

## Stabilized leachates: ozone-activated carbon treatment and kinetics

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### Abstract

Ozone has been used as a pre-oxidation step for the treatment of stabilized leachates. Given the refractory nature of this type of effluents, the conversion of some wastewater quality parameters has been moderate after 1 h of ozonation (i.e. 30% chemical oxygen demand (COD) depletion). Ozone uptake was calculated in the interval 1.3-1.5 g of ozone per gram of COD degraded. An optimum dose of ozone has been experienced in terms of biodegradability of the processed effluent (60 min of treatment,  $1 \times 10^{-3}$  mol L<sup>-1</sup> ozone inlet feeding concentration and 50 L h<sup>-1</sup> gas flow-rate). pH and other typical hydroxyl radical generator systems exerted no influence on the efficiency of the process, suggesting the negligible role played by the indirect route of oxidation (generation of hydroxyl radicals). The ozonated effluent was thereafter treated in a second adsorption stage by using a commercial activated carbon. Removal levels up to 90% of COD in approximately 120 h were experienced for adsorbent dosages of 30 g L<sup>-1</sup>. Both steps, the single ozonation and the adsorption stage have been modelled by using different pseudoempirical models.

Keywords: Leachate; Landfill; Ozone; Activated carbon; Wastewater

### 1. Introduction

Nowadays, in most countries landfilling is the preferred option for the disposal and management of solid urban wastes [1]. Controlled landfilling prevents some of the risks associated to the alternative use of incineration processes. In spite of the number of advantages found when using this waste disposal method, some inherent drawbacks might be experienced. Thus, generation of odors and leachates are the main disadvantages associated to sanitary landfilling. As a consequence, one of the major issues to deal with, is the collection, storage and suitable treatment of highly contaminated leachates. Organic and inorganic substances are released from the urban residues due to different chemical, physical and biological processes [2].

Predictions for the next 15-20 years indicate an upward trend in waste production and, subsequently, in leachate generation. Therefore, studies addressed to the development of feasible technologies to confront leachate purification are of paramount significance.

According to literature [1], technologies meant to leachate treatment can be classified into three major groups: (a) leachate channeling: recycling, lagooning, etc., (b) biodegradation: aerobic and anaerobic processes and (c) chemical and physical methods: oxidation, adsorption, etc. Each of the aforementioned alternatives presents its own advantages and hindrances. Recently, the combination of biological and physical-chemical processes is being considered as the most appropriate technology for manipulation and management of high strength effluents [3]. The integrated chemical-physical-biological processes (whatever the order) ameliorates the drawbacks of individual processes contributing to a higher efficacy of the overall treatment.

Additionally, the changing nature and composition of leachates depending on age, season, climatic conditions, etc., implies that universal treatments of wide application can not be proposed. As a consequence, the methodology adopted to face these effluents must be flexible and adaptable to relatively different inputs. In this sense, the action of a preoxidation and/or adsorption stage might be manipulated depending on the input (high or low intensity) to produce an effluent with roughly similar characteristics for a further biological stage (or direct discharge in case of fulfilling the present regulatory laws for this type of emissions).

In spite of the recognition of leachate environmental impact, the past and recent literature is rather scarce on the development of integrated methods of treatment (i.e. combination of chemical, physical and biological steps). Table 1 displays some of the most relevant works on this particular topic. Moreover, when applied, most of studies completed on the treatment of leachates are restricted to the exposition of experimental data with no inclusion of the kinetics governing the process.

The aim of the present work is to assess the potential of a chemical (ozone)-physical (adsorption)

integrated leachate treatment as a complete treatment or as a pre-treatment to render the effluent more suitable for a final polishing biodegradation. For that purpose, experiments in the presence of ozone and some heterogeneous catalysts have been carried out and the effectiveness of the process analysed. Thereafter, an analysis of the potential benefits of granular activated carbon as a second stage to process the ozonated effluent has been conducted. Biodegradability indexes after each phase have been calculated. The kinetics of both stages have been assessed.

## 2. Experimental

### 2.1. Leachate characterization

Leachates were collected from the landfill site of Badajoz (South West of Spain). Tables 2 and 3 summarize the main characteristics of these leachates from January 2001 to April 2003. Experiments presented in this study have been completed by using leachates taken in December 2001. From Table 2 it is observed that this leachate presents a low value of chemical oxygen demand (COD) and BOD<sub>5</sub> : The rates

Table 1  
Leachate treatment survey

| References | Treatment   | Parameter measured                          | % Remov.   | Age |
|------------|---|---|--|-----|
| [4]        | CF-C <sup>a</sup>   | COD, TOC.                                   | 50-70 color  | –   |
|            | Fenton-C <sup>a</sup>   | Color                                       |  |     |
| [2]        | CF-Aerb-O <sub>3</sub>  | COD, BOD, N-NH <sub>4</sub>                 | 90-95 in all parameters                                    | S&Y |
|            | CF-Aerb-Precp-O <sub>3</sub>  |   |  |     |
|            | H <sub>2</sub> O <sub>2</sub> =UV; O <sub>3</sub> ; O <sub>3</sub> =fixed |   |  |     |
| [5]        | bed catal.  | COD   | > 80   | S   |
| [6]        | Aerb-O <sub>3</sub> =UV-C <sup>a</sup>                                    | COD   | 50-60  | S   |
|            | Aerb-C <sup>a</sup>   |   |  |     |
| [7]        | O <sub>3</sub> -Aerb-Anaerob-C <sup>a</sup>                               | TOC, COD, BOD, UV <sub>260</sub>            | 57 TOC   | S   |
|            |   | COD, TOC, UV <sub>260</sub>                 |  |     |
| [8]        | Lagoon-C <sup>a</sup> /O <sub>3</sub> =CF                                 |   | 50 with CF<br>40-80 depending on MW                        | –   |
| [9]        | Fenton-CF   | TOC   |  | –   |
| [10]       | Aerb-lime-O <sub>3</sub>  | COD   | 88   | S   |
| [11]       | Aerb-CF-Fenton  | COD   | 87   | S   |
| [12]       | Fenton+CF.  | COD   | 67   | S   |
| [13]       | lime-Fe <sup>2+</sup> -CF   | COD   | 39   | I   |
| [14]       | Fenton  | COD   | 35   | I   |
| [15]       | Biolog-Fenton-Biolog  | COD   | 73   | I   |
|            | Aerb, Fenton, O <sub>3</sub> ; precip, C <sup>a</sup>                     |   | 96 TOC   |     |
| [16]       | C <sup>a</sup>  | COD, BOD, TOC (Aerb+precip+C <sup>a</sup> ) |  | S   |
| [17]       | Fenton+UV   | TOC, COD, BOD                               | 70 COD   | –   |
| [18]       | Anaerob-Fenton  | COD   | 97   | Y   |
| [19]       | lime-stripping  | BOD, SS, N                                  | 69 BOD   | –   |
| [20]       | H <sub>2</sub> O <sub>2</sub> ; O <sub>3</sub> ; UV                       | COD, TOC, TOX                               | 89 COD (H <sub>2</sub> O <sub>2</sub> =O <sub>3</sub> =UV) | –   |
| [21]       | ca  | Several                                     | 90 COD   | –   |

<sup>a</sup> C–activated carbon; Aerb–aerobic; Anaerob–anaerobic; CF–coagulation-flocculation; UV–ultraviolet light; COD–chemical oxygen demand; TOC–total organic carbon; BOD–biological oxygen demand; TOX–total halogenated organics; Y–young; S–stabilized; I–intermediate.

