

Treatment of Sanitary Landfill Leachate by Photo-Fenton Process: Effect of the Matrix Composition

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In this study it was evaluated the role of the composition of sanitary landfill leachate on the removal of dissolved organic carbon (DOC) by photo-Fenton process. The composition of the matrix (high turbidity and color, as well as presence of inorganic ions sulfate and chloride) does not reduce the efficiency of DOC removal by photo-Fenton reactions, but influences significantly the reaction time and consumption of H₂O₂. An expressive increase in the efficiency of DOC removal occurred for concentrations of Fe²⁺ between 50 and 100 mg L⁻¹, remaining constant in the range between 100 and 200 mg L⁻¹. On the other hand, the pre-treatment of this effluent by coagulation-flocculation before the photo-Fenton process is recommended, since a similar efficiency of DOC removal, between 70 and 77%, was achieved using only 17% of the time and 7% of H₂O₂ necessary for the treatment of raw leachate treatment.

Keywords: advanced oxidation process, operational parameter, chloride, sulfate, mineralization

Introduction

The population growth brought as one of its main consequences the generation of municipal solid waste (MSW), which constitutes as a major environmental, economic and social problem worldwide. In general, the worldwide average production of MSW capita is 1.2 kg *per day*.¹ Based on these values, considering the current world population, and that 1 ton of MSW produces 0.2 m³ of landfill leachate, an increasing amount of at least 614 million m³ of leachate is produced each year.² Besides, the biological processes are ineffective for the treatment of this type of effluent, what causes great concern.

Landfill leachate is a material highly recalcitrant to degradation, with a complex composition, consisting mainly of a large amount of organic matter, ammonia, inorganic ions (chloride, sulfate, etc.), heavy metals and toxic compounds, possessing therefore acute and chronic toxicity. Studies have identified the presence of more than 200 compounds in municipal landfill leachates,^{3,4} being 35 of them with potential toxicity to human health and environment.^{3,5} This high toxicity has also been reported in studies involving the use of bacteria, crustaceans and fishes.⁶⁻¹¹

Advanced oxidation processes (AOPs) are suitable alternatives for the treatment of toxic and refractory compounds, since the hydroxyl radicals (HO•) generated degrade the organic matter with efficiency and in a non-selective way, converting it into carbon dioxide, water and inorganic ions.¹²⁻¹⁴ With respect to the treatment of leachate, among the AOPs, special attention has been given to heterogeneous photocatalysis and photo-Fenton process due to the low cost of these processes, efficiency, and possibility of using sunlight as radiation source. On the other hand, the photo-Fenton process was chosen to be employed in this work, considering its effectiveness in the treatment of different types of effluents, including landfill leachate,¹⁵ compared to heterogeneous photocatalysis.¹⁵⁻¹⁷

However, a combination of different processes may be the better option to treat this kind of effluent, due to its complex composition, i.e., dark color and presence of suspended solids, which affect the efficiency of an essentially photochemical treatment.

The combination of coagulation and flocculation, using salts of aluminum and iron as coagulants is a good alternative for removal of waste materials in suspended or colloidal form, contributing to the reduction of color and turbidity of the landfill leachate.^{18,19} Although studies have proposed the application of coagulation-flocculation as an alternative to the treatment of sanitary landfill leachate,¹⁸⁻²⁵

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additional studies are still needed in order to evaluate the better combination between type and dosage of these coagulants, considering the complexity of this matrix.

The main reasons for combining chemical coagulation-flocculation and photo-Fenton process are: (i) the coagulation-flocculation process is efficient for the removal of turbidity and color, but not the organic load;²¹ (ii) the photo-Fenton process is efficient in the degradation of the organic matter, but is strongly influenced by the suspended solids and dark color, once these parameters hinder the access of light to the reaction medium.²⁶⁻²⁸ Besides, the presence of inorganic ions, such as chloride, sulfate, among others, can affect the efficiency of the photo-Fenton process.²⁸⁻³¹ So, alternatives to remove the suspended solids and dark color (coagulation-flocculation) or chloride and sulfate ions (precipitation using the appropriate counter ions such as Ag^+ and Ba^{2+}), need to be evaluated. The combination of these processes may have a synergistic effect during the treatment of landfill leachate.

The first objective of this work was to evaluate the photo-Fenton process as an alternative to degrade the organic matter present in the raw sanitary landfill leachate. Secondly, to verify the role of the components of the matrix (turbidity, apparent color and inorganic ions-chloride and sulfate) on the removal of the organic matter, assessing the potential application of a coupled coagulation-flocculation/photo-Fenton process, or the isolated or combined chloride and/or sulfate removal/photo-Fenton as effective treatments, in terms of efficiency, treatment time and consumption of H_2O_2 .

Experimental

Reagents

All solutions, except the landfill leachate, were prepared with distilled water.

