

# Stabilized leachates: sequential coagulation-flocculation + chemical oxidation process

F. Javier Rivas\*, Fernando Beltran, Fatima Carvalho, Benito Acedo, Olga Gimeno

Departamento de Ingeniería Química y Energética, Universidad de Extremadura, Av. Elvas S/N, Badajoz 06071, Spain

## Abstract

The combined sedimentation-chemical oxidation treatment of medium-stabilized landfill leachates has been investigated. The sequence of stages implemented was: (a) coagulation-flocculation by pH decrease (pH 2) to acidic conditions (COD removal 25% related to COD<sub>0</sub> 7500ppm); (b) coagulation-flocculation by Fe(III) addition (0.01 M) at pH 3.5 (COD removal 40% related to COD of supernatant after step (a)); (c) Fenton (Fe(III) = 0.01 M; H<sub>2</sub>O<sub>2</sub> = 1.0M) oxidation (COD removal 80% related to COD of supernatant after step (a)); and (d) coagulation-flocculation of Fenton's effluent at pH 3.5 (COD removal 90% related to COD of supernatant after step (a)). The use of Kynch theory allows for the design of clarifiers based on the amount of solids fed. For a general example of 1000 m<sup>3</sup> day<sup>-1</sup> of a feeding stream, clarifier area values of 286, 111 and 231 m<sup>2</sup> were calculated for compacting indices of 3.7, 2.67 and 2.83 corresponding to the first, second and third consecutive sedimentation processes, respectively, (steps (a), (b) and (d)).

Keywords: Leachate; Landfill; Coagulation-flocculation; Sedimentation; Fenton

## 1. Introduction

Leachates from municipal landfills are defined as the aqueous effluent generated as a consequence of rainwater percolation through wastes, chemical biological processes in waste's cells and the inherent water content of wastes themselves. The combination of the previous factors results in a dark effluent whose properties highly depend on the age of the landfill. Typically, old landfills produce leachates catalogued as stabilized and characterised by a relatively low chemical oxygen demand (COD) in the range 500-5000 ppm, slightly basic pH 7.5-8.5, low biodegradability (ratio BOD/COD below 0.1) and a significant amount of heavy metals and high molecular weight compounds (humic substances).

Given the toxic nature of stabilized leachates, these effluents are difficult to deal with and biological processes are totally inefficient. Therefore, alternative technologies based on physical-chemical stages are required.

Because of implementation and operation simplicity, coagulation-flocculation processes are widely used in drinking and wastewater treatment plants. Thus, precipitation of landfill leachates has been extensively studied in previous works. [Table 1](#) illustrates some investigations published in the specialised literature. As inferred from this table, the efficiency of the process depends on a number of factors such as coagulant nature and dose, leachate age, use of pre- or post-treatment stages, etc. Broadly speaking, due to the low efficiency and addition of hardness to the medium, the use of lime is not normally recommended [7]. Also, iron salts are preferred over aluminium salts.

In spite of the considerable bibliography focused on the coagulation-flocculation of landfill leachates, most of investigations are limited to the study of the effect of different operating variables on the final conversion achieved, measured in terms of COD, colour, TOC, etc. Strikingly, the technical feasibility of the coagulation-flocculation process is not

Table 1  
Coagulation–flocculation leachate treatment survey

Reference	Coagulant	Measured parameter	COD removal (%)	Notes
[1]	FeCl <sub>3</sub> or Al <sub>2</sub> SO <sub>4</sub> (concentration range 0.01–0.07 M)	Turbidity and COD	40–50	Stabilized leachate. Influence of pH, coagulant dose, polymer addition and H <sub>2</sub> O <sub>2</sub> oxidation.
[2]	FeSO <sub>4</sub> (0.3 g L <sup>-1</sup> of Fe)	COD and TOC	70	Young leachate. Precipitation after biological and Fenton oxidations.
[3]	Ca(OH) <sub>2</sub> (6 kg m <sup>-3</sup> )	COD, BOD, metals, etc.	57	Young leachate. Process with and without ammonia stripping. Influence of pH and temperature on metal removal. Economic study.
[4]	Ca(OH) <sub>2</sub> + Al <sub>2</sub> SO <sub>4</sub> (1.5 + 1.0 kg m <sup>-3</sup> )	COD and BOD	42	Stabilized leachate. Combination of biodegradation, chemical oxidation and precipitation.
[5]	FeCl <sub>3</sub> + Al <sub>2</sub> SO <sub>4</sub> (concentration range 0.1–1.0 g L <sup>-1</sup> )	COD, BOD, TOC, etc.	53	Stabilized leachate. Oxidation with ozone and Fenton. Biodegradation and adsorption onto activated carbon.
[6]	Ca(OH) <sub>2</sub> + FeSO <sub>4</sub> (concentration range 0.5–4.0 and 0.0–0.2 g L <sup>-1</sup> )	COD, BOD	39	Stabilized leachate. Influence of different coagulants.
[7]	FeCl <sub>3</sub> + Al <sub>2</sub> SO <sub>4</sub> (concentration range 1.0–5.0 g L <sup>-1</sup> )	COD, BOD, colour, etc.	75 (stabilized leachate)	Young and stabilized leachates. Efficiency of different coagulants with and without polyelectrolyte addition.
[8]	Struvite (Mg:NH <sub>4</sub> :PO <sub>4</sub> = 1:1:1)	COD, NH <sub>4</sub> <sup>+</sup> , TKN, colour, etc.	50	Young leachate. Efficacy of a membrane process. Economic study.
[9]	FeCl <sub>3</sub> ·6H <sub>2</sub> O (concentration range 0.1–1.0 g L <sup>-1</sup> )	COD, colour	24	Stabilized leachate. Efficacy of a photo-oxidation process.
[10]	FeCl <sub>3</sub> (concentration range 0.8–1.0 g L <sup>-1</sup> )	TOC	38–48 (TOC)	Stabilized leachate. Investigation by considering different fractions as a function of MW, Fenton reagent.
[11]	FeCl <sub>3</sub> (concentration range 0.2–1.2 g L <sup>-1</sup> )	COD	39	Stabilized leachate. Fenton reagent with sludge recycle.
[12]	FeSO <sub>4</sub> , FeCl <sub>2</sub> , FeCl <sub>3</sub> , Al <sub>2</sub> SO <sub>4</sub> (concentration range 40–200 mg L <sup>-1</sup> in metal base)	COD, TOC, BOD, etc.	50	Stabilized leachate. Adsorption onto activated carbon and ozone oxidation.

