitamin C and propyphenazone. Low biodegradability was observed in MBR (16 %) for propyphenazone, while the removal of intermediates from the vitamin C-synthesis was moderate, reaching 30 % for diacetone sorbose (DAS) and 69 % for diacetone alpha-keto-gulonic acid (DAG). Ozonation almost completely removed propyphenazone but failed to significantly oxidise intermediates from the vitamin C-synthesis. Nanofiltration of the leachate succeeded to remove 99 % of DAG and 79% of propyphenazone which made it the most efficient among techniques used.

INTRODUCTION

Landfill leachate is a complex wastewater generated during rainwater penetration through landfill, which varies considerably in both composition and volumetric flow. In unprotected landfills, leachate infiltrate vertically through the vadose soil zone below the landfill and eventually reach groundwater aquifer forming anaerobic plumes (Bjerg et al., 1995) that can pose a serious threat to drinking water resources (Christensen et al., 1992; Kerndorff, 1995). In landfills, which include a leachate collection system, it is mandatory to treat the collected leachate before its release into ambient surface waters. The composition and concentration of contaminants are influenced by the type of wastes deposited, by hydro-geological factors and mainly by the age of the landfill. Alvarez-Vazquez et al. (2004) classified landfill leachate into three types: young, medium and old according to different landfill ages (less than a year, 1-5 years and more than 5 years, respectively).
Landfill leachate represents one of the most challenging effluents to treat biologically. While nitrification is generally readily achievable, with >95% removal of ammonia reported through the exclusive application of biological techniques, COD removal is considerably more challenging. Removal efficiency values range from over 90% to as low as 20%, according to leachate characteristics (origin and, more significantly, age), process type and process operational facets. Treatment process schemes generally comprise of some combination of biological, physical and/or chemical treatment. They are designed as modular, multistage units capable of coping with changing leachate contamination over the years. In most cases, the plants' first step is the biological process for ammonia, COD and BOD_5 removal.

Membrane bioreactors which combine activated sludge process and membrane separation have been used for landfill leachate treatment in a number of western European countries since the early 1990s, though they are much less common than conventional biotreatment technologies (Alvarez-Vazquez et al., 2004). Advantages of MBR over conventional activated sludge technology comprise of better effluent quality, smaller footprint, higher concentration of MLSS (mixed liquor suspended solids), less excess sludge production and generally more stable process. The efficiency of contaminant removal with MBR should be as a general rule better then with the conventional activated sludge process. It is due to the

fact that MBR has longer sludge age or sludge retention time, which allows specialized microbial species capable of decomposing compounds with lower biodegradability to develop within the mixed culture in sufficient number.

Among other alternatives for leachate treatment, advanced oxidation with ozone has been investigated for leachate treatment (Monje-Ramirez and Orta de Velasquez, 2004; Silva et al., 2004; Ntampou et al., 2006) since the oxidation power of ozone enhances the degradation of a number of organic compounds found in leachate. Also, chemical oxidation using ozone makes possible the transformation of recalcitrant compounds into more biodegradable products for further biological treatment (Marttinen et al., 2002; Wu et al., (2004). On the other hand, high doses are often required for complete degradation of pollutants by ozonation, rendering the process economically unfeasible.

Membrane technology such as reverse osmosis is often used to remove nearly all pollutants from landfill leachates but concentrate stream fate often presents a problem to be dealt with. Concentrate can be dried and handled further as a solid toxic waste while some authors (Peters, 1998) have proposed concentrate re-injection in the landfill where the compounds of leachate may immobilize on the solid waste of the landfill. Nanofiltration (NF) displays separation characteristics between UF and RO. Compared to RO, NF membranes have a looser structure and enable higher fluxes and lower operating pressures which makes them economically more feasible, while unlike the UF, they are able to reject small organic molecules with molecular weights as low as 200-300 Da. The separation mechanism is explained in term of steric and/or charge effects with sieving mechanism responsible for rejection of uncharged solutes. NF technology has been widely used for the removal of natural organic matter in drinking water**,** as well as in pulp and paper industry. So far, few studies mention the use of nanofiltration to treat landfill leachates **(**Marttinen et al., 2002; Wintgens et al., 2002; Rautenbach and Mellis 1994; Trebuet et al., 2001).