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Vetec) was used to prepare a 14 g L^{-1} Fe^{2+} stock solution in H_2SO_4 3.0 mol L^{-1} . H_2O_2 (30% m/m), NH_4VO_3 , Na_2SO_3 , all from Vetec, AgNO_3 (Synth) and $\text{Ba}(\text{NO}_3)_2$ (Nuclear), were used as received. Aqueous solutions of H_2SO_4 and NaOH (Vetec) were used for pH adjustments. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (F. Marques de Sá) and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (Proquimios) were used in the coagulation-flocculation tests.

Sampling of the sanitary landfill leachate

The leachate under study was collected in a municipal landfill located in the city of Uberlândia, Minas Gerais, Brazil. This landfill is in activity since 2010, receiving

approximately 490 ton of household wastes *per day*. Samples of 50 L of the leachate were collected directly from a collection box at the exit of the landfill cell, just before to be mixed in the sewage treatment plant of the domestic effluent. The sampling of the leachate was done using plastic bottles, followed by pH adjustment close to 3, using H_2SO_4 , to preserve the landfill leachate, as suggested by the Standard Methods³² and refrigerated at $4 \text{ }^\circ\text{C}$ until use. The option for the use of sulfuric acid was based on studies that highlight the advantage of its use rather than HCl or of the mixture $\text{HCl}/\text{H}_2\text{SO}_4$.^{28,30} The main chemical-physical characteristics of the landfill leachate collected were quantified.

Experiments using the photo-Fenton process

The experiments were done at lab scale using two 10 W black light lamps as radiation source. The lamps were positioned in parallel (separated by a distance of 3.5 cm) and at 1 cm of the top of a square container with 0.13 m side, made of dark glass, with 5.5 cm deep (volume and surface area of, respectively, 0.8 L and 0.016 m^2). This container was filled with the leachate, resulting in a depth of 5 cm. The irradiance was measured using a radiometer PMA 2100 Solar Light Co. in the UVA (320-400 nm), with the sensor placed at the same angle and distance defined for the incidence of radiation in the reactor, being obtained at the surface of the effluent an irradiance of 35 W m^{-2} .

A total volume of 800 mL of the landfill leachate was irradiated immediately after addition of the solution containing Fe^{2+} , pH adjustment to 2.5-2.8 (with further adjustment), and addition of H_2O_2 .

Three set of assays were done using this system: (i) the effect of Fe^{2+} concentration (50, 100 and 200 mg L^{-1}) on the removal of dissolved organic carbon (DOC) and H_2O_2 consumption, during 20 hours of exposition of the raw landfill leachate. The levels of Fe^{2+} used in this study were based on previous studies.^{15,26} The concentration of H_2O_2 was maintained in excess, between 200 and 2000 mg L^{-1} during the experiment, by adding more of this additive to compensate its consumption, as indicated by the analyses performed throughout the experiments; (ii) experiments carried out under the best condition obtained in step (i) (using $100 \text{ mg L}^{-1} \text{ Fe}^{2+}$), applied to the landfill leachate after pre-treatment with $240 \text{ mg L}^{-1} \text{ Fe}^{3+}$, at pH 3; (iii) effect of chloride and sulfate ions (isolated or integrated) during the photo-Fenton reactions, applied to the raw effluent, under the best concentration of Fe^{2+} (100 mg L^{-1}). The chloride and sulfate ions were precipitated using, respectively, AgNO_3 and $\text{Ba}(\text{NO}_3)_2$, according to the stoichiometry of the respective reactions and number of moles of the ions.

After sampling and before all analyses, an excess of $1.0 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_3$ solution was added to the samples (except in H_2O_2 and iron analyses), according to the stoichiometry between H_2O_2 and Na_2SO_3 , and the number of moles of the remaining H_2O_2 , to ensure the removal of the residual H_2O_2 , interrupting the Fenton reactions. Further, the pH was adjusted between 6 and 8, inducing iron precipitation, followed by filtration through membranes with mean pore size of $0.45 \mu\text{m}$.

Treatment by coagulation-flocculation

Before integration between the coagulation-flocculation and photo-Fenton treatment of landfill leachate, experiments at lab-scale were performed at pH 3, to evaluate the action of the coagulants FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$, represented by simplicity as Fe^{3+} and Al^{3+} ion concentration. This pH value was used since H_2SO_4 was added to preserve the landfill leachate after its sampling, as recommended by a Standard Method³² and literature.^{28,30} The effect of dosage of coagulant ion (5, 15, 30, 60, 120, 240, 480 and 960 mg L^{-1} , equivalent to 0.09, 0.27, 0.54, 1.1, 2.14, 4.28, 8.57 and 17.1 mmol L^{-1} of Fe^{3+} and 0.2, 0.56, 1.1, 2.2, 4.44, 8.89, 17.8 and 35.6 mmol L^{-1} of Al^{3+}) was evaluated monitoring the removal of turbidity, apparent color and DOC. The concentration of coagulant ion was defined on the basis in the literature¹⁹ and studies performed in our research group.³³ The experiments were carried out using beakers containing 50 mL of the landfill leachate. After the addition of coagulant, the solution was maintained under magnetic stirring at 120 rpm during 5 min, for coagulation. After, the stirring rate was reduced to 20 rpm being maintained for 20 min for flocculation. Finally, the stirring was turned off, for sedimentation of the flocculate. For this it was established a 60 minutes interval. The supernatant was withdrawn from a point located about 1.5-2.0 cm below the top of the liquid level and submitted to analyses.

