Characterization and detoxification of a mature landfill leachate using a combined coagulation–flocculation/photo Fenton treatment

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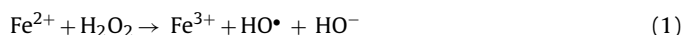
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ABSTRACT

The aim of the present work was to characterize and treat a mature landfill leachate using a coagulation/flocculation process followed by a photo-Fenton oxidation treatment. The leachate was obtained from a landfill in Tetlama, Morelos (Mexico) during the drought season and was characterized in terms of its major pollutants. Considerable levels of chemical oxygen demand (COD), total carbon (TC) and NH_4^+ were identified, as well as high concentrations of Hg, Pb, and As. Other heavy metals such as Ni, Co, Zn, Cd, and Mn were detected at trace levels. The lethal concentration (LC_{50}) of the leachate, evaluated on *Artemia salina*, was $12,161 \pm 11$ mg/L of COD, demonstrating an antagonistic interaction among the leachate's components. The treatment of this effluent consisted of a coagulation–flocculation process using an optimal dose of $FeCl_3 \cdot 6H_2O$ of 300 mg/L. The supernatant was treated using a photo-Fenton process mediated with $FeCl_2 \cdot 4H_2O$ and H_2O_2 in a compound parabolic concentrator (CPC) photo-reactor operating in batch mode using an R ratio ($R = [H_2O_2]/[Fe^{2+}]$) of 114. The global removal efficiencies after treatment were 56% for the COD, 95% for TC, and 64% for NH_4^+. The removal efficiencies for As, Hg, and Pb were 46%, 9%, and 85%, respectively.

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1. Introduction

A landfill leachate is defined as the residual liquid generated during the biochemical decomposition of waste or as the result of water percolation through solid wastes undergoing a degradation process [1]. Christensen [2] proposed the classification of pollutants present in a landfill leachate, into the following four broad categories: (i) dissolved organic matter (DOM), expressed as COD (chemical oxygen demand) or TOC (total organic carbon), including methane, volatile fatty acids (VFA), and biorecalcitrant compounds such as fulvic and humic substances; (ii) metallic ions, such as Ca, Mg, Na, K, NH_3, Fe, Mn, and the anions Cl^-, SO_4^{2-}, S^{2-}, CO_3^{2-}, and potentially toxic ion metals such as Cd, Cr, Pb, Ni, Cu, Zn, and As; (iii) xenobiotic organic compounds, which can include a huge variety of halogenated and phenolic compounds, alcohols, aldehydes, and ketones; and (iv) trace compounds [3].

The degradation of these recalcitrant organic compounds and the removal of nitrogen can be achieved by advanced oxidation processes (AOP) [1,4,5]. The photo-Fenton process has proven to be a good alternative for treating a wide variety of pollutants more efficiently, thus increasing the effluents' biodegradability. The hydroxyl radical ($HO^\bullet$) is the major intermediate reactive responsible for organic substrate oxidation (2.8 V vs. NHE) in the Fenton oxidation. In a heavily organic (RH) and strongly acidic effluent, a complex redox reaction set would be expected, which produces additional hydroxyl radicals according to Eqs. (1)–(3) [6,7]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + HO^- \tag{1}$$

$$RH + HO^\bullet \rightarrow H_2O + R^\bullet \tag{2}$$

$$R^\bullet + H_2O_2 \rightarrow ROH + HO^\bullet \tag{3}$$

Because landfill leachates are ultimately complex effluents, it is difficult to establish an adequate stoichiometric dose of reagents. Peroxide-to-iron molar ratios ($R = [H_2O_2]/[Fe^{2+}]$) employed in landfill leachates are typically 100–1000 for photo-Fenton processes [6]. However, obtaining an optimal R ratio value for a specific leachate is difficult because of its chemical complexity and because at times high doses of iron salts may reinitiate coagulation–flocculation phenomena [8].

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The main difficulties observed during the treatment of leachates under conventional processes are associated with high concentrations of organic matter, a high concentration of nitrogen as ammonia, toxic organic compounds, and heavy metals [9]. Physicochemical procedures for the treatment of landfill leachates are also used in the treatment line (pre-treatment or final polishing) aimed at treating a specific pollutant [10].