Table 2

Leachate characterization from Badajoz landfill site (units in g L<sup>-1</sup>, except for N-Kjeldahl in mg L<sup>-1</sup>)

|                | January<br>2001 | March<br>2001 | April<br>2001 | Septem<br>ber<br>2001 | Decemb<br>er<br>2001 | March<br>2002 | May<br>2002   | October<br>2002 | April<br>2003 |
|----------------|-----------------|---------------|---------------|-----------------------|----------------------|---------------|---------------|-----------------|---------------|
| COD            | 2:3070:<br>05   | 2:3070:<br>04 | 2:9670:<br>02 | 4:1070:<br>09         | 4:8570:<br>10        | 4:1270:<br>03 | 2:3070:<br>30 | 39:472:<br>3    | 4:9770:<br>5  |
| BOD5           | 0:6070:<br>07   | 0:8570:<br>03 | 0:6370:<br>11 | 0:5470:<br>06         | 0:5270:<br>03        | 0:4170:<br>05 | 0:4570:<br>05 | 0:5270:<br>07   | 0:2970:<br>03 |
| N-<br>Kjeldahl | 12374           | 8575          | 10972         | –                     | 8573                 | 250715        | –             | 700735          | 331           |
| TC             | 1:2370:<br>04   | 1:3170:<br>02 | 1:3870:<br>06 | –                     | 1:6470:<br>05        | 1:970:0<br>5  | 0:8370:<br>08 | 16:570:<br>4    | –             |
| IC             | 0:4870:<br>04   | 0:3970:<br>04 | 0:4070:<br>02 | –                     | 0:5870:<br>08        | 0:6670:<br>02 | 0:1770:<br>08 | 2:370:0<br>4    | –             |
| pH             | 8.88            | 8.29          | 8.52          | 8.75                  | 8.20                 | 7.90          | 8.35          | 9.02            | 8.39          |

Table 3

Metal characterization of leachates from Badajoz landfill site (mg L<sup>-1</sup>)

|    | January<br>2001 | March<br>2001 | April<br>2001 | Septembe<br>r<br>2001 | Decembe<br>r<br>2001 | March<br>2002 | May<br>2002 | October<br>2002 | April<br>2003 |
|----|-----------------|---------------|---------------|-----------------------|----------------------|---------------|-------------|-----------------|---------------|
| Al | 1070            | 1650          | 1240          | 1380                  | 1590                 | 1610          | 950         | 1770            |               |
| Sb | 188.3           | 61.7          | 0.1           | 3.2                   | 0.1                  | 0.1           | 24.1        | –               |               |
| As | 0.1             | 0.1           | 0.1           | 0.1                   | 0.1                  | 0.1           | 0.1         | –               |               |
| Cd | 7.3             | 1.4           | 0.1           | 0.1                   | 0.1                  | 0.4           | 0.1         | 1.96            | 30            |
| Cu | 3405            | 254           | 0.1           | 16                    | 21                   | 0.1           | 0.1         | 110.2           | 70            |
| Cr | 656.8           | 670.1         | 750.3         | 615                   | 534                  | 972           | 588.7       | 8346            | 1090          |
| P  | 5430            | 520           | –             | 2060                  | 1980                 | –             | 10          | 4318            | 1933          |
| Fe | 23109           | 16248         | 15511         | 20125                 | 16685                | 17720         | 10385       | 29990           | 0             |
| Mn | 4316.4          | 707.1         | 703.2         | 2069                  | 1533                 | 3978          | 276.4       | 751             | 670           |
| Hg | 0.1             | 0.1           | 0.1           | 0.1                   | 0.1                  | 0.1           | 0.1         | 0.1             |               |
| Ni | 13470           | 1358          | –             | 397                   | 212                  | 0.1           | 0.1         | 1261            | 280           |
| Ag | 0.1             | 0.1           | 0.1           | 0.1                   | 0.1                  | 0.1           | 0.1         | 1.58            |               |
| Pb | 0.1             | 0.1           | 38            | 0.1                   | 9                    | 0.1           | –           | 2.51            | 20            |
| Se | 0.1             | 0.1           | 29            | 2.1                   | 0.1                  | 1.2           | 0.1         | –               |               |
| Zn | 16500           | 2.5           | 0.1           | 0.1                   | 0.1                  | 0.1           | 0.1         | 355             | 240           |

BOD5 = COD and TOC/COD situated in the range 0.1-0.3 and 0.2-0.4, respectively, and pH above 7 indicate that this leachate may be defined as intermediate-stabilized [2]. This type of aged leachates is normally catalogued as refractory towards conventional biodegradation processes and in most cases necessitates an intensive and sophisticated physico-chemical process to meet the standards of quality set by the regulating authorities. Among metallic species analysed, Al, Fe, Cr, Mn and Ni show the highest concentrations with other metals detected at trace levels.

## 2.2. Experimental set-up

Experiments were carried out in a glass bubble column of 1 L of capacity (see Fig. 1). When needed, a mixture of ozone/oxygen was fed through a porous plate located at the column base. To avoid contamination of the gas ozone analyzer, a foaming trap made of Raschig rings was situated at the top of the column. Additionally, re-circulation of the liquid from the trap was also implemented by means of a peristaltic pump. For experiments carried out in the presence of a heterogeneous catalyst, the liquid inside the reactor was passed through a column bed containing the catalyst and pumped back to the bubble column.

Adsorption experiments of ozonated leachates (60 min of treatment,  $1 \times 10^3$  mol L<sup>-1</sup> ozone inlet feeding concentration and 50 L h<sup>-1</sup> gas flow-rate) were carried out by using a commercial activated carbon (AC), Norit 08. This pelletized alkaline adsorbent shows a specific surface area of 1150 m<sup>2</sup> g<sup>-1</sup>, bulk density of 0.39 g cm<sup>-3</sup>, moisture content of 2 wt%, ash content of 7.0wt% and particle size below 0.6

mm as the main physical properties. Its microporous structure is described in more detail elsewhere [22].

Isotherms of leachate adsorption were determined by using the bottle point technique whereas kinetic experiments were carried out in an isothermal agitated glass reactor of 1 L of capacity.

### 2.3. Analytical determinations

Leachates were characterised measuring the following parameters: COD was determined in a Dr. Lange spectrophotometer, the method based on the standard

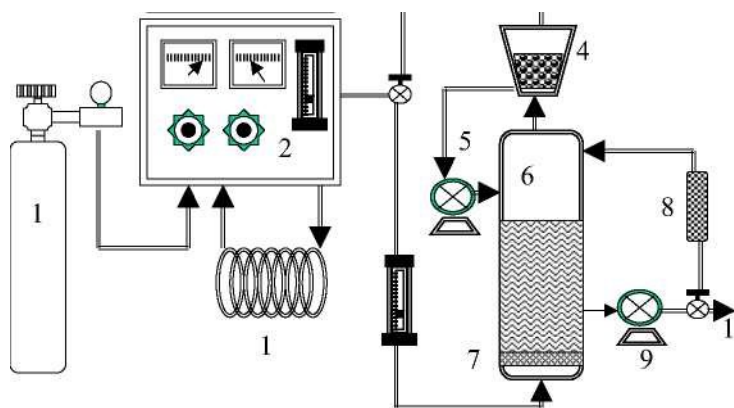


Fig. 1. Experimental set-up. 1–Oxygen cylinder, 2–ozone generator, 3–ozone analyser, 4–foam trap, 5–peristaltic pump, 6–bubble column, 7–porous plate, 8–catalytic bed, 9–peristaltic pump, 10–sampling port, 11–cooling water.