Chemical analyses and bioassays

Turbidity, pH and the apparent color at 465 nm were measured using, respectively, a turbidimeter 2100Q (Hach), a pH meter (Bel Engineering), and a spectrophotometer (Shimadzu UV 1800), after calibration with standard solutions.

DOC was measured using a total organic carbon (TOC) analyzer (Shimadzu TOC-VCPH/CPN) equipped with an ASI-V autosampler. The quantification limit (LOQ) of the equipment was 0.22 mmol L^{-1} (2.7 mg L^{-1}). Chemical oxygen demand (COD) determinations were carried out

according to the Standard Method 5220D³² being the LOQ equal 0.42 mmol L^{-1} (13 mg L^{-1}). Biochemical oxygen demand (BOD_5) measurements were performed following the Standard Method 5210D³² using an Oxitop IS-6 WTW and a BOD incubator (TE-371 Model-TECNAL) to keep the temperature at $20 \text{ }^\circ\text{C}$. The LOQ estimated for this measurement was 0.16 mmol L^{-1} (5.1 mg L^{-1}).

The H_2O_2 concentration was determined photometrically using a method proposed by Nogueira *et al.*,³⁴ which presents a LOQ of 0.36 mmol L^{-1} (11 mg L^{-1}). The concentration of total dissolved iron, after reduction with hydroxylamine, was determined directly via methodology based on the reaction between Fe^{2+} and 1,10-phenantroline, which presents a detection limit (LOD) of $0.77 \mu\text{mol L}^{-1}$ (0.043 mg L^{-1}).³²

The concentration of total solids, suspended solids, dissolved solids, total nitrogen, ammoniacal nitrogen, sulfate and total phosphorus were quantified according to the respective Standard Methods,³² and chloride by Mohr method. For total or ammoniacal nitrogen the determination procedure involves distillation and titration when the concentration of nitrogen is greater than 5 mg L^{-1} . The LOQ for the turbidimetric method for sulfate is 0.10 mmol L^{-1} (9.6 mg L^{-1}), while for total phosphorus the LOD is $10 \mu\text{mol L}^{-1}$ (0.32 mg L^{-1}).

Results and Discussion

Landfill leachate

The main chemical-physical characteristics of the sanitary landfill leachate, before and after pH adjustment with H_2SO_4 , are summarized in Table 1.

The sampled leachate at natural pH (7.8) exhibited a BOD_5/COD ratio of 0.58, consistent with a biodegradable material (Table 1).^{35,36} However, after pH adjustment close to 3, a decrease in the BOD_5/COD ratio to 0.35 was obtained, indicating a sample with poor biodegradability (Table 1).^{35,36} This result can be associated with the preferential precipitation (50%) of the biodegradable components, since the BOD_5 value decreased from 2,211 to 1,090 $\text{mg O}_2 \text{ L}^{-1}$. A significant decrease in the DOC and COD values (31 and 22%, respectively) was also achieved before and after the acidification step (Table 1).

In contrast, there was an increase in the values of apparent color, turbidity and suspended solids after acidification (Table 1). This is associated to the humic substances, composed by humin, humic and fulvic acids. The humin is insoluble in water at any pH, while fulvic acids are soluble in water at all pH conditions, being responsible by the bright yellow or brownish-yellow color.³⁷ On the

other hand, the solubility of humic acids (responsible by the brownish color) is strongly pH-dependent, being insoluble at $\text{pH} < 2$.^{2,37,38} The difference of solubility between humic and fulvic acids is due to their elemental composition, content of functional groups, interval of molar mass, etc. The average elemental composition of fulvic acids extracted from water is 55.03% C, 5.24% H, 36.08% O, 1.42% N and 2.00% S, while for humic acids is 54.99% C, 4.84% H, 33.64% O, 2.24% N and 1.51% S.¹ So, the higher the levels of oxygen, the greater the concentration of functional groups, making them more hydrophilic. Besides, the greatest concentration of oxygenated groups makes them more acidic, favoring the complexation of metal species. Therefore, during the acidification step, most of the humic acids end up precipitating, justifying the increasing in the apparent color, turbidity and suspended solids (Table 1). In addition, a pronounced increase (from < 10 to $6,741 \text{ mg L}^{-1}$) in sulfate concentration occurred as consequence of the step of acidification (Table 1). The increase in the amount of total and dissolved solids is justified by the addition of H_2SO_4 .