The United States Environmental Protection Agency (US EPA) has shown that effluents with COD values up to 3000 mg/L can be treated using a photo-Fenton process, yielding removal efficiencies of approximately 98% [11]. Therefore, the same technique, incorporating a previous coagulation–flocculation treatment, was chosen for application to a landfill leachate [12]. This coagulation stage is necessary at the beginning of the process because the leachate's dark color is due to the presence of humic substances, which account for most of the organic components in the leachate [13]. Because UV light must penetrate through the solution to trigger the photo-Fenton reaction, anything that prevents light from reaching the reactive species will obviously affect the removal efficiency. Suspended matter can also affect UV transmission by either scattering or absorbing it. Furthermore, humic substances are considered to be hydroxyl radical scavengers [7].

Landfill leachate treatment through coagulation–flocculation procedures has been extensively studied [12,14,15]. Iron salts have proven to be more efficient than aluminum salts; therefore, hexahydrated ferric chloride solutions were used for this purpose because they are widely available and relatively cheap, compared to organic coagulants–flocculants [16]. For the removal of color, ferric chloride has performed well and has produced better results than other salts at acidic pH values [15].

Applying a coagulation–flocculation process as a first step in the landfill leachate treatment seems reasonable because it has been shown that the removal percentage of chemical oxygen demand (COD) and total solids (TS) achieved is generally 50–65% with stabilized leachates [13]. The decontamination of leachates through the photo-Fenton process has also been reported to produce results efficiently [17–19]. Therefore, it seems appropriate to couple the aforementioned treatments to achieve a deep-level detoxification. Moreover, the combination of the two processes enhances the removal of heavy metals and other species that are refractory to biological oxidation.

The first objective of this study was to fully characterize the leachate in terms of its most abundant toxicants and through the assessment of its potential impacts from a biological perspective. The second objective was to evaluate the potential of a coupled coagulation–flocculation/photo-Fenton process as an effective treatment for stabilized leachates, in terms of the efficiency of removal for each of the studied toxicants.

2. Materials and methods

2.1. Sample preparation and collection

The landfill from which the studied leachate was obtained is located near Tetlama, in the Mexican state of Morelos. The stabilized leachate was collected at the landfill site in May 2009, during the drought season, and was kept in refrigeration at 3 °C until used [20].

Four concentrations of $FeCl_3 \cdot 6H_2O$ were prepared to determine an adequate coagulant dose: 100 mg/L, 300 mg/L, 500 mg/L, and 1000 mg/L. The COD values were measured for each concentration. The solutions were prepared with $FeCl_3 \cdot 6H_2O$ (purity: 97.0%) provided by Quimicos Monterrey (Monterrey, Mexico). The supernatant resulting after 2 h of sedimentation was collected and further subjected to photo-Fenton treatment. The pH was adjusted
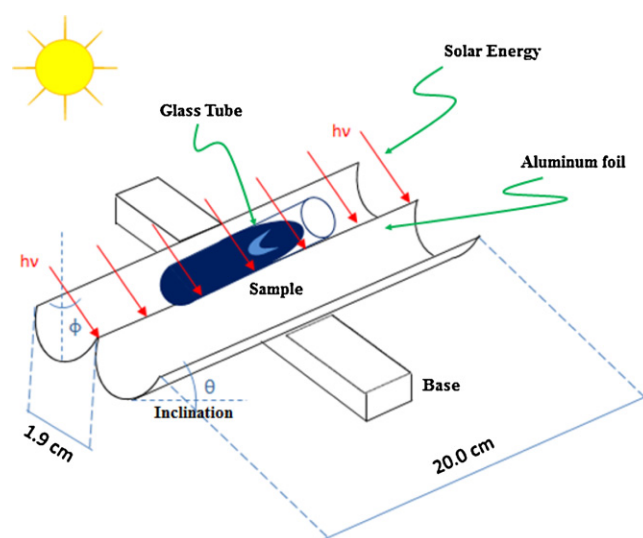

Fig. 1. Schematic representation of a two-slot Compound Parabolic Collector (CPC). θ is the geographic latitude and φ is the azimuth.

with concentrated J.T. Baker sulfuric acid (96%) using a Thermo Orion 4 Star potentiometer.