Table 2  
Landfill leachate characterisation. (units in mg L<sup>-1</sup> except metals in µg L<sup>-1</sup>)

Parameter	
COD	7400–8800
BOD <sub>5</sub>	475 ± 25
N-Kjeldahl	99.5 ± 5
Co	100
Cd	10
Cu	260
Cr	1200
Fe	7450
Mn	170
Ni	430
Pb	10
Zn	20

normally considered. Thus, aspects like sludge volume, settling velocity, solid's concentration, etc. are not usually taken into account. However, the aforementioned parameters are of paramount importance at the time of scaling-up and design of clarifiers.

Consequently, in this work, the flocculation-coagulation-oxidation of landfill leachates has been studied. Additionally, the process has been improved by implementing a pre-sedimentation stage by simple acidification. Based on Kynch's theory, the design of clarifiers has been conducted.

## 2. Experimental

### 2.1. Leachate characterization

Leachates were collected from the landfill site of Badajoz (South West of Spain). The main characteristics of this leachate are chemical oxygen demand in the range 7000–8000 mg L<sup>-1</sup>, biological oxygen demand after 5 days (BOD<sub>5</sub>) of 450 mg L<sup>-1</sup>, pH 8.5–9.0. Table 2 summarizes the rest of parameters analysed. From Table 2, it is observed that this leachate presents a relatively low value of COD and BOD<sub>5</sub>. The rate BOD<sub>5</sub>/COD situated in the proximity of 0.05 and pH above 7 indicate that this leachate may be defined as intermediate stabilized. As stated previously, this type of aged leachate is characterised by its refractory nature towards conventional biodegradation processes, necessitating, therefore, of an intensive and sophisticated physical-chemical process to meet the standards of quality set by the regulating authorities.

Coagulation-flocculation and further sedimentation experiments were carried out in a FC-4 SBS conventional jar-test apparatus equipped with four cylindrical beakers of 1 L of capacity. Agitation was mechanically implemented at 40 rpm by using an impeller with a 1 cm x 5 cm blade. Sedimentation experiments were conducted in 1 L capacity and 34 cm height standard graduated glass cylinders. Fenton's reagent oxidation runs were accomplished in 1 L glass recipients under magnetic stirring with no control either of pH or temperature.

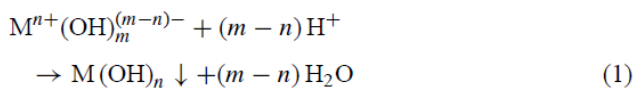
## 2.2. Analytical determinations

Leachates were characterised measuring the following parameters: chemical oxygen demand was determined in a Dr. Lange spectrophotometer, the method based on the standard dichromate reflux method [13]. Biological oxygen demand (BOD) was measured by following the respirometric method [14]. For this purpose, non-acclimated microorganisms from the municipal wastewater plant of the city of Badajoz were used. Total suspended solids (TSS) and volatile suspended solids (VSS) were obtained by following the standards methods [13]. Metals in leachates were determined by induced coupled plasma. Absorbance of samples at 254 and 410 nm after dilution were determined by means of a U2000 model HITACHI spectrophotometer.