Table 1. Characterization of the sanitary landfill leachate before and after pH adjustment using H_2SO_4

Parameter	Value	
	Before	After
pH	7.8	3.0
Apparent color / ($\text{mg L}^{-1} \text{ Pt/Co}$)	4,100	5,064
Turbidity / NTU	149	410
Suspended solids / (mg L^{-1})	163	237
Dissolved solids / (mg L^{-1})	7,630	9,743
Total solids / (mg L^{-1})	8,144	10,223
DOC / (mg C L^{-1})	981	679
COD / ($\text{mg O}_2 \text{ L}^{-1}$)	3,965	3,085
BOD ₅ / ($\text{mg O}_2 \text{ L}^{-1}$)	2,211	1,090
BOD ₅ /COD	0.58	0.35
Chloride / (mg L^{-1})	2,651	2,074
Total nitrogen / (mg L^{-1})	915	n.d.
Ammoniacal nitrogen / (mg L^{-1})	776	n.d.
Sulfate / (mg L^{-1})	$< 10^a$	6,741
Total phosphorus / (mg L^{-1})	7.5	5.7
Total dissolved iron / (mg L^{-1})	n.d.	20.5

^aLimit of quantification = 10 mg L^{-1} ; n.d. = not determined.

Treatment using the photo-Fenton process

Influence of Fe^{2+} concentration

Since it is known that an excess of Fe^{2+} in the Fenton reactions tends to compromise the degradation efficiency^{15,39-41} since it can compete with the organic matter by HO^\bullet or act as a radiation filter,^{39,40} the appropriate

concentration of this reactive needs to be defined for the treatment of landfill leachate by the photo-Fenton process.

Figure 1 presents the DOC removal of raw leachate by photo-Fenton process, using three different concentrations of Fe^{2+} (50, 100 and 200 mg L^{-1}).

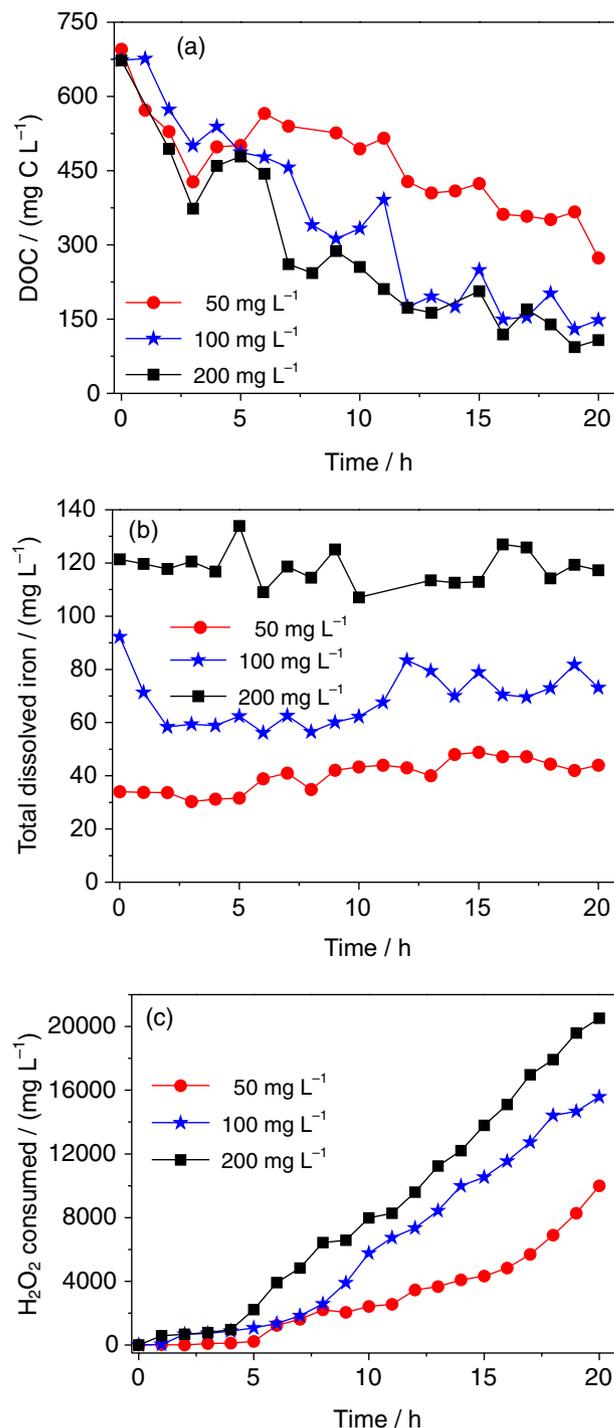


Figure 1. Effect of Fe^{2+} concentration on (a) DOC removal; (b) concentration of total dissolved iron; (c) H_2O_2 consumption, during the raw landfill leachate treatment by the photo-Fenton process. Initial conditions: $\text{DOC} = 680 \pm 13 \text{ mg C L}^{-1}$; $\text{H}_2\text{O}_2 = 2000 \text{ mg L}^{-1}$ (replaced when close to 200 mg L^{-1}); $\text{pH} = 2.5\text{-}2.8$.