The Fenton reagent solution was prepared by mixing 10 mL of a $FeCl_2 \cdot 4H_2O$ solution (20 mg/L) with the leachate sample. The $FeCl_2 \cdot 4H_2O$ reagent (purity: 98.0%) was also provided by Quimicos Monterrey (Mexico) and used as received. The hydrogen peroxide solution (30% by volume) was provided by J.T. Baker. The initial hydrogen peroxide concentration required for the degradation of the leachate was calculated through the COD of the raw leachate, as shown in Eq. (4) [21]:

$$[H_2O_2] = (34/16)(COD_{leachate}) \tag{4}$$

2.2. Photoreactor and light source

The tests were performed in a series of batch reactors (Pyrex 50-mL glass tubes, transmittance: $\lambda = 290$ nm) mounted on a CPC with 16 slots and covered with aluminum foil. The non-concentrating CPC collectors were built using the design ratios recommended by Blanco and Malato [22]. The CPC was placed 20° above the horizontal, in a shadow-free, westward-oriented yard of the F Building of the Universidad Iberoamericana in Mexico City. The experimental set-up is depicted in Fig. 1. The only light used was sunlight. The experiments were conducted on a fixed time schedule from 9:00 a.m. to 2:00 p.m., beginning on April 10th, 2010, and ending on July 16th, 2010. The total accumulated radiation was measured using a calibrated Solar® Light PMA 2100 radiometer equipped with a PMA 2110 UVA (USA) detector with a 320–400 nm spectral range, which was placed over the CPC. Samples were removed from sunlight after 45 kJ/L and 90 kJ/L of irradiation. The accumulated radiation per unit of volume was determined from Eq. (5) [22]:

$$E_{UV,n} = E_{UV,n-1} + \left(\frac{\Delta t_n \times UV_n \times A_{collector}}{V_{Total}} \right) \tag{5}$$

where $E_{UV,n}$ is the accumulated radiation per unit of volume at interval n [kJ/L], $E_{UV,n-1}$ is the accumulated radiation per unit of volume at interval $n-1$ [kJ/L], Δt_n is the elapsed time at interval n [s], UV_n is the incident radiation [kW/m^2], $A_{collector}$ is the reactor area of exposure [m^2], and V_{Total} is the total treated volume [L].

2.3. Analyses

The decrease in the leachate's pollutant concentrations was evaluated indirectly. Total carbon (TC) was measured using a Shimadzu TOC-V CPH analyzer (Japan). The COD measurements were conducted according to standard methods [23] by digestion with $K_2Cr_2O_7$ in a closed reflux reactor using high-range Hach COD digestion vials and a heating system and then measuring the characteristic absorbance of each sample using a Milton Roy Spectronic 21D spectrophotometer. NH_4^+ concentration was evaluated via the $K_2S_2O_7$ digestion method using high range vials, supplied by Hach, and then measuring the characteristic absorbance at $\lambda = 410$ nm, using a Milton Roy Spectronic 21D spectrophotometer [23].

The concentrations of the metallic ions Fe, Hg, As, Pb, Cd, Zn, Ni, Mn, Ca^{2+}, and Co were measured using a Varian Spectra AA 250 atomic absorption spectrophotometer (USA). The PO_4^{3-}, S^{2-}, and Cl^- concentrations were determined by ion chromatography using a Dionex ICS-5000 DC chromatograph, a pre-packed IonPac AS11-HC column, an IonPac AG11-HC precolumn, and a self-regenerating suppressor ASRS 300. The mobile phase was 30 mM sodium hydroxide and the flow rate was fixed at 1.5 mL/min. The operation temperature was 35 °C.