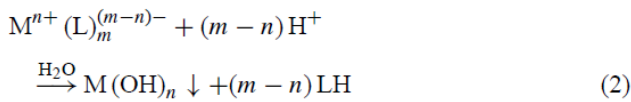
## 3. Results and discussion

### 3.1. Precipitation by simple acidification

From previous experiences [15], it is known that a decrease in leachate pH from 8 to 9 (initial pH) to values below four leads, after a short period of time to the formation of a precipitate that is finally settled down at the bottom of the containing recipient. The reason for the generation of this precipitate and its nature are out of the scope of this work, however, some basic explanations might account for these experimental facts. Thus, the existence of metallic species of amphoteric character according to:



The displacement of soluble complexes by insoluble oxides or hydroxides according to:



or likely, the existence of substances (i.e. humic substances) of different solubility depending on pH can be considered to account for the formation of the precipitate at low pH.

In any case, regardless of the acid precipitation mechanism, the best operating conditions were investigated by varying the value of the pH in the range 4.0 to 1.0. Fig. 1 illustrates some of the variable changes once the precipitation had been conducted. As inferred from this Fig. 1A, COD conversions in the range of 25% were experienced for final pH values below 3, with no appreciable effect in runs conducted at pHs 3 and 4 (although the precipitate was formed). Nevertheless, if the supernatant of the latter experiments (pHs 3 and 4) is acidified to pH values of 2 and 1 (notation pHs 4:2 and 3:1), respectively, similar results were obtained if compared to the process conducted in one unique step. Consequently, since no significant differences were found between the precipitation

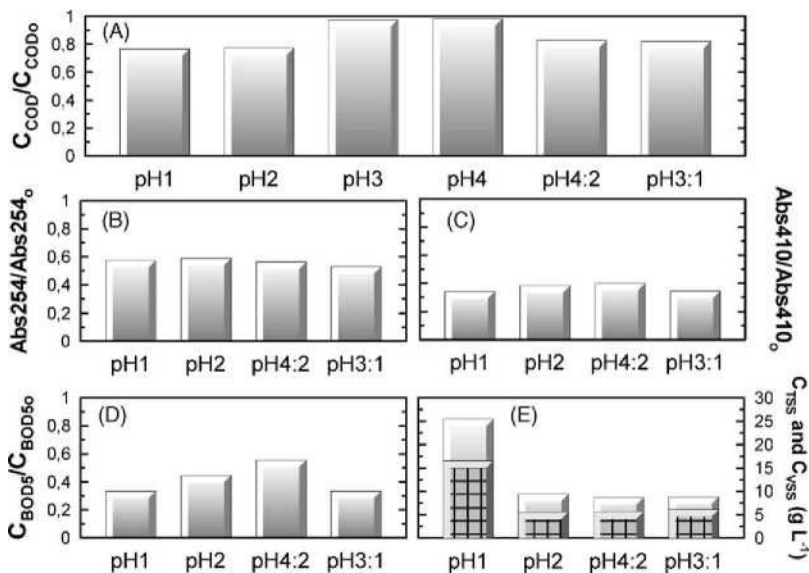


Fig. 1. Landfill leachate precipitation by acid pH. Experimental conditions: T = 20 °C; pH<sub>0</sub> 8.9; C<sub>COD0</sub> = 7500mgL<sup>-1</sup>; C<sub>BOD50</sub> = 450mgL<sup>-1</sup>; absorbance at 254nm(1:31 dilution) = 1.56; and absorbance at 410nm (1:6 dilution) = 0.985.

processes carried out at pHs 1 and 2 based on economic criteria (lower consumption of mineral acid), the latter value was taken as the optimum pH. Moreover, the settling velocity of the formed sludge was also similar,

regardless of the acid pH used (results not shown).

Fig. 2(A1) shows the sludge volume profile as a function of time for quadruplicated experiments carried out under similar conditions. Hence, the curve height-time (derived from the previous plot) can be fitted to the following model proposed by Renko and Sirvio [16]:

$$h(t, h_0) = \frac{\alpha X_0 h_0}{\beta} + \left[ h_0 - \frac{\alpha X_0 h_0}{\beta} \right] \exp\left(-\frac{\beta}{X_0 h_0} t\right) \quad (3)$$

Where  $t$  stands for time,  $h(t, h_0)$  is sludge height at time  $t$ ,  $h_0$  is initial sludge height;  $a$  and  $P$  are adjustable parameters for the sedimentation process and  $X_0$  is initial total solid concentration (TSS). Thus, from data taken from Fig. 2(A1) and the following initial conditions:  $h_0 = 34 \text{ cm}$  and  $X_0 = 1360 \text{ mgL}^{-1}$ ; the following values for the adjustable parameters were obtained:  $a = 0.154 \text{ cm min}^{-1}$  and  $P = 1.014 \text{ mgcmL}^{-1} \text{ min}^{-1}$  ( $R^2 \ll 0.99$ ).

Additionally, the solid concentration as a function of height can also be calculated from the following expression [17]:

$$X(t, h) = \frac{X_0 h_0}{h(t, h_0) - \left[ \alpha - (\beta / X_0 h_0) h(t, h_0) \right] t} \quad (4)$$

or from Kynch's theory by considering the corresponding correlation [18]:

$$X(h, t) = X_0 \frac{h_0}{h_i} \quad (5)$$

where  $h_i$  is the intercept in the Y-axis of the tangent plotted at the point of height  $h$  in the curve sludge height versus time.