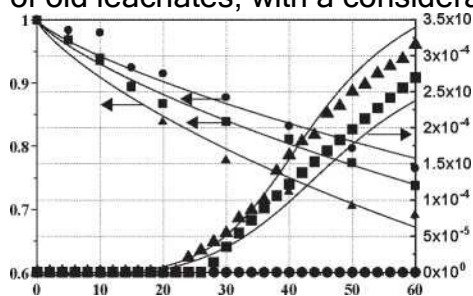
dichromate reflux method [23]. Total carbon (TC) and inorganic carbon (IC) concentrations were obtained by means of a DC-190 Dohman analyzer. BOD was measured following the respirometric method [24]. For this purpose, non acclimated microorganism from the municipal wastewater plant of the city of Badajoz were used. Metals in leachates were determined by Induced Coupled Plasma. Toxicity of samples was measured by using a luminometer (ToxAlert<sup>s</sup>); this method based on the inhibition percentage of a bioluminescent bacteria (*Vibrio fischeri* NRRL B-11177). Absorbance of samples at 254 and 410 nm after dilution were determined by means of a U2000 model HITACHI spectrophotometer.

Ozone in the gas phase was analysed by absorbance at 254 nm (GM109 Anseros ozone analyser). The apparent ozone concentration in the liquid phase was measured by the Indigo method [25].

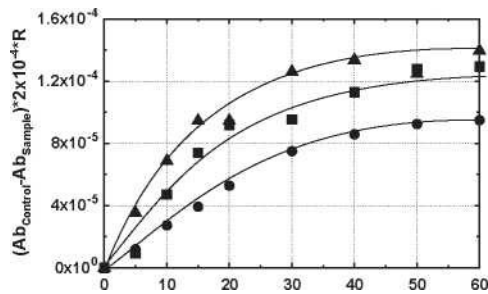
## 3. Results and discussion

### 3.1. Single ozonation

In this study, the efficiency of ozone as a pre-treatment step of leachates has been assessed. As a first approach, a series of experiments was carried out by increasing the ozone dose fed to the bubble column. Fig. 2 illustrates the evolution of normalized COD, gas ozone outlet ( $CO_3_{out}$ ) and apparent dissolved ozone in the liquid phase. As observed from this figure, under the operating conditions used in this study, COD conversion achieved after 1 h of reaction is rather limited with a maximum value in the proximity of 30% elimination for this parameter. The reason for these low values rests on the composition of old leachates, with a considerable



(A) Time, min



(B) Time, min

Fig. 2. Ozonation of stabilised leachates. Experimental conditions:  $COD_0 = 5:0 \text{ g L}^{-1}$ ;  $T = 20^\circ\text{C}$ ;  $Q_g = 50 \text{ L h}^{-1}$ . (A) Evolution of normalized COD and ozone outlet (Lines = model 2 simulation). (B) Analysis results of Indigo assay ( $R = \frac{\text{Sample volume} \times \text{Indigo}}{\text{volume} \times \text{me}}$ ). Ozone inlet:  $K, 5.4 \times 10^{-4} \text{ mol L}^{-1}$ ;

Indigo volume

\,  $10.4 \times 10^{-4} \text{ mol L}^{-1}$ ;  $m, 14.6 \times 10^{-4} \text{ mol L}^{-1}$ .

fraction of substances with high molecular weight and recalcitrant characteristics [4]. Also, an increase in the ozone concentration supplied to the reactor led to the corresponding increase of both dissolved and outlet ozone concentrations. The apparent presence of dissolved ozone in the aqueous phase from the beginning of the process would indicate the development of slow reactions. However, as discussed later in the paper, the absence of ozone at the reactor outlet and the simultaneous accumulation of dissolved ozone in the liquid are contradictory facts. In this sense, there are not reported data on kinetic regimes developed during the ozonation of stabilised leachates, however, in most of previous cases the low conversion in COD has also been experienced. Thus, Ince [20] and Baig and co-workers [2] have reported COD conversion values of 36 (after 60 min treatment) and 33% (time not specified), respectively, when dealing with this type of stabilised leachates.

Other parameters related to the water standards of quality such as absorbance at 254 and 410 nm and TC also experienced a moderate decrease throughout the ozonation stage. UV spectrophotometry has regularly been proposed and used for water and wastewater quality control for 50 years [26]. The absorbance at 254 nm of a wastewater is related to the presence of aromatic and unsaturated structures (chromophores). Absorbance at 410 nm is used in this study to assess the colour removal from leachates (from darkened brown to lightly yellow). Fig. 3 depicts the evolution of normalized absorbance at 254 nm and colour (410 nm) with time for experiments conducted under different inlet ozone partial pressures.

Ozone consumption was calculated by considering the decrease in COD, ozone in the gas outlet and dissolved in the liquid (negligible in comparison to ozone in the gas outlet) and, finally, the physico-chemical characteristics of the experimental installation (dead time, scavenging effect of surfaces, etc.). Thus, ozone uptake (mass of ozone per mass of COD degraded) depends on the amount of ozone absorbed when oxidizing the leachate, the amount of ozone absorbed/decomposed when ultrapure water is ozonated (water exp.) and, finally, the COD conversion. Subtraction of ozone absorbed when oxidising leachates and ozonating pure water should result in the actual amount of this reagent used to degrade COD. Mathematically, ozone uptake is calculated as follows

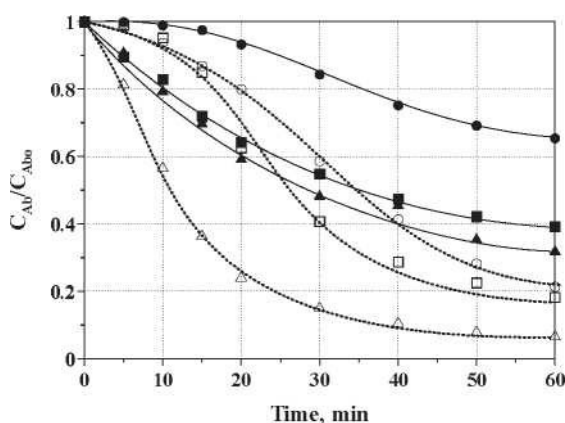


Fig. 3. Ozonation of stabilised leachates. Experimental conditions:  $COD_0 = 5,0 \text{ g L}^{-1}$ ;  $T = 20^\circ\text{C}$ ;  $Q_g = 50 \text{ Lh}^{-1}$ ; absorbance 254 nm = 1:45 after dilution 1:30 with ultrapure water; absorbance 410 nm = 1:50 after dilution 1:4 with ultrapure water. Evolution of normalized absorbance (254 nm solid symbols; 410 nm open symbols) Ozone inlet:  $K O_3, 5:4 \times 10^4 \text{ mol L}^{-1}$ ;  $10:4 \times 10^{-4} \text{ mol L}^{-1}$ ;  $m W, 14:6 \times 10^{-4} \text{ mol L}^{-1}$ .