2.4. Biodegradability tests

The degree of biocompatibilization of the samples was evaluated by measuring the BOD_5 using the ready biodegradability test method (OECD 301). The test was applied using six BOD VELP Scientifica bottles equipped with BOD manometric Oxytop®-type sensors. The average concentration of the biomass was 160 mg of suspended solids per liter of mineral nutrient medium, calculated according to the standard methods for the examination of water and wastewater [23,24]. The inoculum used for the test was activated sludge from the wastewater treatment facility at the Universidad Iberoamericana.

2.5. Toxicity testing

Assessing the toxicity of the landfill leachate is an additional characterization procedure that is necessary to determine the interaction of the pollutants present in the leachate with living organisms. Artemia salina (brine shrimp) has gained popularity as a test organism because of its ease of culture and short generation time and the commercial availability of its dormant eggs. Because test animals hatching from cysts are of similar age, genotype, and physiological condition, test variability is greatly reduced [25]. Moreover, the use of A. salina is adequate for aqueous media such as landfill leachate and for environments that have been affected by active oxygen species (AOS) [26]. The toxicity assessment conducted to determine the median concentration was conducted using brine shrimp (A. salina), according to the technique described by Sam [27] and Svensson [28], for the raw leachate at four volumetric dilutions (0%, 25%, 50%, and 75%).

2.6. Toxicity evaluation model

Because leachates have been shown to be very complex mixtures, a toxicity evaluation model was implemented to search for synergistic or antagonistic effects. Verslycke et al. [29] proposed a mixed toxicity model in which the expected toxicity of the mixture is expressed in toxic units (T.U.) and is the sum of the ratios of the actual pollutant concentration (C_i) to their lethal concentrations (LC_{50}), according to Eq. (6):

$$\text{Expected toxicity} = \sum \frac{C_i}{LC_{50,i}} \tag{6}$$

Given that there is a median lethal concentration associated with each toxicant identified in the leachate, it is possible to assess whether each one presents either synergetic or antagonistic effects [29].

3. Results and discussion

3.1. Characterization of the landfill leachate

The sampled raw leachate exhibited a BOD_5/COD ratio of 0.102, which indicated poor biodegradability. This is a major hindrance to the use of any biological treatment as a sole depuration technique [30]. The raw leachate showed a relatively low COD value that accounted for 16% and 9% of the maximum values reported by the US EPA [31] and Kjeldsen et al. [32], respectively, as shown in Table 1. This is a characteristic behavior of a stabilized or mature landfill leachate, whose low biodegradability does not necessarily depend on its high content of organics [33]. Moreover, its high pH (pH 8.04) was also indicative of its age [12]. The SO_4^{2-}/S^{2-} ratio is a measure of the degree of anaerobiosis and also a useful indicator for estimating the stability of the leachate because methanogenic bacteria convert sulfate into sulfide; a landfill can be considered free from bacterial transformations when a leachate exhibits a very small SO_4^{2-}/S^{2-} ratio [32].

It is also evident from Table 1 that NH_4^+ is present in significant amounts and always between the reported ranges. Apart from a low degree of biodegradability, if NH_4^+ is present to a significant degree, the leachate cannot be treated by conventional biological processes. A high ammonia concentration in a leachate is known to inhibit nitrification when subjected to such treatments. Several authors have found that this is the primary cause of acute toxicity of municipal landfill leachates [10,34]. This leachate also appeared to be especially saline, showing values above the two reported ranges in Table 1.

Among the metals that were identified in the leachate, mercury and lead exhibited dangerously high concentrations that were far above the ranges reported by the US EPA [31] and Kjeldsen et al. [32]. Mercury may be present as inorganic Hg^{2+} or Hg^+ compounds, or as organic mercury, and its presence in the leachate may be attributed to the disposal of mercury batteries and household appliances [35]. Lead appears as inorganic Pb^{2+} compounds from car batteries or accumulators, as well as old pipelines [36]. Some metals, such as As, Cd, Fe, and Zn, were detected at concentrations within the ranges reported in Table 1. Cr and Ni, which are toxic and carcinogenic, were detected at trace levels below 0.1 mg/L, as was Co.