Fig. 2(A2) depicts the  $X(h, t)$  profiles calculated by the two methods.

To proceed with the design of a suitable clarifier, two different criteria are considered, the volumetric flow rate of leachates fed to the clarifier ( $\text{m}^3 \text{ day}^{-1}$ ) or the solid flow rate fed to the clarifier per surface unit ( $\text{kgm}^{-2} \text{ day}^{-1}$ ). For effluents with a high content in solids ( $>500 \text{ ppm}$ ), the latter gives the minimum area needed for the clarifier.

The graphical method used for the design consists of a first representation of GB against X [18]. GB is the solid flow rate in the clarifier due to gravity and is given by:

$$G_B = X_j v_j \quad (6)$$

where  $v_j$  is the settling velocity corresponding to a sludge height of concentration  $X_j$ . The plot GB versus X for leachates treated at pH 2 is shown in Fig. 2(A3). A simple exponential correlation of the type  $GB = A_0 + K(1 - \exp(-rX))$  was used to fit experimental data (fitting parameters:  $A_0$ ,  $K$  and  $\tau$ ).

The design of a continuous clarifier depends on the compacting index,  $\gamma$ , a design variable set from the beginning. This parameter is defined as the ratio solid concentration in the concentrated sludge ( $X_U$ ) withdrawn from the clarifier to solid concentration fed ( $X_0$ ). Thus, if  $\gamma = 3.7$  ( $X_U = 5000 \text{ mgL}^{-1}$ ), the following step consists of plotting the tangent to the GB curve containing the point  $(5000, 0)$ , that is, intercepting the axis of abscissa at  $X = 5000 \text{ mgL}^{-1}$ . Now, the Y-axis intercept of this tangent gives the value  $G_T$ , which accounts for the global solid flow rate ( $G_T = G_B + G_u$ ) due to gravity (GB) plus the one due to the movement resulting from sludge outlet at the clarifier bottom ( $G_u$ ). For  $\gamma = 3.7$ , this value is approximately  $G_T = 4.75 \text{ kgm}^{-2} \text{ day}^{-1}$  (see Fig. 2(A3)).

The minimum area needed for the clarifier is given by  $AT = Q_0 X_0 / G_T$ , being  $Q_0$  the volumetric flow rate fed. Thus,

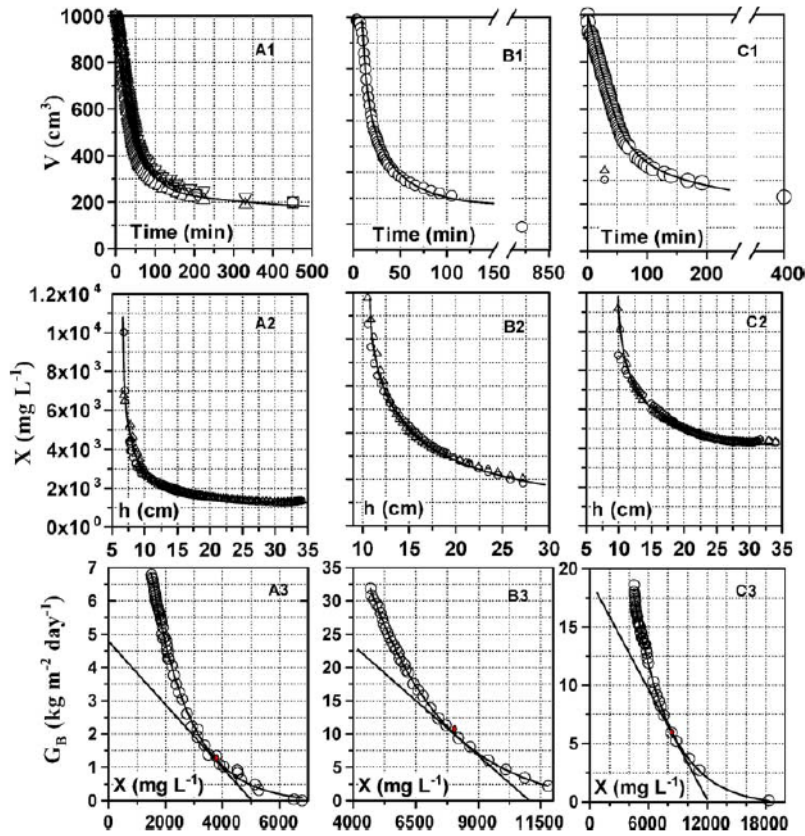


Fig. 2. Landfill leachate precipitation. (A) Precipitation by acidification (pH 2). (B) Precipitation in the presence of  $\text{Fe(III)} = 0.01 \text{ M}$  at pH 3.5. (C) Precipitation after Fenton's oxidation ( $\text{Fe(III)} = 0.01 \text{ M}$ ;  $\text{H}_2\text{O}_2 = 1.0 \text{ M}$ ) at pH 3.5. (1) Sludge settling velocity, (2) sludge concentration as a function of height. (3) Mass flow rate as a function of solid concentration. O, according to Eq. (3);  $\Delta$ , according to Eq. (4).

if  $Q_0$  is considered to be  $1000 \text{ m}^3 \text{ day}^{-1}$ ,  $A_T = 276 \text{ m}^2$ , that is, the diameter of a cylindrical clarifier should be 18.7 m, approximately. Fig. 3(A) illustrates the value of  $AT$  as a function of the compacting index for a generic value of  $Q_0 = 1000 \text{ m}^3 \text{ day}^{-1}$ .