Fig. 4 outlines the amount of COD degraded with time and consumption of ozone per gram of COD depleted with and without considering the downtime and wastage of ozone due to self-decomposition along the experimental set-up. As inferred from Fig. 4, after 60 min of chemical oxidation, the ozone dose was calculated in the range 1.3-1.5 g  $O_3$  consumed/g COD degraded. This global stoichiometric coefficient is in the same order as the reported values of Steensen [5] (1.22.2) or Baig [2] (3.2), indicating the refractory nature of these effluents if compared to wastewaters of different nature (i.e. 0.5-0.7 for table olive wastewater [27]). For comparison purposes, a rough analysis of the reaction rate (simplified to a first order kinetics) gave the following values of 0.4, 0.25 and  $0:18 \text{ h}^{-1}$  for the kinetic constants of COD, TOC and TC depletion rates. These values are slightly higher than those reported by Ince [20] when using other similar advanced oxidation processes. However, it has to be pointed out that leachates used by this author had a lower contaminant

$$\frac{gO_3}{gCOD} = \frac{[C_{O_3inlet}Q_g t - \int_0^t C_{O_3outlet}Q_g dt - C_{O_3}V]_{leachates} - [C_{O_3inlet}Q_g t - \int_0^t C_{O_3outlet}Q_g dt - C_{O_3}V]_{water}}{[COD_0 - COD]_{MW \text{ of } O_3}}$$

In expression (1),  $C_{O_3inlet}$ ;  $C_{O_3outlet}$  and  $C_{O_3}$  stand for the concentrations of ozone (in  $\text{mol L}^{-1}$ ) fed to the reactor, leaving the reactor and dissolved in the aqueous matrix, respectively. Additionally,  $COD_0$  and  $COD$  are the chemical oxygen demand (measured in  $\text{g L}^{-1}$ ) at time zero and time  $t$ , respectively, and  $V$  is the reaction volume load, and presumably, substances present in that leachates were more refractory than those found in the present case.

Enhancement in biodegradability (if any) of the ozonated sample was analysed by measuring several parameters like  $BOD_5$ ; percentage of inhibition in

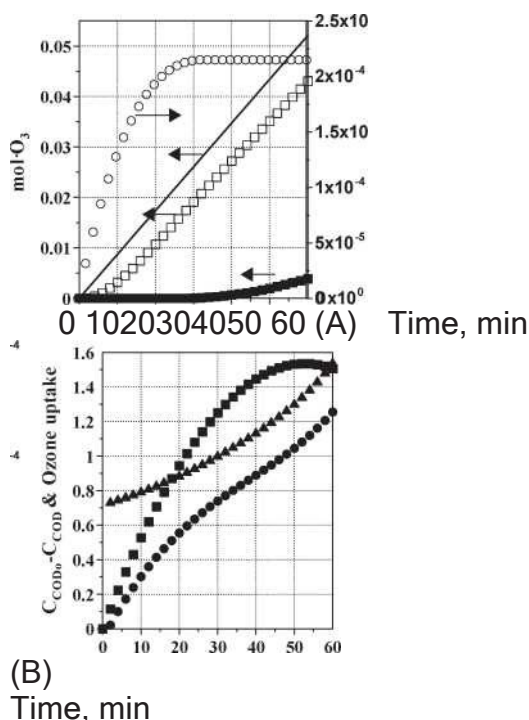


Fig. 4. Ozonation of stabilised leachates. Experimental conditions:  $COD_0 = 5:0 \text{ g L}^{-1}$ ;  $T = 20^\circ\text{C}$ ;  $Q_g = 50 \text{ L h}^{-1}$ . (A) Moles of ozone fed (solid line), leaving the reactor (squares) and accumulated in the liquid (circles). Open symbols correspond to ultrapure water, solid symbols correspond to leachates. (B) grams of COD eliminated;  $m$ ; overall ozone uptake;  $K$ ; ozone uptake by reaction with COD.

ToxAlert<sup>®</sup>; the ratios BOD<sub>5</sub>=COD and BOD<sub>5</sub>=TOC and the increase on the average oxidation state of carbon (DAOSC): In most cases, oxygenated species (higher oxidation state of C) presents better biodegradability properties than non-oxygenated compounds. Additionally, DAOSC is defined as follows:

$$\Delta\text{AOSC} = 4 \left[ \frac{\text{COD}_0}{\text{TOC}_0} - \frac{\text{COD}}{\text{TOC}} \right] \frac{12}{32} \quad (2)$$

In Eq. (2) units are in g L<sup>-1</sup>. Fig. 5 shows the initial and final values for the aforementioned parameters after 60 min of ozone oxidation. As deduced from this figure, all parameters indicate a higher biodegradability of the ozonated sample if compared to initial conditions. It is noteworthy to note the total disappearance of inhibition when exposing the effluent to *Vibrio fischeri* bacteria. These tests were repeatedly accomplished for experiments carried out at the same conditions showing a high reproducibility of this parameter (62-69% inhibition for raw leachates and 0% inhibition after ozonation). Nevertheless, this bioassay should be taken with caution since it does not show a regular behaviour when diluting the samples (in this work all bioassays were accomplished without dilution).

Another feature investigated was the optimum reaction time to achieve the highest biodegradability of the effluent. For this purpose, an ozonation experiment was extended over 4 h and BOD<sub>5</sub> measured at different times along the process.

Some authors have experienced a maximum in biodegradability depending on the ozone dose fed. Thus, Imai and coworkers [7] reported an optimum reaction time of 60 min for the ozonation of leachates feeding an ozone concentration of 35 mg L<sup>-1</sup> at a gas flow-rate of 37.8 L h<sup>-1</sup>. Baig and Liechti [10] also reported a maximum in BOD<sub>5</sub> for an ozone dose of 200 mg L<sup>-1</sup>: In this work, experimental conditions were quite similar to those used by Imai et al. (50 mg L<sup>-1</sup> of ozone inlet concentration and 50 L h<sup>-1</sup> gas flow-rate).

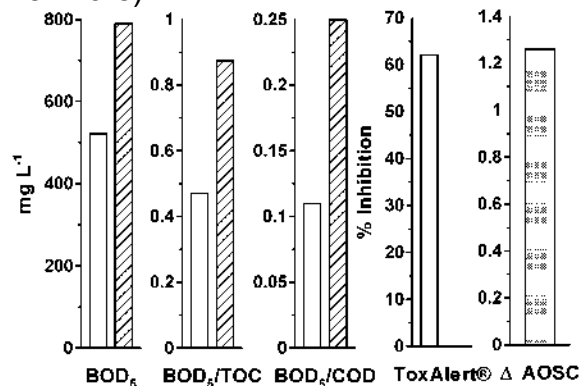


Fig. 5. Ozonation of leachates. Evolution of some biodegradability parameters after 1 h treatment. &, Before ozonation; ijg, After ozonation.

Fig. 6a shows the evolution of normalized COD, apparent dissolved ozone concentration and normalized absorbances at 254 and 410 nm for the single ozonation of leachates. Additionally, Fig. 6b depicts the evolution profiles of TC, TOC, BOD<sub>5</sub> and BOD<sub>5</sub>=COD and BOD<sub>5</sub>=TOC ratios for the same run. As seen in this figure, a general trend is experienced in terms of biodegradability since a maximum in this parameter is achieved after roughly 60 min of treatment.