3.2. Toxicity assessment on Artemia salina

The LC_{50} of the leachate had a value of 12,161 ± 11 mg/L of COD. The median lethal concentration for A. salina is reported in COD concentration units because it has been demonstrated that a negative relationship between LC_{50} and COD exists, which indicates that the substances responsible for the toxic effects require the formation of complexes with organic matter to elicit their biological activity [37]. Other studies have suggested that NH_4^+/NH_3 compounds or metals seem to affect A. salina minimally [10,37]. These premises, however, do not rule out the possibility that the combination of organic pollutants and metal ions may yield either synergetic or antagonistic effects for the studied leachate.

Table 2 reports the concentration of toxicants present in the leachate in toxic units (T.U.). The reported values suggested that strong antagonistic effects might be expected among the leachate's compounds (ΣT.U. > 1) [29], as its toxic strength was ΣT.U. = 6.97 ± 2.32 T.U. This means that any biological response to

Table 1
Characteristics of the studied leachate, its comparison with reported range–concentrations in [mg/L].

Parameter	Range reported by US EPA [31]	Range reported by Kjeldsen et al. [32]	Pollutant concentration
BOD_5	2–55,000	20–57,000	1500 ± 500
COD	9–90,000	140–152,000	$14,680 \pm 3225$
Total carbon (TC)	–	30–29,000	8089 ± 800
Ammonium (NH_4^+)	0–2400	50–2200	381 ± 3
Calcium hardness ($CaCO_3$)	200–25,000	–	8418 ± 549
pH	3.7–9.0	4.5–9.0	8.04 ± 0.17
Arsenic (As)	–	0.01–1	0.233 ± 0.224
Cadmium (Cd)	0–17	0.0001–0.4	0.433 ± 0.057
Chlorides (Cl^-)	2–5000	150–4500	3501 ± 1987
Chromium (Cr)	0–33	0.02–1.5	<0.1
Cobalt (Co)	–	0.005–1.5	<0.1
Iron (Fe)	2–5500	3–5500	65 ± 5
Lead (Pb)	0–12	0.001–5	19.59 ± 18.54
Manganese (Mn)	–	0.03–1400	<0.1
Mercury (Hg)	0–0.2	0–0.16	33.27 ± 105.57
Nickel (Ni)	0–9	0.015–13	<0.1
Orthophosphates (PO_4^{3-})	0–155	–	<1
Sulfates (SO_4^{2-})	1–1825	8–7750	<1
Sulfides (S^{2-})	–	–	10.68 ± 1.68
Zinc (Zn)	0–1000	0.03–1000	0.333 ± 0.057

exposure to the multiple substances present in the leachate would be less than the one expected if the known effects of the individual substances were added together. A number of causes might be the reason for this antagonistic effect. Heavy metals, for instance, do not always follow the same toxicity mechanism as their free forms, while organic matter may reduce bioavailability and toxicity [37].

3.3. Study of an adequate coagulant dose

The efficiency of the treatment process depends on the characteristics of the leachate and on the type and concentrations of the chemical products used [38]. The collected leachate was distinctly alkaline (pH 8.04) and was adjusted to a value of 3 at which landfill leachates exhibit an efficient response to coagulation [18]. Charge neutralization has been shown to apply preferably at acidic pH, favoring the precipitation of dissolved organic matter (DOM) [39].

As pH increases, the removal efficiency of COD, turbidity, and color decreases [12,15], although at alkaline pH values, the reduction of turbidity is hindered by the precipitation of $Fe(OH)_3$ and $Fe(OH)_2$. Presumably, a pH value of 3 is sufficiently acidic to favorably flocculate organic colloids [18]. An initial low pH value is also important to guarantee good removal efficiencies from the subsequent photo-Fenton process [40].

From Fig. 2, it is evident that for this specific landfill leachate, there was indeed a coagulant concentration that provided the best COD removal efficiency for the raw effluent (300 mg/L $FeCl_3$). This concentration happened to be the lowest of the four studied concentrations, which is certainly favorable in terms of the economy of the process. Fig. 2 also shows that the removal efficiencies were more dramatic as concentration increased within the

Table 2
Expected toxicity of the pollutants present in the landfill leachate [T.U.].[a]

Toxicant	Expected toxicity [T.U.]
COD	1.21 ± 0.26
Total carbon (TC)	1.22 ± 0.26
Ammonium (NH_4^+)	0.83 ± 0.01
Arsenic (As)	1.23 ± 1.23
Cadmium (Cd)	1.23 ± 0.31
Lead (Pb)	0.20 ± 1.10
Mercury (Hg)	1.06 ± 3.37
Zinc (Zn)	1.21 ± 0.37

[a] According to the model proposed by Verslycke et al. [29].