As observed from Fig. 3,  $XU$  exerts a higher influence than  $X_0$ , exponentially increasing  $AT$  as  $XU$  is increased.

An attempt was made to improve the quality of the flocs by adding a commercial polyelectrolyte (A-201) to the media, however, no significant influence was appreciated either in the floc size or settling velocity of the sludge.

### 3.2. Precipitation with Fe(III)

Next to the acidic precipitation, the following phase to be implemented was a priori, to carry out the chemical oxidation stage. Due to the possibility of a post-oxidation precipitation step, the Fenton's process was chosen as the oxidising reagent. Moreover, given the similarities between  $\text{Fe(II)}$  and  $\text{Fe(III)}$  to treat landfill leachates by Fenton's reagent [19], ferric species instead of ferrous salts were used. Thus, after adding up a given amount of  $\text{Fe(III)}$  to the supernatant of the acidic precipitation, pH was adjusted to a value close to 3.0-3.5 (optimum Fenton's working pH). However, after a few minutes and before addition of  $\text{H}_2\text{O}_2$ , a new precipitate was formed. In the absence of appropriate ligands, formation of hydroxylated species of  $\text{Fe(III)}$  is expected even at this low pH.

Consequently, it was decided to study this new process by assessing the influence of  $\text{Fe(III)}$  dose. Fig. 4 shows the normalized remaining concentration of COD and absorbance reduction after precipitation at pH 3.5 in the presence of different amounts of  $\text{Fe(III)}$ . Normalization is determined regarding the COD of the supernatant of the previous stage instead of the raw leachate COD.

As observed from Fig. 4, in a parallel way to a higher sludge production, the COD removal slightly increases as the amount of  $\text{Fe(III)}$  added is raised from 0.005 to 0.08 M. Absorbance reduction at 254 nm is not appreciably affected by  $\text{Fe(III)}$  dosage. However, a negative influence is experienced for values of absorbance at 410 nm, likely due to a higher presence of dissolved  $\text{Fe(III)}$  in the supernatant after precipitate elimination.

### 3.3. Fenton's oxidation

The chemical oxidation stage was implemented by adding  $\text{Fe(III)}$  again to the supernatant of the previous iron pre-precipitation and concentrated hydrogen peroxide to achieve a value of 1.0 M in this reagent. In previous

experiments, it was observed how H<sub>2</sub>O<sub>2</sub> concentration exerted a positive effect up to values of roughly 1.0 M, a further increase of this concentration did not lead to proportional benefits.

Fig. 5A depicts the results obtained once the chemical oxidation was applied to the supernatant of the precipitation with

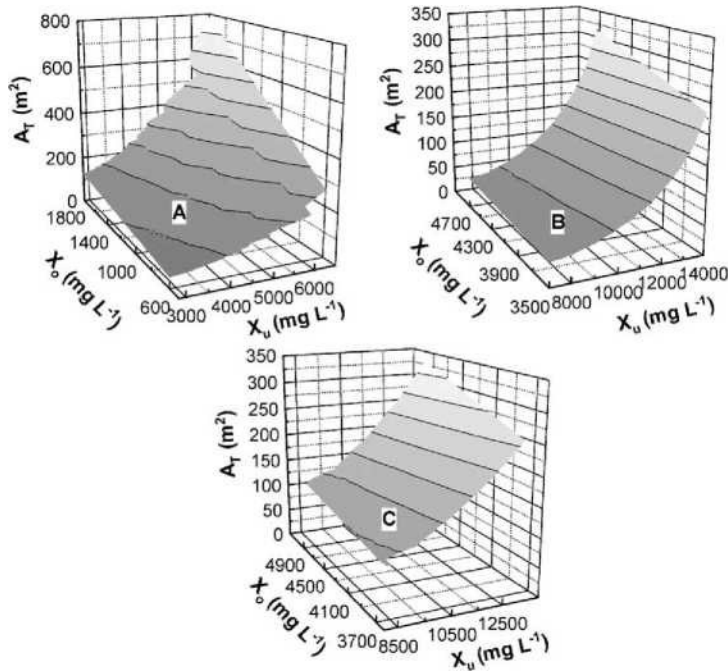


Fig. 3. Landfill leachate precipitation. Minimum clarifier area as a function of solid concentration at the inlet and outlet streams. (A) Precipitation by pH shift to 2. (B) Precipitation in the presence of Fe(III) = 0.01 M at pH 3.5. (C) Precipitation after Fenton oxidation (Fe(III) = 0.01 M; H<sub>2</sub>O<sub>2</sub> = 1.0 M) at pH 3.5.