Figure 1 shows a fast decay of DOC concentration during the first three hours of reaction, followed by an increase up to 5-7 hours. It is probable that the initial high rate of DOC removal occurred due to the simultaneous acidification and coagulation-flocculation, and in a minor extension by the photo-Fenton process. Although, after sampling, the pH of the landfill leachate was adjusted close to 3, a new adjust was necessary to fix the pH in the range between 2.5 and 2.8, to favor the photo-Fenton process. As is well known, the solubility of humic acids is reduced when the pH of the solution decreases.^{2,15,19,28,38} As shown in Table 1, a decrease of 31% was observed in the step of acidification. Similar behavior was obtained by Amor *et al.*,¹⁹ a reduction of about 42% in DOC of a leachate sample when the pH was decreased to around 3. In addition, it is expected a contribution of the coagulation-flocculation process for removal of the humic acids, since the initial concentration of total dissolved iron was approximately 23-51% lower than the theoretical values (Figure 1b), considering the content of dissolved iron in the leachate (20.5 mg L⁻¹) (Table 1). In general, the concentration of dissolved iron is the sum of these 20.5 mg L⁻¹ of iron ions naturally found in the raw leachate with the amount added. These concentrations of dissolved iron available during the photo-Fenton process is always lower than the values previously defined (50, 100 and 200 mg L⁻¹). In our experiments, for example, the average concentrations determined during the 20 h of experiment (Figure 1b) were, respectively, 40.2 ± 6.0, 68.9 ± 10.0 and 118.3 ± 6.5 mg L⁻¹. The decrease in the concentration of iron can also be due to its complexation with fulvic acids as well as by chloride and sulfate ions.^{28,30,31,42} The low effectiveness of the photo-Fenton process in the first 3 hours can be evidenced by the low consumption of hydrogen peroxide (Figure 1c). From 3 up to 5-7 hours, the degradation of the insoluble humic acids should be probably occurring, which tends to increase the amount of DOC (Figure 1a). From this point, the photo-Fenton reactions are prevalent since a considerable consumption of DOC, combined with a higher consumption of H₂O₂, was observed (Figures 1a and 1c).

Doubling the concentration of Fe²⁺ from 50 to 100 mg L⁻¹, the DOC consumption was favored (Figure 1a). On the other hand, duplicating it to 200 mg L⁻¹, no improvement was observed (Figure 1a), suggesting that an iron concentration of 100 mg L⁻¹ can be enough to trigger efficiently the photocatalytic process. So, it can be affirmed that using 100 mg L⁻¹ Fe²⁺, the photocatalytic regeneration of ferrous ions from ferric should be fast enough (Figure 1b), ensuring the availability of ferrous ions to produce more hydroxyl radicals from H₂O₂ consumption. These results are in agreement with the reported in other

studies.^{15,26} In addition, it is known that an excess of iron tends to compete with the organic matter by the hydroxyl radicals.^{39,40} The higher consumption of H₂O₂ observed in the presence of 200 mg L⁻¹ when compared to the results obtained using 100 mg L⁻¹ (consumption of H₂O₂ and DOC) evidence this (Figure 1c). Additionally, the excess of iron ions tends to increase the turbidity, limiting the access of light into the reaction medium and therefore compromising the regeneration of ferrous ions. As mentioned above, due to complexation reactions and precipitations, an initial concentration of 100 mg L⁻¹, corresponds to a concentration of (68.9 ± 10.0) mg L⁻¹ of iron in solution, during the photo-Fenton process, is enough to promote efficiently the treatment of the raw leachate. This result agree with the reported by Rocha *et al.*¹⁵ where the best DOC removal was reached starting with an initial iron concentration of 60 mg L⁻¹. It is important to emphasize that the experimental setup used in this work is different from the used by Rocha *et al.*,¹⁵ although the same path length (5 cm) is verified in both cases, which justifies the results obtained.

Influence of chloride and sulfate ions and coupling of the treatments

Considering the complexity of the matrix studied, it is important to evaluate the effect of its composition³¹ on the efficiency of the treatment, time and consumption of H₂O₂ during the photo-Fenton treatment. Therefore, the possibility of coupling between processes, such the coagulation-flocculation and photo-Fenton treatment, or the isolated or integrated removal of chloride/sulfate combined with a photo-Fenton process were evaluated as alternatives of treatment to this effluent.

Operational parameters such as the type and dosage of the coagulant, time of treatment, pH, rate of stirring and presence of inorganic and organic substances, can influence the efficiency of the treatment based on coagulation-flocculation, and therefore its role needs to be evaluated.¹⁹ In this study the type and dosage of the coagulant were evaluated, once that after sampling the initial pH was adjusted to close 3 with H₂SO₄, as suggested by Standard Methods³² and literature.^{28,30}

Analyzing the Figure 2, it can be observed that the type of coagulant ion influences strongly the removal of the apparent color and turbidity, parameters that compromise the photocatalytic process, mainly in concentrations up to 480 mg L⁻¹. In addition, considering concentration up to 480 mg L⁻¹ of each coagulant ion, better results were obtained using Fe³⁺ (Figure 2). On the other hand, the same removal efficiency can be obtained for Al³⁺ using 960 mg L⁻¹ (Figure 2). Therefore, despite the claim in the literature that iron salts are more efficient than aluminium,^{43,44} our results

demonstrate that the choice depends on the dosage of the coagulant. However, it is important to emphasize that the use of iron is even more feasible considering its concentration in mol L^{-1} , since the molar mass of iron (56 g mol^{-1}) is almost twice the molar mass of aluminum (27 g mol^{-1}). This means that to get the same concentration (in mg L^{-1}) of Fe^{3+} as coagulant, a molar concentration twice of Al^{3+} is required.