100–300 mg/L range of $FeCl_3$, with removal efficiency decreasing for higher concentrations [15]. This fact could be attributed to a restabilization of the colloidal particles accentuated by an ever-increasing coagulant dose [12].

For the purposes of this study, a dose of 300 mg/L of ferric chloride was used to achieve the desired COD for further treatment with photo-Fenton oxidation.

3.4. Study of the coagulation–flocculation process

After treatment, a volume of sedimentable solids of 287.4 ± 138.5 mL/L of raw leachate was obtained. This might be attributed to the soil type found at the site, and if the soil's predominant type is clay, colloidal particles might be expected in the leachate mixture [41]. Gama-Castro et al. [42] thoroughly studied the soil composition of the zone in the state of Morelos where the landfill is located and determined that its clay content ranges from 26% to 35%, with clay almost always being the predominant component. The calcium concentration is a strong indicator of this fact. Clay minerals exhibit high cation exchange capacities and are thus able to bind and remove metals and phenolic compounds from water; they are also susceptible to being coagulated and charge-neutralized [43].

As can be observed from Fig. 3, the coagulation–flocculation treatment removed approximately 81.9% of the initial TC concentration, 17.8% of the initial COD, and 36.1% of the initial NH_4^+. Among these removal efficiencies, the highest was for the TC, presumably because of the removal of high-molecular-weight compounds (>10 kDa) [1,44]; these account for more than 42% of the COD value of an aged landfill leachate [44,45]. Moreover, the relatively low BOD_5/COD value (BOD_5/COD < 0.102) strongly suggests the presence of high-molecular-weight substances that are biorecalcitrant [32,46].

Humic substances almost always interact with mineral surfaces because they have a very high affinity for the external surface of mineral oxides [46,47]. As mineral oxides usually respond to flocculation treatment, high removal efficiencies of TC and of color and turbidity were thus found. NH_4^+ removal does not seem to be efficient because, at this stage, it is strongly related to the removal of colloidal matter present as albuminoid-type nitrogen [39,48], which did not abound because the leachate is evidently stabilized. Porto-Dantas et al. [49] did not register any removal of NH_4^+ in solution by coagulation.

Fig. 2. COD removal efficiency and FeCl$_3$·6H$_2$O concentration of the supernatant against ferric chloride (FeCl$_3$) coagulant dose for the studied mature landfill leachate water.

The coagulation–flocculation treatment also produced changes in the concentration of metals. Fig. 4 shows that Pb underwent a 27.5% removal efficiency, which is the greatest value reported for the metals present. However, As and Hg seem to be refractory to this stage of the treatment, showing removal efficiencies of 7.7% and 0.3%, respectively.

As mentioned before, the high pH of the leachate (pH 8.04) led to the consideration that most metals might be adsorbed onto suspended solids [43]. At such a pH value and within the stability zone of water, Pb is present as an insoluble hydroxide (Pb(OH)$_2$), while As and Hg are solubilized as As^{5+} and Hg^{2+}, respectively. When pH decreases during acidification prior to the addition of the coagulating agent, neither Hg nor As change their solubility equilibrium; Pb, on the contrary, would change to Pb^{2+} at pH < 7. However,

when acidification starts, flocs begin to settle and until the solution reaches an acidic pH, lead will not cease to be scavenged by this effect. Even so, Pb^{2+} could suffer complexation from the still-abundant humic substances in the leachate and thus be removed by this treatment. The removal of metals such as Pb, Zn, Cd, and even Hg could be explained by the ability of phenolic groups in humic substances (Ar) to bind divalent metal ions, according to Eq. (7) [7]:

$$Ar(OH)_2 + M^{2+} + H_2O \rightarrow ArO_2M + 2H^+ + H_2O \qquad (7)$$
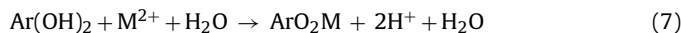
One of the main drawbacks of this treatment process was the great volume of sludge that it generated. For this particular landfill leachate, the volume of sludge amounted to more than one-fourth of the initial volume. It is therefore important to find economical
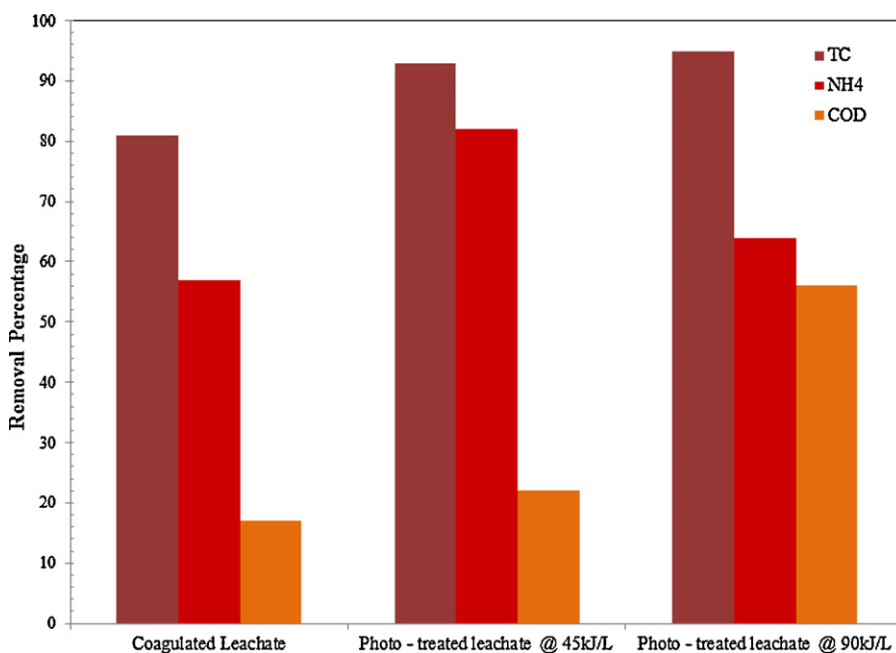

Fig. 3. Chemical oxygen demand (COD), total carbon (TC), and ammonium (NH$_4^+$) removal efficiencies against treatment stage.
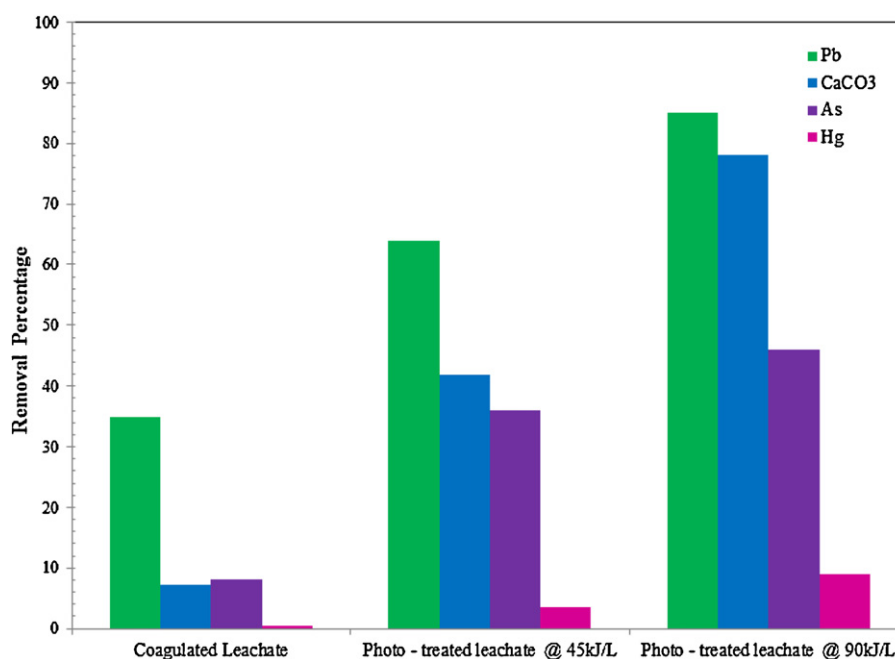
Fig. 4. Arsenic (As), calcium hardness (CaCO$_3$), mercury (Hg) and lead (Pb) removal efficiencies against treatment stage.

and effective ways to treat and dispose of this sludge appropriately [50].