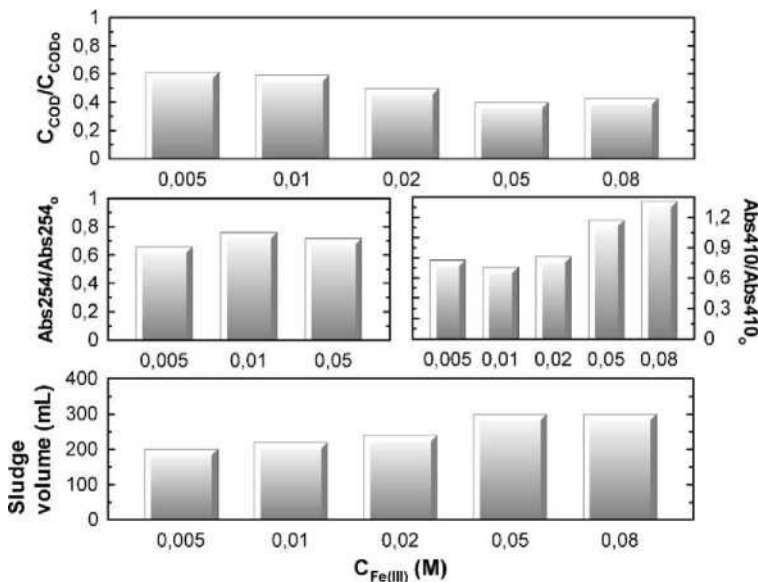


Fig. 4. Landfill leachate precipitation at pH 3.5. Experimental conditions: T = 20 °C; pH 2; C<sub>COD0</sub> = 5890 mg L<sup>-1</sup>; absorbance at 254 nm (1:51 dilution) = 0.760; and absorbance at 410 nm (1:11 dilution) = 0.290.

different amounts of Fe(III). Reductions figures are related to parameter values after precipitation at pH 2. As observed from Fig. 5A, COD removals approached an 80% regardless of the amount of Fe(III) used in the previous stage. The exception was experienced with the lowest amount of Fe(III) = 5 × 10<sup>-3</sup> M, in this case there was an increase of COD, undoubtedly due to the presence of unreacted H<sub>2</sub>O<sub>2</sub> not decomposed during the process.

### 3.4. Precipitation after Fenton's oxidation

Dissolved Fe(III) after Fenton's oxidation was removed by increasing the pH of the media. Three pH values were tested, for instance pHs 3.5, 5.5 and 7.0. Fig. 5B shows the final COD conversion obtained (related to the COD after acidic precipitation). As inferred from this figure, the final COD removal achieved was close to 90%, experiencing minimum

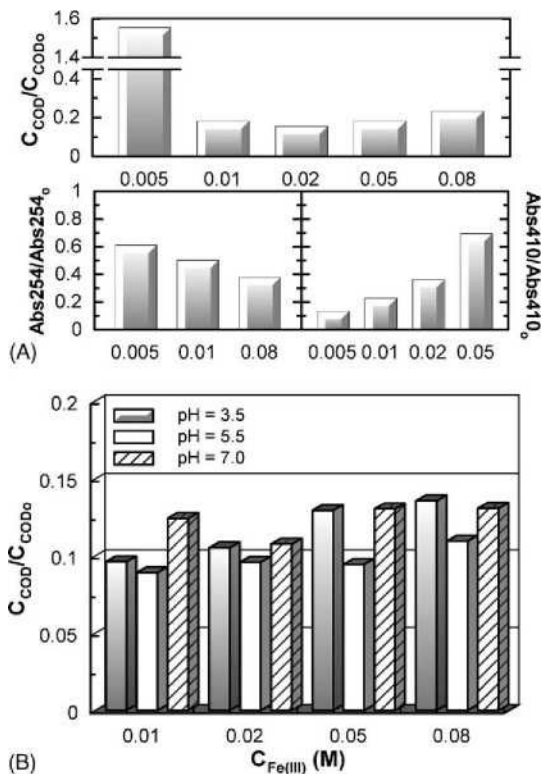


Fig. 5. (A) Landfill leachate oxidation ( $Fe(III) = 0.01$  M;  $H_2O_2 = 1.0$  M) after precipitation with  $Fe(III)$  at pH 3.5. Experimental conditions:  $T = 20$  °C;  $CCOD_0 = 3530$  mg L<sup>-1</sup>; absorbance at 254nm (1:51 dilution) = 0.760; and absorbance at 410 nm (1:11 dilution) = 0.290. Values related to parameters after acidic precipitation. (B)  $Fe(III)$  precipitation after Fenton's oxidation. Influence of precipitation pH. Experimental conditions:  $T=20$  °C and  $CCOD_0 = 1200$  mg L<sup>-1</sup>. Values related to parameters after acidic precipitation.

differences either in terms of  $Fe(III)$  used in the precipitation stage previous to the chemical oxidation or final pH used for the removal of  $Fe(III)$  after the oxidation.