Another important parameter when using ozone as the oxidising agent is pH. In this work experiments were completed under acidic, alkaline and circumneutral conditions and the results analysed. Fig. 7 shows the aforementioned experimental series for runs completed at initial pH of 10, 8.2 and 3.2. Changes in pH led to some important features. Thus, after addition of HCl to leachates to attain acidic conditions, a brownish gel was formed. As a consequence, in acid media COD rapidly decreased achieving a higher COD conversion for this experiment than those obtained at neutral and basic pHs (similar results were obtained for absorbance depletion,

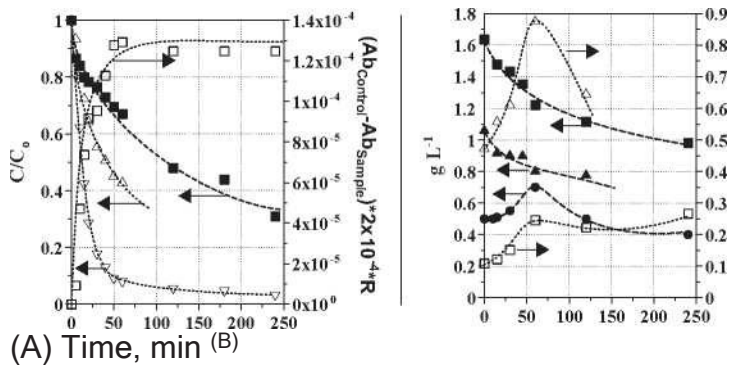


Fig. 6. Ozonation of stabilised leachates. Experimental conditions:  $COD_0 = 5:0 \text{ g L}^{-1}$ ;  $T = 20^\circ\text{C}$ ;  $Q_g = 50 \text{ L h}^{-1}$ ; absorbance 254 nm = 1:45 after dilution 1:30 with ultrapure water; absorbance 410 nm = 1:50 after dilution 1:4 with ultrapure water. (A) Evolution of normalized COD concentration (solid symbols), Indigo assay results  $R = \frac{Ab_{control}}{Ab_{sample}} \times 2 \times 10^4 \times R$ , and normalized Indigo volume (absorbance 254 nm; up triangles; 410 nm; down triangles). (B) Evolution of  $\lambda$ ; TC; m; TOC; K; BOD5; &; BOD5=COD; W; BOD5=TOC:

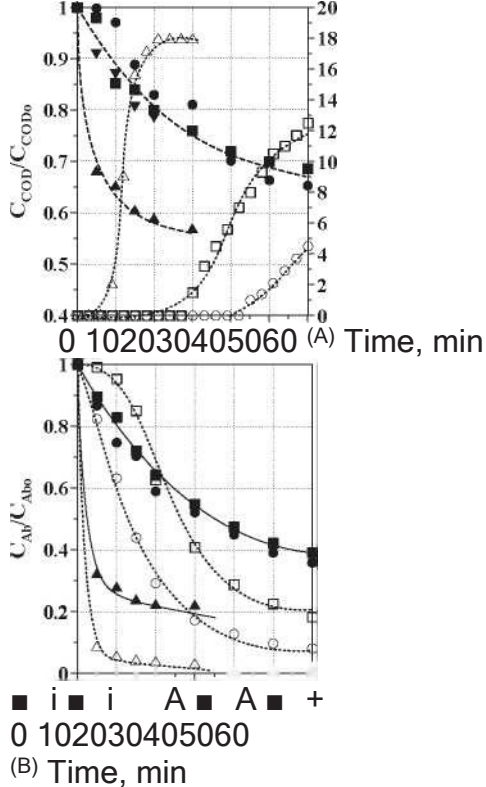


Fig. 7. Ozonation of stabilised leachates. Influence of initial pH. Experimental conditions:  $COD_0 = 5:0 \text{ g L}^{-1}$ ;  $T = 20^\circ\text{C}$ ;  $Q_g = 50 \text{ L h}^{-1}$ ; absorbance 254 nm = 1:45 after dilution 1:30 with ultrapure water; absorbance 410 nm = 1:50 after dilution 1:4 with ultrapure water. (A) Evolution of normalized COD (solid symbols) and ozone outlet (open symbols) concentration with time. pH: m W; 3.2; & 8.2; KJ; 10.0; .; 3.2 (after removal of precipitate). (B) Evolution of normalized absorbance at 254 nm—open symbols and at 410 nm—solid symbols. pH: m W; 3.2; & 8.2; KJ; 10.0.

see Fig. 7b). Filtration of this precipitate was an arduous task since membranes become easily plugged. Nevertheless, considering the fraction of COD removed by precipitation, the efficiency of the ozonation process at pH 3.2 (down triangles in Fig. 7a) was similar to the rest of operating conditions. As expected, ozone at the gas outlet increased as initial pH of the media was decreased.

The similarity in the results obtained, no matter the initial pH used, suggests that the substances present in this particular leachate mainly react through direct reaction with molecular ozone, the radical route playing a minor role. It is likely that, given the unselective nature of hydroxyl radicals generated, this species is wasted in parallel reactions with scavenging compounds of low or null COD content. In this sense it has to be pointed out the high content of carbonate/bicarbonate ions in this effluent (approx.  $500 \text{ mg L}^{-1}$ , i.e.  $0:04 \text{ M}$ ), a well-known hydroxyl radical scavenger.

The previous hypothesis was corroborated by results obtained when utilizing other oxidising systems



characterized by their efficient production of hydroxyl radicals (advanced oxidation processes, AOP). The following processes were tested: (a) O<sub>3</sub>=UV; (b) O<sub>3</sub>=H<sub>2</sub>O<sub>2</sub>; (c) O<sub>3</sub>=UV=H<sub>2</sub>O<sub>2</sub> and (d) O<sub>3</sub>=heterogeneous catalyst (including supported Pt or Co<sub>2</sub>O<sub>3</sub> on alumina).

Experiments were completed for a 2 h period and results compared to data obtained for the single ozonation of leachates. The procedure was as follows,

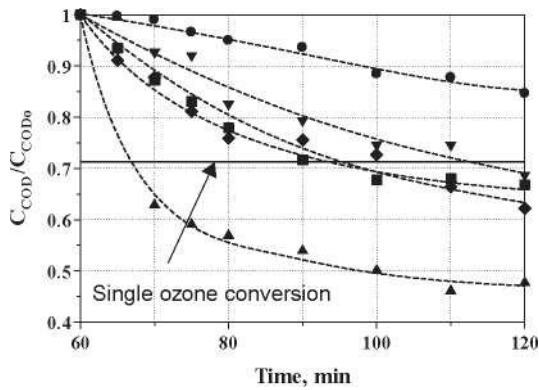


Fig. 8. Catalytic ozonation of stabilised leachates (second hour results). Experimental conditions: COD<sub>0</sub> – 5.0 g L<sup>-1</sup>; pH – 8.2; T – 20°C; Q<sub>g</sub> – 50 L h<sup>-1</sup>; flow-rate through the catalytic bed – 130 mL min<sup>-1</sup>; K, Pt on alumina (19 g); Co<sub>2</sub>O<sub>3</sub> on alumina (19 g); 1 use; ▲, second use; third use; fourth use.

for the first hour only ozone was used, being the AOP used during the second hour. In no case any significant improvement in the analyzed parameters was observed. Moreover, in some cases some inhibition of the process was experienced (i.e. Pt catalyst). Only the use of the cobalt based heterogeneous catalyst gave a slight increment of the COD conversion compared to the single ozonation (see Fig. 8).

Repeated use of this catalyst did not lead to a consistency in the conversion attained at the end of the second hour. The second use resulted in an anomalous high conversion (> 50%); probably due to experimental errors or leaching of cobalt into the leachate, which would act as a homogeneous catalyst [28].