Since the Jakuševec landfill contains waste from both domestic and industrial origin (Ahel et al., 1998; Ahel et al., 2004; Mijatović et al., 2004), the composition of leachate formed in the landfill is very complex and includes a wide spectrum of organic and inorganic contaminants having both biogenic and anthropogenic origins. Like in many other municipal solid waste landfills, the main inorganic constituents are ammonia and chloride, while in the organic fraction macromolecular humus-like materials dominate (Mikac et al., 1998). However, some xenobiotic organic compounds of pharmaceutical origin were also found in rather high concentrations (Ahel et al., 1998). Among these compounds the most abundant ones were isopropylidene derivatives of monosaccharides, which originate from the production of vitamin C. Both macromolecular humic organic matter (determined as chemical oxygen demand - COD) and vitamin C by-products have been detected in high concentration in the adjacent groundwater aquifer (Mikac et al., 1998), indicating that these constituents are rather resistant to microbial degradation. Therefore, the removal of these compounds from the leachate by conventional biological treatment is expected to be very difficult.

The development of technologies for leachate treatment is far from completed since leachate varies significantly as a function of landfill's age and the types of waste deposited. The aim of this work was to evaluate different methods for treatment of specific leachate with emphasis on specific pollutants of pharmaceutical origin, efficiency of each method and their combination for possible application.

METHODS

Leachate sampling and analytical methods

The leachate was collected from the retention basin at Jakuševec, the main landfill of the city of Zagreb, Croatia, which produces around 350 000 m^3 of leachate per year. The leachate samples were collected over a period of 9 months. The analyses conducted based on standard methods were: pH, conductivity, total dissolved solids, COD, BOD_5, and TOC. Identification and quantitative analysis of pharmaceutical intermediates from the vitamin C production and propyphenazone were performed using liquid chromatography – mass spectrometry (LC/MS). Briefly, samples were extracted using solid-phase extraction on Oasis HLB cartridges and subsequently analysed using C_{18} reversed phase chromatography coupled with positive electrospray ionisation mass spectrometry. The most prominent compounds in leachate extracts deriving from the vitamin C-production were diacetone sorbose (DAS) and diacetone alpha-keto-gulonic acid (DAG). The concentration of the target compounds was determined using external calibration.

Table 1 Concentration ranges of main constituents of the leachate from the Jakuševec landfill (Zagreb, Croatia)

Parameter	Concentration range
pH	7.4-7.8
Conductivity (µS/m)	8000-10000
COD (mg O_2/L)	1400-2800
BOD_5 (mg O_2/L)	650-1300
TOC (mg/L)	570-1100
Average BOD_5/COD	0.46
Average TOC/COD	0.39
Total nitrogen (mg/L)	480-620
DAG (µg/L) [CAS: 68539-16-2]	80-430
DAS (µg/L) [CAS: 17682-70-1]	1420-2570
Propyphenazone (µg/L) [CAS: 479-92-5]	85-130

Membrane bioreactor treatment

The experiments were conducted on a pilot plant MBR with a hollow fibre membrane (Zenon ZeeWee^{TM}-10, 0.4 µm pore size, 0.92 m^2 surface area) vertically submerged directly in the 40 L (useful volume) rectangular based (24x24x93 cm) bioreactor. The pilot plant consisted of laboratory pumps for feed flow and permeate suction; a blower with a diffuser placed under the membrane; a pressure gauge. The membrane was bubbled, with a blower with 3.4 m^3 h^{-1} of air flow, which helped to avoid fouling of the membrane through promoting shear over its surface and produced stable dissolved oxygen concentration of 2-5 mg/L in the bioreactor. The membrane was also backflushed with effluent for 10 seconds every 9.75 minutes with the backflush rate 1.5 times greater than the effluent flow rate in order to remove deposits on the membrane surface. The flow rate of feed water was 7 L h^{-1} which gave a permeate flux of 7.6 L m^{-2} h^{-1} and 5.7 h hydraulic retention time (HRT). The bioreactor was inoculated with activated sludge from a full-size leachate treatment plant on the landfill site with initial 9.8 g L^{-1} of mixed liquor suspended solids (MLSS) in the

bioreactor. During continuous duration of the experiment over 51 days on the landfill site, MLSS was slowly increasing and reached 12.9 g/L at the end of the experiment.