As a consequence and taken into account economic (lower consumption of  $Fe(III)$ ) and operating criteria (lower sludge production) a concentration of  $Fe(III)$  of 0.01 M can be considered an appropriate value to be used in the second precipitation step.

Once the complete process was evaluated, the clarifier design was carried out for the  $Fe(III)$  precipitation before and after the chemical oxidation stage was implemented. Thus, in the first case (precipitation in the presence of  $Fe(III) = 0.01$  M at pH 3.5) the sludge settling velocity is shown in Fig. 2(B1), while Fig. 2(C1) corresponds to  $Fe(III)$  precipitation after Fenton's oxidation ( $Fe(III) = 0.01$  M;  $H_2O_2 = 1.0$  M).

By using Eq. (3) and the initial conditions  $h_0 = 34$  cm,  $X_0 = 4124$  mg L<sup>-1</sup> (TSS before oxidation) and  $X_0 = 4320$  mg L<sup>-1</sup> (TSS after oxidation), the values of the adjustable parameters were obtained:  $a = 0.411$  cm min<sup>-1</sup>;  $P = 5798$  mg cm L<sup>-1</sup> min<sup>-1</sup> and  $a = 0.132$  cm min<sup>-1</sup>;  $P = 2504$  mg cm L<sup>-1</sup> min<sup>-1</sup>, for curves derived from Fig. 2(B1) and (C1), respectively. With the previous values of  $a$  and  $P$  and Eq. (4), the GB profiles as a function of solid concentration are shown in Fig. 2(B3) and (C3) for precipitation experiments before and after conducting the chemical oxidation.

As an example, the value of AT was calculated for compacting indices of 2.67 ( $XU = 11000$  mg L<sup>-1</sup>) and 2.83 ( $XU = 12250$  mg L<sup>-1</sup>) corresponding to precipitation experiments before and after Fenton's implementation, respectively. The calculated AT values were 111 and 231 m<sup>2</sup> ( $Q_0 = 1000$  m<sup>3</sup> day<sup>-1</sup>).

Fig. 3(B) and (C) show the minimum clarifier area determined as a function of solid concentration at the inlet and outlet streams. As expected, AT highly depends on XU being higher as XU is increased.

### 3.5. Comparison of the chosen sequence performance to a modified working route

Finally, to ascertain if the procedure adopted was optimized if compared to an alternative route of operation, it was

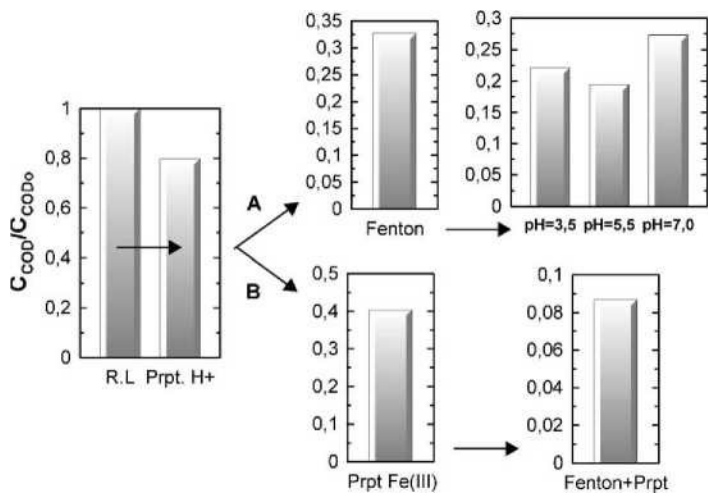


Fig. 6. Landfill leachate treatment by coagulation-flocculation + precipitation. Comparison of treatment sequences. Route A: precipitation at pH 2 + Fenton oxidation (Fe(III) = 0.02 M; H<sub>2</sub>O<sub>2</sub> = 1.0M) + Precipitation at pHs 3.5, 5.5 and 7.0. RouteB: precipitation at pH 2 + precipitation with Fe(III) = 0.01M pH 3.5 + Fenton oxidation (Fe(III) = 0.01 M; H<sub>2</sub>O<sub>2</sub> = 1.0 M) + Precipitation at pH 3.5. Experimental conditions: T =20 °C and C<sub>cod0</sub> = 7390mgL<sup>-1</sup>.

decided to conduct a new experimental series by eliminating the second precipitation stage (precipitation with Fe(III) = 0.01 M at pH 3.5) and directly implement the chemical oxidation step after the acidic precipitation.

Thus, for comparative purposes, the concentration of Fe(III) used in the Fenton's reaction was doubled to 0.02 M. Again the final Fe(III) removal was carried out at three different pHs. The results in terms of COD depletion related to the raw leachate (R.L.) are shown in Fig. 6. As observed from this figure, if the precipitation with Fe(III) previous to Fenton's oxidation is eliminated, the final COD conversion attained approaches 75-80% if compared to >90% achieved when this stage is added.