### 3.1.1. Kinetics of single ozonation

At the sight of Fig. 2, an abnormal behaviour of this system is observed. Thus, on one hand, it is seen how regardless of the inlet ozone dose used, dissolved ozone accumulates from the beginning of the process even when no ozone is detected at the reactor outlet. However, on the other hand, the absence of ozone leaving the reactor necessarily involves the development of instantaneous or fast kinetic regimes of ozone absorption. Consequently, ozone can not accumulate in the reaction bulk and the analysis conducted seems to mislead about the actual dissolved ozone concentration. The reason for this positive analysis can be attributed to the presence of other oxidants generated in the ozonation capable of degrading the indigo trisulfonate. Among these potential oxidants, hydrogen peroxide is reported to both interfere in the assay and be generated in ozonation processes [29,30].

To describe the single ozonation kinetics, two models have been tested.

Model 1: Following the above reasons, in the first model it has been supposed that the kinetic regime of ozone absorption, until ozone at the gas outlet is detected, proceeds under the fast kinetic regime. By assuming a fast pseudofirst order kinetic regime and a mean value for the concentration of ozone in the gas, C% O<sub>3g</sub>; throughout the column (plug-flow), the expression governing the removal of COD is

$$\frac{dC_{COD}}{dt} = z_{O_3} a \frac{\bar{C}_{O_{3g}} RT}{H} \sqrt{\epsilon_{O_3} C_{COD} D_{O_3}} \quad (3)$$

In Eq. (3)  $\epsilon_{O_3}$  stands for the apparent kinetic parameter of the process,  $z_{O_3}$  is the stoichiometric coefficient (approximately 1.5 g O<sub>3</sub> per gram of COD, that is 1 mol of O<sub>3</sub> per mol of COD), R is the universal gas constant, T is the temperature, H is the Henry's constant and  $D_{O_3}$  is the ozone diffusivity coefficient (9.0 × 10<sup>-8</sup> m<sup>2</sup> min<sup>-1</sup>) at the operating conditions. According to expression (3), after integration,

a plot of the square root of the remaining COD versus time should lead to a straight line of slope:

$$\text{Slope} = -z_{O_3} a \frac{\bar{C}_{O_3g} RT}{H} \sqrt{\varepsilon_{O_3} D_{O_3}}. \quad (4)$$

From the aforementioned plots, slope values of  $-7.0 \times 10^{-4}$ ,  $-11.7 \times 10^{-4}$  and  $-16.1 \times 10^{-4} \text{ COD}^{1/2} \text{ min}^{-1}$  ( $R^2=0.99$  in all cases) were found for experiments completed with inlet ozone gas concentrations of  $5.4 \times 10^{-4}$ ,  $10.4 \times 10^{-4}$  and  $14.5 \times 10^{-4} \text{ mol L}^{-1}$ , respectively. By considering a typical value in a bubble column of the individual mass transfer coefficient  $k_L = 5 \times 10^{-5} \text{ s}^{-1}$  [31], the value of  $a$  is  $37.2 \text{ m}^{-1}$  ( $k_L a$ , the global liquid mass transfer coefficient was obtained through ozone absorption experiments in water;  $k_L a = 1.86 \times 10^{-3} \text{ s}^{-1}$ ;  $R^2 = 0.99$ ). Finally, assuming  $H$  to have a similar value than obtained in clear water ( $116 \text{ atm M}^{-1}$ ),  $\varepsilon_{O_3}$  was calculated to be in the proximity of  $1 \times 10^5 \text{ M}^{-1} \text{ min}^{-1}$ .

Once ozone at the gas outlet was detected, a moderate-slow regime was supposed to develop. In this case the following general set of reactions applies (plug-flow for the gas phase and totally mixed flow for the liquid phase):

$$\begin{aligned} \frac{d\bar{C}_{O_3g}}{dt} (1 - \beta)V &= 2Q_g(C_{O_3\text{inlet}} - \bar{C}_{O_3g}) \\ &- k_L a \frac{\bar{C}_{O_3g} RT}{H} E \beta V, \end{aligned} \quad (5)$$

$$\frac{dC_{O_3}}{dt} = r_{O_3} + k_L a \left[ \frac{\bar{C}_{O_3g} RT}{H} - C_{O_3} \right], \quad (6)$$

$$\frac{dC_{\text{COD}}}{dt} = k_L a \frac{\bar{C}_{O_3g} RT}{2} E. \quad (7)$$

In the above expressions  $\beta$  is the gas-hold-up,  $C_{O_3}$  dissolved ozone concentration,  $r_{O_3}$  the net ozone rate reactions in the liquid phase and  $E$  the reaction factor defined as  $k_L a \sinh(Ha) \cosh(Ha) \beta \varepsilon_{O_3} C_{\text{COD}} + k_L a \tanh(Ha)$ .

being  $Ha$ ; the Hatta number defined as

$$E = \frac{Ha}{\tanh(Ha)} \left[ 1 - \frac{k_L a \frac{Ha}{\sinh(Ha) \cosh(Ha)}}{\beta \varepsilon_{O_3} C_{\text{COD}} + k_L a \frac{Ha}{\tanh(Ha)}} \right] \quad (8)$$

being  $Ha$ , the Hatta number defined as

$$Ha = \frac{\sqrt{C_{\text{COD}} \varepsilon_{O_3} D_{O_3}}}{k_L}, \quad (9)$$

where  $k_L$  is the individual mass transfer coefficient in the liquid phase. By minimizing the square error function between theoretical and calculated COD concentrations with time the kinetic constant  $k_{\text{COD}}$  was determined. Thus, a value of  $0.6 \text{ M}^{-1} \text{ min}^{-1}$  was capable of simulating COD profiles with time with no significant deviations from experimental data. However, for the case of dissolved ozone concentration and specially, ozone concentration at the reactor outlet, the model overestimates the actual values for these parameters (data not shown). In fact, according to the model, ozone at the reactor outlet immediately reaches a plateau value close to the inlet ozone concentration. Accordingly, dissolved ozone also achieves its saturation concentration in few a seconds. Given the discrepancies between empirical and simulated results, it is clear that the model lacks of some important steps difficult to evaluate given the complexity of both, the effluent and the oxidation system used. Consequently, a pseudo-empirical model was adopted to conveniently describe the process.

Model 2: The next model was adopted based on the following considerations:

\*  
 $C_{O_3g} -$   
 $[C_{O_3}$   
 $1 + \exp[-$   
 $X N_p Z b$

$$-\frac{dC_{COD}}{dt} = \alpha(C_{O_3inlet} - C_{Descomp})^n C_{COD} \quad (11)$$

\* Given the null effect experienced by systems in which the hydroxyl radical plays an important role, it has been supposed that COD is eliminated by direct reaction with molecular ozone.

\* The wide range of substances constituting the leachates implies that the apparent rate constant of the assumed COD–ozone reaction undoubtedly varies with time. For instance, for the first reaction moments, substances readily oxidisable by ozone will react immediately. As the reaction progresses, less reactive substances accumulate and the rate constants of the corresponding reactions will therefore diminish. Mathematically:

$$-\frac{dC_{COD}}{dt} = k'_{COD} t^n C_{COD} \quad \text{for } n < 1. \quad (10)$$

Due to the similarity between the adsorption of contaminants into a fixed adsorbent bed and absorption of ozone fed into a column, a typical model found to simulate the first process has been used for the second one. The adopted model was the Bed Depth Service Time Model [32] with some modifications specified below.