In contrast, the coagulation-flocculation was inefficient for removal of the organic load (Figure 2). The low efficiency of COD removal is due the previous acidification step, where most of the humic acids were precipitated by the decrease of the pH. So, only a residual fraction of humic acids was removed by the coagulation-flocculation process. It should be emphasized that it is necessary a pH value below 2 for the complete precipitation of these acids. Then, since fulvic acids are not precipitated by iron, they should form soluble complexes with iron.^{2,38} Considering that a lower coagulant concentration tends to reduce the operational costs, a concentration of Fe^{3+} equal to 240 mg L^{-1} was defined as the best concentration for the pre-treatment using coagulation-flocculation. We choose to use $240 \text{ mg L}^{-1} \text{ Fe}^{3+}$ instead of 480 mg L^{-1} , once the gain in efficiency duplicating the concentration is not justified. Using Fe^{3+} at an initial pH equal to 3, decreases of, respectively, 60, 80 and 11% in the apparent color, turbidity and DOC were obtained (Figure 2). This same percentage of turbidity removal was achieved by Amor *et al.*¹⁹ in the pre-treatment of landfill leachate using FeCl_3 . However, a higher concentration of Fe^{3+} (415 mg L^{-1}) and initial pH equal to 5 was employed, demonstrating the need for a prior assessment of the role of each component of the matrix.

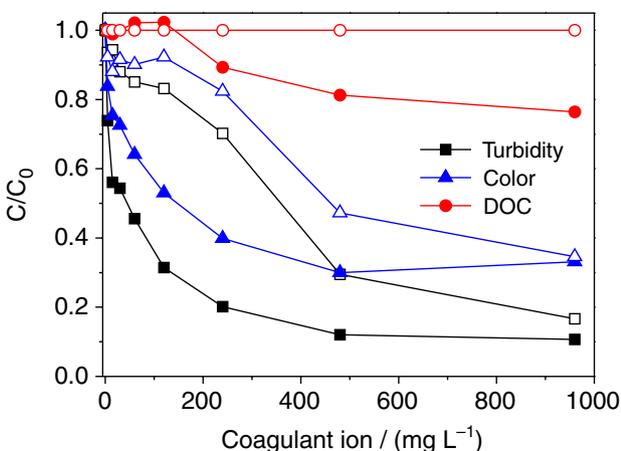


Figure 2. Effect of dosage of coagulant ion on the removal of turbidity, apparent color and DOC from raw landfill leachate by coagulation-flocculation using Fe^{3+} (solid symbols) and Al^{3+} (open symbols).

After determining the best coagulant and its dosage ($240 \text{ mg L}^{-1} \text{ Fe}^{3+}$), a comparison was done on the efficiency of the photo-Fenton process applied directly to the raw

leachate and to a sample previously pre-treated using Fe^{3+} (Figure 3a). The isolated or combined influence of sulfate and chloride was also evaluated during the treatment of the raw leachate using the photo-Fenton process (Figure 3a).