Nanofiltration

Nanofiltration was performed on a pilot plant unit consisting of a membrane pressure vessel, centrifugal pump and corresponding pipes, valves, pressure gouges and flow meters. The membrane used in these experiments was an NF 70 polyamide spiral wound membrane (Film Tec, Dow Chemical USA). Membrane had 2.2 m^2 of useful area and a 200 Da molecular weight cut-off. Water recovery was 0.7 with applied transmembrane pressure of 17 bar. All of the experiments were conducted as a one-through system without recirculation of the concentrate. Nanofiltration pilot plant was situated on location of the landfill where all filtration experiments were conducted, and the samples were transported to the laboratory.

Ozonation

Ozone was generated from air oxygen by using an ozone generator (Ozotech INC, Yerka) and it was introduced in the solution through a porous diffuser which produced fine bubbles. The gas stream was fed to the bottom of the tank/vessel. Ozonation was carried out with 1.24 mg O_3/ mg COD ozone dose in a 1.5 L glass column, while rate of ozone transfer to the aqueous phase was determined with iodometric titration method.

RESULTS AND DISSCUSION

From the analyses of the leachate samples it can be seen that the pH value of these samples was typically about 7.4-7.7, with the BOD_5/COD ratio of 0.39. Since the investigated landfill is still in intensive use while having a history of more than 30 years of operation, it is rather difficult to classify it. High BOD_5/COD ratio is a consequence of intensive deposition of new waste while low COD concentration, high concentration of nitrogen and pH value above 7 reflects the landfill's age and size. Moreover, the landfill leachate from the Jakuševec landfill was heavily contaminated with pharmaceutical chemicals such as the diacetonated (di-isopropylidene) intermediates from the vitamin C-synthesis reaching the total concentration in the range from 27-55 mg/L. This represented about 3-5 % of the total organic carbon. Very little is known, so far, about the ecotoxicological properties of these diacetonated compounds. Our study of the groundwater contamination near the Jakuševec landfill indicated their biorefractory behaviour in the aquifer (Ahel et al., 1998). As to their biological effects, sodium salt of DAG is used as a plant growth regulator, which can remarkably influence the germination of seeds kept under adverse storage (Maity, 2002).

We were able to remove only 23 % of the present COD with the treatment of the leachate by MBR. The poor degradation of COD is not in concordance with BOD_5/COD ratio of the raw leachate which indicated that nearly half of the organics in the leachate were biodegradable. However, the BOD was measured after five days according to the protocol, while microorganism in the MBR had only an 8 h HRT. Fig 1. shows the results of DAS removal by MBR. Unlike other two investigated contaminants whose removal efficiency was constant during the experiment, DAS removal efficiency by MBR steadily rose during the 51 day of the experiment from 5 % to 50 % indicating development and adaptation of the mixed microbial culture able to degrade the contaminant.