\* ozone consumption is associated to both reaction with coD and inefficient decomposition in the reaction matrix (i.e. metal catalytic decomposition, wastage with species not contributing to coD, etc.). By considering these features, the expression for ozone outlet concentration results:

$$C_{O_3g} = \frac{[C_{O_3inlet} - \alpha(-\frac{dC_{COD}}{dt}) - C_{Descomp}]}{1 + \exp[\frac{\xi N_0 Z \beta}{u} - \xi [C_{O_3inlet} - \alpha(-\frac{dC_{COD}}{dt}) - C_{Descomp}] t]} \quad (11)$$

In Eq. (11),  $\alpha$  stands for the coefficient relating ozone absorption and COD consumption,  $u$  is the gas velocity,  $C_{Descomp}$  accounts for the fraction of ozone decomposed not leading to a decrease in COD (inefficient decomposition),  $\xi$  is the kinetic constant of ozone absorption,  $Z$  the height of the liquid in the column and  $V$  the liquid volume. Additionally,  $N_0$  is a representative parameter of the type of effluent ozonated. Fig. 2 illustrates the experimental and calculated results obtained by this model for the series of experiments carried out with different ozone concentrations fed to the bubble column. As observed both COD and outlet ozone profiles are acceptably well simulated by the model. Table 4 shows the fitted parameters for this model.

### 3.1.2. Economy estimation

A rough estimation of the economy of the process can be carried out by considering the electrical energy per order EE/O. EE/O for a batch reactor is defined as follows:  $EE/O = P/(Vk)$ ; where  $P$  is the rated power of the system (watts),  $V$  is reaction volume ( $m^3$ ) and  $k$  is the first-order rate constant ( $h^{-1}$ ). According to this, EE/O values were calculated for COD, TOC and TC with values of 123:3 kW  $h=order=m^3$ ; 197:2 kWh  $h=order=m^3$  and TC 273:9 kW  $h=order=m^3$ ; respectively. These values are lower than those reported by Ince, although it has to be reminded that leachates used by

Table 4  
Kinetics parameters of single ozonation. Model 2

| $C_{O_3inlet}$ (M)   | $H_{COD}$ (min 1:8)   | $n$ | $a$ (min) | $C_{Descomp}$ (M)    | $x$ (M <sup>-1</sup> mn) | $N_0$ (M)            |
|----------------------|-----------------------|-----|-----------|----------------------|--------------------------|----------------------|
| $5.4 \times 10^{-4}$ | $9.33 \times 10^{-3}$ | 0.8 | 1.30      | $1.7 \times 10^{-4}$ | 303.7                    | $6.2 \times 10^{-3}$ |

|                      |                        |     |      |                   |       |                      |
|----------------------|------------------------|-----|------|-------------------|-------|----------------------|
| $1.0 \times 10^{-3}$ | $11.40 \times 10^{-3}$ | 0.8 | 1.30 | $1.5 \times 10^4$ | 303.7 | $6.2 \times 10^{-3}$ |
| $1.5 \times 10^{-3}$ | $15.01 \times 10^{-3}$ | 0.8 | 1.35 | $1.9 \times 10^4$ | 303.7 | $6.2 \times 10^{-3}$ |

Ince [20] had a stronger refractory nature than leachates used in the present work.

### 3.2. Single ozonation+adsorption onto activated carbon

As stated in the previous section, single ozonation of stabilized leachates for 1 h increases the biodegradability of the effluent in comparison to the raw effluent. However, the results obtained, i.e.  $BOD_5 = CODE_0:25$ ; reveal that the oxidised effluent can not be considered as suitable either for a further biodegradation stage or direct discharge (COD too high). Consequently, an additional stage is therefore needed. Hence the adsorption onto a commercial activated carbon (Norit 0.8) was tested. The reason for choosing the adsorption after the ozonation step is based on the formation of substances more suitable for the adsorption process (smaller size) than the hypothetical big molecules (i.e. humic substances) normally present in stabilized leachates [4].

Firstly, a series of equilibrium experiments were conducted to assess the capacity of the adsorbent to remove the contaminant load from the leachate. Thus, Fig. 9 depicts the isotherm curves corresponding to COD, absorbance at 410 nm and absorbance at 254 nm:

The aforementioned curves were then fitted to a series of isotherm models taken from the literature (for instance Langmuir, Freundlich, Dubinin-Radushkevich, Toth, Sips, Temkin and Redlich Peterson) by minimizing the sum of squared errors. Among them, the Sips isotherm (Eq. (12)) gave the lowest values of the error function. Fig. 9 shows the best fits found for the isotherms, additionally Table 5 presents the Sips isotherm parameters.

$$Q_e = \frac{\Omega_S(\omega_S C_e)^\delta}{1 + (\omega_S C_e)^\delta}, \quad (12)$$

where  $Q_e$  and  $C_e$  are the equilibrium concentrations in the solid and liquid phases, respectively.

As seen from Fig. 9 the monolayer capacity for COD adsorption ranges in the proximity of 0:2 g COD per gram of AC. Not many data can be found on the leachate adsorption onto activated carbon, nevertheless, the value obtained is close to those reported for other authors [4].

After having checked the suitability of the adsorption as an auspicious technology to deal with leachates, the kinetics of the process was thereafter investigated. For that purpose, experiments in the presence of different amounts of adsorbent were carried out and the evolution of the contaminant indexes monitored with time. Fig. 10 displays the evolution profiles of dimensionless COD and absorbances at 410 and 254 nm: As

inferred from this figure, Norit 0.8 ( $30 \text{ g L}^{-1}$ ) is capable of removing up to 90% of the initial COD in hardly 120 h: As a consequence, the final remaining COD is approximately  $0:3 \text{ g L}^{-1}$  which can finally be polished in

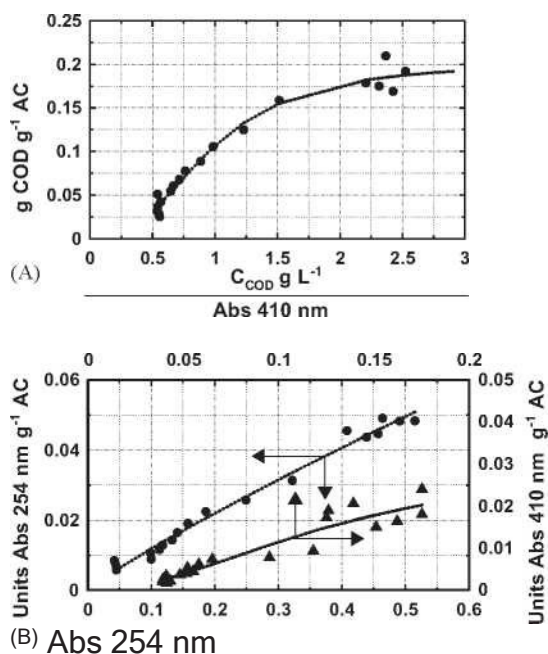


Fig. 9. Adsorption isotherms of pre-ozonated leachates onto

Norit 0.8 Experimental conditions:  $COD_0 = 3.5 \text{ g L}^{-1}$  (average value); absorbance 254 nm = 0.6 after dilution 1:31 with ultrapure water; absorbance 410 nm = 0.8 after dilution 1:6 with ultrapure water. pH = 7.0; T = 20°C. Lines: Sips iso-therm.