#### 4. Conclusions

From this work, the following conclusions are withdrawn:

- A pH drop below 4 involves the formation of a precipitate. A maximum 25% in COD removal is achieved for values lower than 3.
- A new precipitation of the previous acidic supernatant with Fe(III) at pH 3.5 leads to a further COD elimination in the interval 40-60% depending on the Fe(III) concentration used.
- Oxidation with Fenton's reagent followed by precipitation of dissolved Fe(III) results in a >90% final COD conversion regarding the COD content after the acid precipitation.
- By using Kynch's theory, the clarifier design corresponding to the different precipitation stages can be conducted.
- Additionally given the low COD removal experienced after precipitation of Fe(III) once the oxidation has taken place, it is likely that sludge composition is mainly due to hydroxylated species of Fe(III). These sludges can, therefore, be re-dissolved and recycled to the oxidation step with the subsequent savings in reactants.

#### Acknowledgements

Authors thank the economic support received from Junta de Extremadura and European Social Funds through project IPR00-A002.

#### References

- [1] A. Amokrane, C. Comel, J. Veron, Landfill leachates pretreatment by coagulation-flocculation, *Water Res.* 31 (1997) 2775.
- [2] P. Wang, I. Lau, H. Fang, D. Zhou, Landfill leachate treatment with combined UASB and Fenton coagulation, *J. Environ. Sci. Health A35* (2000) 1981.
- [3] J. Keenan, R. Steiner, A. Fungaroli, Chemical-physical leachate treatment, *J. Environ. Eng.* 109 (1983) 1371.
- [4] A. Papadopoulos, D. Fatta, M. Loizidou, Treatment of stabilized landfill leachate by physico-chemical and bio-oxidation processes, *J. Environ. Sci. Health A33* (1998) 651.
- [5] U. Welander, T. Henrysson, Physical and chemical treatment of a nitrified leachate from a municipal landfill, *Environ. Technol.* 19 (1998) 591.
- [6] M. Loizidou, N. Vithoulkas, E. Kapetanios, Physico-chemical treatment of leachate from landfill, *J. Environ. Sci. Health A27* (1992) 1059.
- [7] A. Tatsi, A.I. Zouboulis, K.A. Matis, P. Samaras, Coagulation- flocculation pre-treatment of sanitary landfill



leachates, *Chemosphere* 53 (2003) 737.

- [8] I. Ozturk, M. Altinbas, I. Koyuncu, O. Arikan, C. Gomec-Yangin, Advanced physico-chemical treatment experiences on young municipal landfill leachates, *Waste Manag.* 23 (2003) 441.
- [9] Z. Wang, Z. Zhang, Y. Lin, N. Deng, T. Tao, K. Zhuo, Landfill leachate treatment by a coagulation-photooxidation process, *J. Haz-ard. Mater.* B95 (2003) 153.
- [10] J. Yoon, S. Cho, Y. Cho, S. Kim, The characteristics of coagulation of Fenton reaction in the removal of landfill leachate organics, *Water Sci. Technol.* 38 (1998) 209.
- [11] H. Yoo, S. Cho, S. Ko, Modification of coagulation and Fenton oxidation processes for cost-effective leachate treatment, *J. Environ. Sci. Health A36* (2001) 39.
- [12] K. Takamizawa, I. Fukunaga, O. Yamamoto, Z. Inoue, A. Honda, Tertiary treatment of leachate from a sea-based solid waste disposal site, *Environ. Technol.* 12 (1991) 117.
- [13] AOAC, Official Methods of Analysis of the Association of Official Analytical Chemistry, Horwitz W, Arlington, US, 1984.
- [14] J.L. Means, S.J. Anderson, Comparison of five different methods for measuring biodegradability in aqueous environments, *Water Air Soil Poll.* 16 (1981) 301.
- [15] F.J. Rivas, F.J. Beltran, O. Gimeno, B. Acedo, F. Carvalho, Stabilized leachates: ozone-activated carbon treatment and kinetics, *Water Res.* 37 (2003) 4823.
- [16] E. Renko, H. Sirvio, Optimal sampling design for a sludge blanket interface settling model, *Water Res.* 31 (1997) 1148.
- [17] E. Renko, Modelling hindered batch settling part II: a model for computing solids profile of calcium carbonate slurry, *Water SA* 24 (1998) 331.
- [18] R.S. Ramalho, *Tratamiento De Aguas Residuales*, Reverte, Barcelona, 1996.
- [19] F.J. Rivas, F.J. Beltran, O. Gimeno, F. Carvalho, Fenton like oxidation of landfill leachates, *J. Environ. Sci. Health Part A A38* (2003) 371.

This is a post-peer-review version of an article published in *Journal of Hazardous Materials*, 2004 following peer review. The version of record Javier Rivas, F., Beltrán, F., Carvalho, F., Acedo, B. & Gimeno, O. (2004). Stabilized leachates: Sequential coagulation–flocculation + chemical oxidation process. *Journal of Hazardous Materials*, 116(1-3), 95–102. <https://doi.org/10.1016/j.jhazmat.2004.07.022>