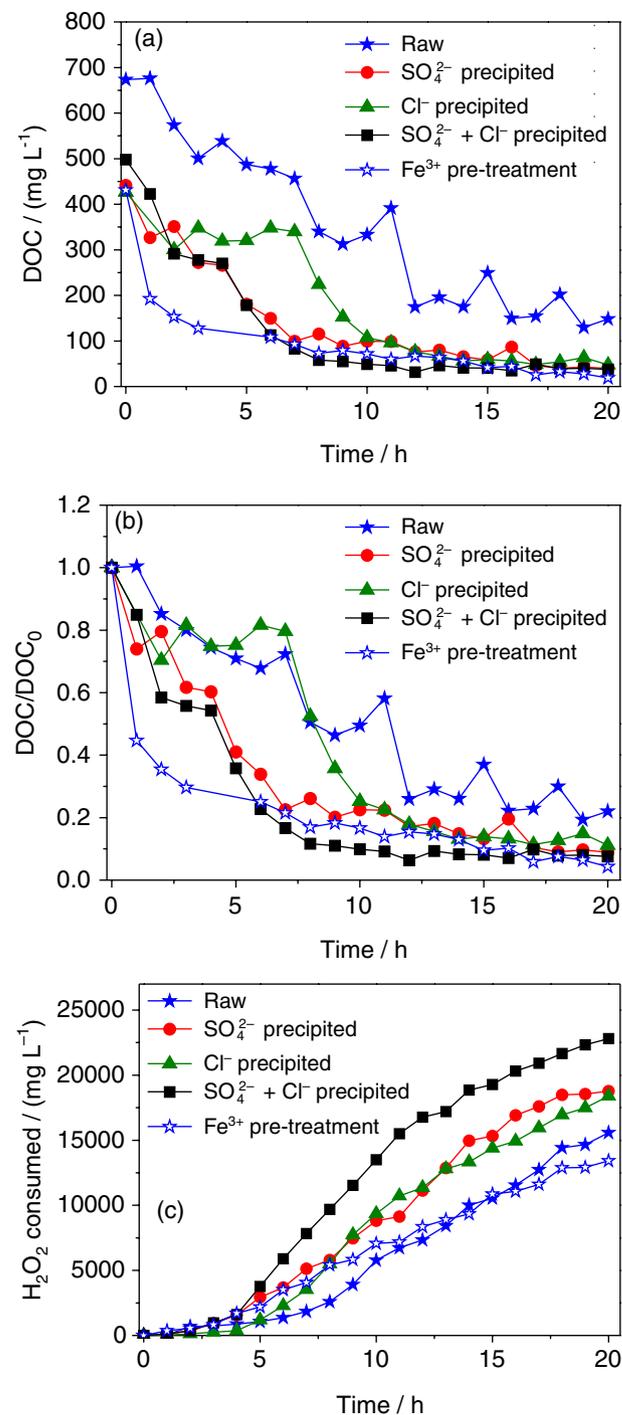


Figure 3. Influence of chloride and sulfate and of the pre-treatment on (a) DOC degradation; (b) normalized DOC; (c) H_2O_2 consumption, during the photo-Fenton process applied to the raw (solid symbols) and the pre-treated leachate using Fe^{3+} (open symbols), using 100 mg L^{-1} of Fe^{2+} . Initial conditions: $\text{DOC}(\text{raw leachate}) = 673 \text{ mg C L}^{-1}$ and $\text{DOC}(\text{after pre-treatment}) = 449 \pm 33 \text{ mg C L}^{-1}$; $\text{H}_2\text{O}_2 = 2000 \text{ mg L}^{-1}$ (replaced when close to 200 mg L^{-1}); $\text{pH} = 2.5-2.8$.

All photo-Fenton experiments were carried out using the better Fe^{2+} concentration (100 mg L^{-1}).

By precipitation of the ions sulfate ($6,741 \text{ mg L}^{-1}$, 70 mmol L^{-1}) and chloride ($2,041 \text{ mg L}^{-1}$, 58 mmol L^{-1}) or by the pre-treatment using Fe^{3+} , it was achieved an average reduction of 33% in the DOC content (Figure 3a). In addition, it was observed that the precipitation of these ions favors the photo-Fenton process when compared to its direct application to the raw leachate (Figure 3a).

Sulfate ions commit much more the photo-Fenton process than chloride, as demonstrated by the normalized DOC results (Figure 3b). It was observed that a better DOC removal was obtained when sulfate was previously precipitated and that a similar efficiency was reached when chloride and sulfate were simultaneously precipitated (Figure 3b). For example, removing the sulfate, a residual DOC concentration of 181 mg C L^{-1} was reached after 5 hours (Figure 3a), while removing only chloride a similar removal was achieved only with 9 hours of treatment (152 mg C L^{-1} of residual DOC). For the raw leachate, (Figure 3a) 12 h were required for the same reduction. On the other hand, a lower consumption of H_2O_2 was verified in the absence of sulfate ($2,937 \text{ mg L}^{-1}$), against $7,727$ and $7,345 \text{ mg L}^{-1}$, respectively in the absence of chloride and in the treatment of the raw leachate (Figure 3c).

The lower efficiency of DOC removal in the treatment of the raw leachate directly by the photo-Fenton process can be attributed to four possible reasons: (i) impairment of hydroxyl radicals generation due the formation of Fe^{2+} and Fe^{3+} complexes, such as FeCl^+ , FeCl_2^+ , FeCl_2^+ , FeSO_4^+ , $\text{Fe}(\text{SO}_4)_2^-$, affecting the distribution and reactivity of the iron species; (ii) scavenging of hydroxyl radicals and formation of inorganic radicals (Cl^\bullet , $\text{Cl}_2^{\bullet-}$ and $\text{SO}_4^{\bullet-}$), much less reactive than HO^\bullet ; (iii) increasing of H_2O_2 consumption due to its decomposition mediated by the less reactive (chloride and sulfate) radicals, and (iv) oxidation reactions involving these inorganic radicals.^{29,45} It is important to emphasize that high concentrations of chloride ($> 50\text{-}100 \text{ mmol L}^{-1}$) are needed to inhibit the formation of peroxocomplexes of Fe^{3+} for a significant decrease in the rate of decomposition of H_2O_2 .⁴⁵ On the other hand, De Laat and Le⁴⁵ reported a reduction of 50% in the rate of decomposition of H_2O_2 by action of Fe^{3+} when using a concentration of sulfate around 7 mmol L^{-1} . The higher influence of sulfate ions on the efficiency of the photo-Fenton process should be related to its ability to establish more stable chemical bonds in the complexes with the Fe^{3+} , when compared to chloride. Silva *et al.*,²⁸ comparing the type of acid used (H_2SO_4 , HCl or the mixture $\text{H}_2\text{SO}_4/\text{HCl}$) and the pH of the reaction medium on DOC removal efficiency in sanitary landfill leachate by the photo-Fenton process,