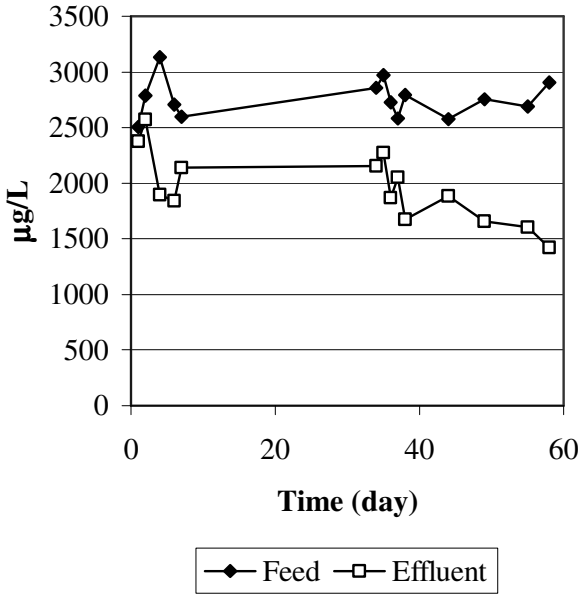

Fig. 1 Removal of DAS by MBR

The average removal efficiencies for all three contaminants for various removal techniques are presented on Fig. 2, 3 and 4. The biological treatment with MBR averagely succeeded to degrade DAG by 68 %, while degradation of DAS reached 50 % by the end of the experiment. Propyphenazone was degraded by only 16 %. In a review by Alvarez-Vazquez et al. (2004), the MBR-based treatment schemes appear to achieve greater COD removal, a mean of around 80 % across all installations, for less biotreatable leachates (BOD/COD=0.03-0.16), than conventional systems which achieve COD removals of around 63% at feedwater BOD/COD ratios of 0.21-0.3. Moreover, they do so at generally lower HRTs, and thus correspondingly higher loading rates (1-3 kg COD m^{-3} d^{-1} compared to less than 0.25 kg COD m^{-3} d^{-1} for conventional treatment).

High rejection rates of common wastewater contaminants for the organic load (more than 90 % for both COD and TOC) were obtained by nanofiltration with NF 70 membrane, while for the collective inorganic parameters (conductivity and total dissolved solids), the rejection rate was more than 75 %. The removal of the total hardness was 90 % which leads to a conclusion that used nanofiltration membrane exhibits a salt rejection typical of charged membranes where divalent ions are better rejected than monovalent.
The rejection rates of individual compounds were 79 % for propyphenazone (M. w. 230 Da) and 99 % for diacetone α-keto-gulonic acid (M.w. 274 Da), respectively. As in a previously published work from our group (Ahel et al., 2004), results indicated that size of the molecule rather than their polarity determined the efficiency of the removal. The results from DAS removal by NF are not presented here because they need further clarification.