Table 5  
Leachate adsorption onto Norit 0.8. Sips isotherm parameters

|             | $Q_s$                | $Q_s$                | $d$                  | $S(\text{error})^2$ |
|-------------|----------------------|----------------------|----------------------|---------------------|
|             |                      |                      |                      | 1.69 x              |
| COD         | 0.20                 | 1.00                 | $2.59 \cdot 10^{-3}$ |                     |
| Abs. 254 nm |                      | $1.92 \cdot 10^{-2}$ | $0.89 \cdot 10^{-5}$ | 6.97 x              |
| Abs. 410 nm | $3.24 \cdot 10^{-2}$ | 7.00                 | $1.99 \cdot 10^{-4}$ | 1.08 x              |

conjunction with urban wastewaters in a conventional treatment plant or reduced by biological methods. In this sense, it has to be pointed out that the biodegradability index in terms of  $BOD_5=COD$  increased up to a value in the interval 1.2-1.7. Likely the conspicuous removal of dissolved metals contributed to the increase of biodegradability. Thus, metals like Al, Cu, Cr, Fe, Mn, Co, Ni, Pb and Zn suffered a reduction ranging in the interval, 78%, 43%, 99.3%, 93.7%, 91%, 99.1%, 99.4%, 63% and 81.6%, respectively.

### 3.2.1. Kinetics of the adsorption onto Norit 0.8

The modified Lagergren equation used by Ho and McKay [33] was used to model the adsorption of leachates onto Norit 0.8. The applicable expression was

$$\ln[Q_e - Q_t] = \ln[Q_e] - k_{\text{Ads}}(t + t_0), \quad (13)$$

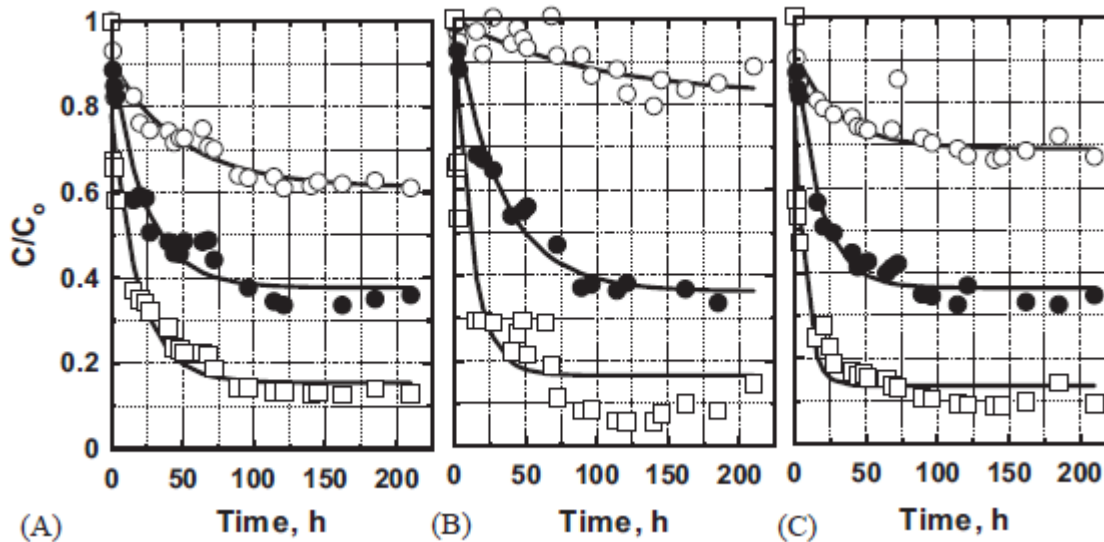


Fig. 10. Adsorption kinetics (A–COD, B–abs. 410 nm; C–abs. 254 nm) of pre-ozonated leachates onto Norit 0.8 Experimental conditions:  $COD_0 = 3.5 \text{ g L}^{-1}$  (average value); absorbance 254 nm = 0.8 after dilution 1:31 with ultrapure water; absorbance 410 nm = 0.8 after dilution 1:6 with ultrapure water. pH = 7.0; T = 20°C. Lines: Lagergren model. □, 30 g L<sup>-1</sup> AC; ●, 15 g L<sup>-1</sup> AC; ▲, 5 g L<sup>-1</sup> AC.

Table 6  
Lagergren equation parameters

| AC concentration (g L <sup>-1</sup> ) | COD                      |                    |       | Absorbance 410 nm        |                    |       | Absorbance 254 nm        |                 |       |
|---------------------------------------|--------------------------|--------------------|-------|--------------------------|--------------------|-------|--------------------------|-----------------|-------|
|                                       | $Q_e$                    | $k_{\text{Ads}}$   | $t_0$ | $Q_e$                    | $k_{\text{Ads}}$   | $t_0$ | $Q_e$                    | $k_{\text{Ad}}$ | $t_0$ |
|                                       | (g COD g <sup>-1</sup> ) | (h <sup>-1</sup> ) | (h)   | (g COD g <sup>-1</sup> ) | (h <sup>-1</sup> ) | (h)   | (g COD g <sup>-1</sup> ) | (s)             | (h)   |

|    | AC)   |      | AC)  |                        | AC)  |      | (h <sup>-1</sup> ) |
|----|-------|------|------|------------------------|------|------|--------------------|
|    |       | 0.02 | 13.2 |                        | 0.01 | 0.33 | 0.03 10.1          |
| 5  | 271   | 1    | 1    | 0.010                  | 1    | 3    | 0.050              |
| 15 | 140.3 | 0.04 | 3.41 |                        | 0.03 | 0.33 | 0.033              |
|    |       | 3    |      | 0.012                  | 1    | 3    | 8                  |
| 30 | 88.8  | 0.05 | 5.62 | 7.8 x 10 <sup>-3</sup> | 0.08 | 0.46 | 0.022              |
|    |       | 3    |      |                        | 2    | 4    | 0.14 2.19          |
|    |       |      |      |                        |      |      | 3                  |

where  $Q_e$  and  $Q_t$  are the concentration of the adsorbed species into the solid at equilibrium and time  $t$ ; respectively, and  $k_{Ads}$  and  $t_0$  adjustable parameters related to the kinetics of the process.

Fig. 10 shows the experimental and simulated results obtained from the model, the fitted parameters are also presented in Table 6. As observed, Eq. (13) adequately models the adsorption process in terms of COD and absorbance depletion. Values of  $Q_e$  obtained after the fitting process approximate to those obtained by using the isotherms of Fig. 9 and the operating line of slope the ratio liquid volume to activated carbon mass. Only values of  $Q_e$  obtained by both methods differ slightly when measuring absorbance at 254 nm: It is because even with the same dilution factor, the initial absorbance in isotherm experiments and kinetic experiments were also different, i.e. 0.6 and 0.8, respectively.

#### 4. Conclusions

Application of ozone to stabilised leachates results in a moderate reduction of the contaminant load. pH seems to exert no influence in the process. Moreover, other advanced oxidation processes tested does not contribute significantly to the COD reduction if compared to results of the single ozonation. The generation of oxygenated species involves a higher biodegradability of leachates; however the presence of dissolved metals impedes the adequate implementation of a biological stage. Adsorption of the ozonated leachate seems to be a plausible post-treatment since this technology is capable of both adsorbing the remaining organic material and metallic species present in solution. The low COD values achieved and high values of biodegradability allows for the use of a final biological step.

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