verified that at pH 2.8, also used in the present work, the predominant iron species in solution are (in percentage): FeSO_4^+ (59.4), $\text{Fe}(\text{SO}_4)_2^-$ (29.5), Fe^{3+} (4.4), $\text{Fe}(\text{OH})_2^+$ (2.9), FeOH^{2+} (2.4) and FeCl_2^+ (1.3). These species can induce by photolysis the simultaneous formation of $\text{SO}_4^{\bullet-}$, HO^\bullet , Cl^\bullet and $\text{Cl}_2^{\bullet-}$.¹⁴ However, considering the low quantum yield of photolysis of FeSO_4^+ and the acidic condition, the main source of sulfate radicals appears to be through the scavenging of hydroxyl radicals by hydrogenosulfate ions.⁴⁶ This justify the results obtained in the present work, since a higher amount of H_2O_2 was needed to reach the same residual DOC obtained in the absence of chloride, but in the presence of sulfate and in the treatment of the raw leachate, when compared to the effluent containing only chloride. It is important to emphasize that although $\text{Cl}_2^{\bullet-}$ and $\text{SO}_4^{\bullet-}$ are strong oxidants ($E^\circ(\text{Cl}_2^{\bullet-}/2\text{Cl}^-) = 2.09 \text{ V}$; $E^\circ(\text{SO}_4^{\bullet-}/\text{SO}_4^{2-}) = 2.43 \text{ V}$), being able to oxidize H_2O_2 and Fe^{II} , they are more selective and less reactive than the hydroxyl radicals.^{47,48} It is noteworthy that sulfate radicals may contribute in the degradation of organic species only if it is present in high concentrations: $[\text{SO}_4^{2-}] > 1 \text{ mol L}^{-1}$.⁴⁹

Regarding the pre-treatment using Fe^{3+} followed by the photo-Fenton process, it can be observed a synergistic effect favoring the DOC removal when compared to the isolated process (Figure 3a), since after only 2 h of reaction, a residual DOC of 153 mg C L^{-1} (Figure 3a) was obtained with the consumption of 549 mg L^{-1} of H_2O_2 (Figure 3c). The coupling implies in a result better than the obtained only by removing the sulfate ions. As shown in Figure 3a, applying Fe^{3+} as coagulant, there was 36% of DOC removal, a result similar to that obtained by precipitation of sulfate and chloride. It is important to emphasize that there was no removal of these ions during the pre-treatment using coagulant, as determined by the analyses. However, although has been obtained initially a similar capability of DOC removal by both strategies, a practically colorless solution was only obtained when the pre-treatment was based in coagulation-flocculation mediated by Fe^{3+} . An effluent with slightly dark color was obtained after precipitation of chloride and sulfate, suggesting that the interference of such anions ends up being offset by the higher light penetration in the solution, favoring the photo-Fenton reactions.

The higher consumption of H_2O_2 (Figure 3c) when the DOC removal remained almost constant (Figure 3a) must be due to the occurrence of inefficient reactions, which compromises the application of the photo-Fenton process in long periods of reaction.^{26,39,40}

In general, it can be observed that the presence of inorganic ions (sulfate and chloride), and mainly the turbidity and apparent color, affect strongly the rate of

mineralization of the organic load (Figures 3a and 3b) and consumption of H₂O₂ (Figure 3c), since a higher reaction time was necessary to reach the same efficiency of DOC removal, between 70-77%, in raw leachate (Figures 3a and 3b). Therefore, in terms of application and based on the results obtained, the best protocol is the application of a pre-treatment using Fe³⁺, followed by the photo-Fenton process, since after only 2 hours a residual DOC concentration of 153 mg C L⁻¹ was reached, with a consumption of 549 mg L⁻¹ of H₂O₂, while a time and concentration of H₂O₂ 6 and 13 times higher, respectively, was necessary to treat the raw leachate. Although the pre-treatment implies in additional costs due to the use of ferric chloride, the lower H₂O₂ consumption should compensate it. Besides, it is possible to treat large volumes of landfill leachate due to the lower time of treatment.

Conclusions

This study demonstrates that the composition of the matrix (high turbidity and apparent color, as well as presence of inorganic ions sulfate and chloride), in the concentration found in the leachate, does not reduce the efficiency of the photo-Fenton process, but influences strongly on the reaction time and consumption of H₂O₂, by increasing them. Therefore, to work around this problem, it is recommended the implementation of a pre-treatment step prior the photo-Fenton process, because in this way the same DOC removal efficiency can be achieved in 17% of the treatment time and using only 7% of the hydrogen peroxide needed to treat the raw leachate using directly the photo-Fenton process.

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