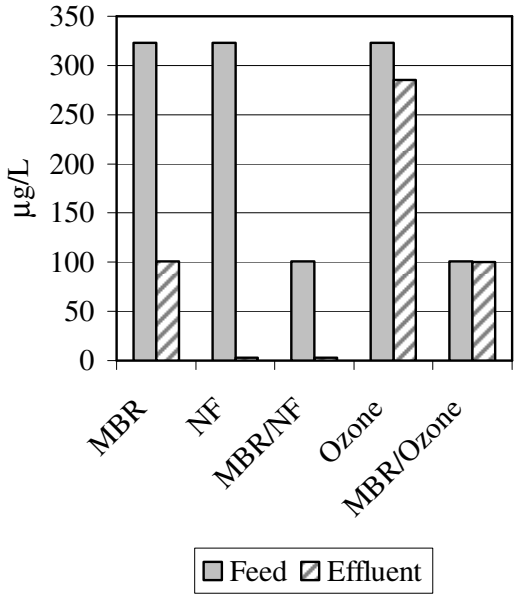

Fig. 2 Average removal of DAG by various techniques

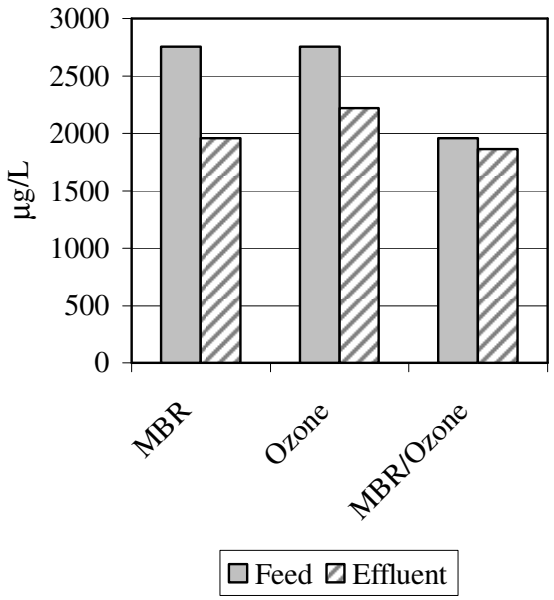

Fig. 3 Average removal of DAS by various techniques

In comparison with reverse osmosis, NF can be run at lower pressures thus decreasing operating costs for energy consumption and possibly decreasing membrane fouling rate. The problem with the membrane processes which operate in cross-flow mode is the fate of the produced concentrate stream, which is usually highly polluted. In the case of landfill leachate, concentrate stream may be re-injected into the landfill in order to immobilize pollutants on the landfill solids or alternatively, evaporated under vacuum and further disposed as a dangerous solid waste (Peters, 1998; Van der Bruggen et al., 2003). Alternatively, it could be treated in a bioreactor for treatment of leachate. Such

sequentional treatment was shown to significantly increase biodegradation rate (Rautenbach and Mellis 1994).

Ozonation was performed on raw leachate and on effluent from MBR. Removal efficiencies for the DAG, DAS and propyphenazone for the raw leachate experiments were 12%, 19% and 99%, respectively. Results suggest that ozone oxidation worked very well for propyphenazone, which, in contrast, was resistant to biological oxidation in MBR, while DAG and DAS were less prone to chemical oxidation with ozone then to biological oxidation. It should be noted that removal of organic matter by ozonation may not be complete since the organic molecules present in the leachate can be oxidised to by-products other than gaseous such as CO_2 and therefore not completely removed from the leachate. This can be concluded from the fact that COD removal by ozonation was 56%, while removal of TOC was only 35%. These values suggest that only a portion of organic carbon present in the leachate was completely removed by ozonation.

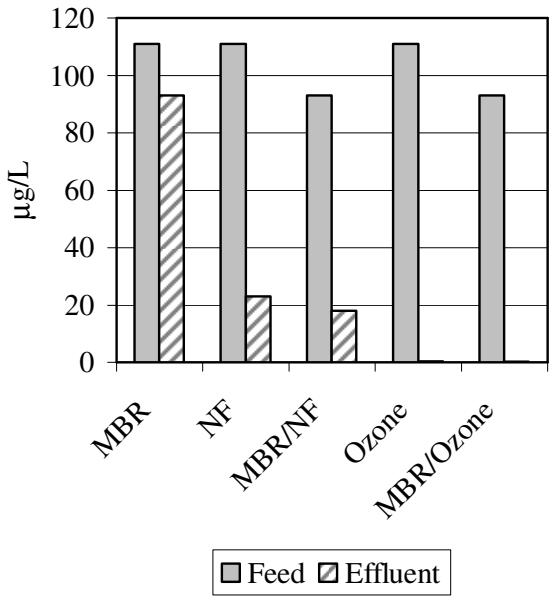

Fig. 4 Average removal of propyphenazone by various techniques

A combination of MBR treatment followed by NF had roughly the same efficiency as NF employed alone for all investigated contaminants and therefore does not justify the use of combined processes. Similarly, ozonation of the MBR effluent did not achieved significant improvement of the overall removal efficiency. Several researchers (Marttinen et al., 2002; Monje-Ramirez and Orta da Velasquez, 2004; Wu et al., 2004) observed an increase in the BOD of the leachate after ozonation due to a transformation of recalcitrant organic matter into a more degradable form probably due to its fractionation. It would, therefore, be of interest for further investigation to apply ozonation before biological treatment to observe the possible enhancement of removal efficiency for selected compounds.

CONCLUSIONS

Results obtained through leachate treatment by MBR, ozonation and NF showed low biodegradability in MBR for propyphenazone and modest removal of intermediates from

the vitamin C-synthesis. Ozonation removed propyphenazone almost completely but failed to significantly oxidise intermediates from vitamin C-synthesis. Nanofiltration of the leachate succeeded to remove 99 % of DAG and 79% of propyphenazone, which made it the most efficient among techniques used. Taken together, results showed diversity of contaminants' behaviour in response to various treatment techniques, which should be taken into consideration when deciding upon the technology to be used for leachate treatment.

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