3.5. Study of the photo-Fenton process

For the photo-Fenton process, a mass ratio ($R = [H_2O_2]/[Fe^{2+}]$) of 114 was used, which corresponds to $[Fe^{2+}] = 5.5$ mg/L and $[H_2O_2] = 630$ mg/L [6]. The pH after the coagulation–flocculation treatment did not change significantly (pH 3), and no further adjustments were made. Wang et al. [34] reported that treatment of leachate using a coagulation–photooxidation process yielded better results at lower pH values. This also prevented iron and other metallic ions from precipitating as insoluble species [34].

For this treatment stage, removal efficiencies tended to be higher than those obtained after the coagulation–flocculation treatment. Fig. 3 shows that the removal efficiencies for TC, COD, and NH$_4^+$ increased to 80.9%, 55.0%, and 66.3%, respectively, compared to the removal efficiencies obtained in the previous stage. This resulted in global removal efficiencies of 96.5%, 63.0%, and 75.9%, respectively, compared to the values reported for the raw landfill leachate. The TC concentration removed via the photo-Fenton reaction corresponded to that fraction of solids that is not susceptible to being settled out by coagulation–flocculation treatments and to the fraction of dissolved organic matter (DOM). Although most of the high-molecular-weight substances were removed previously, the percentage increase for TC removal was not substantial.

In the case of COD, its reduction is attributed to the high oxidative power provided by the photo-Fenton treatment in the form of HO$^•$ because the organic matter increases through transformation into mineralized forms of carbon. In contrast with the previous treatment stage, which was purely physical, the photo-Fenton reaction marked a chemical transformation in the organic matter. Furthermore, the COD removal rate is usually related to irradiation intensity, the concentration of H$_2$O$_2$ and Fe^{2+} in the system, its pH value, and the initial COD [34].

Although the basic aim of landfill leachate treatments is to reduce the concentration of pollutants, the efficiency of the treatment is often not quantified. Kang and Hwang [51] defined the efficiency in the COD degradation of a landfill leachate as a function of [H$_2$O$_2$] and the oxidized COD concentration, [COD]$_{ox}$, as shown in Eq. (8):

$$\eta = 2.21 \times \frac{[COD]_{ox}}{[H_2O_2]} \tag{8}$$

According to the values obtained in this study, [COD]$_{ox}$ = 6636 mg/L, which corresponded to 55.0% of the initial COD value at this stage and 63.0% of the COD concentration for the raw leachate, and considering the oxidized COD concentration during treatment and Eq. (8), the process efficiency for this landfill leachate was 47.0%. However, considering that there was a reduction in the COD value due to the coagulation–flocculation stage, the global efficiency becomes $\eta = 65.5\%$, which is obviously indicative of the contribution of the previous treatment.

In the case of NH$_4^+$, good removal efficiencies were achieved during the earlier treatment stage, but the photo-oxidation treatment greatly enhances its removal. This might be explained by the conversion of ammonia into oxidized nitrogen species, mainly nitrate (NO$_3^-$). Nitrogen (as ammonia) can be converted into NO$_3^-$ if the R ratio is sufficiently high [49]. Zoh and Stenström [52] reported that organic nitrogen and ammonia undergoing a photo-Fenton treatment with a sufficiently high hydrogen peroxide concentration ultimately reach their nitrate (NO$_3^-$) form.

This treatment stage produced different degrees of removal for metals. The removal efficiency for Pb increased to 77.3% at this stage, and that of As increased to 61.8%. Nevertheless, Hg increased its removal efficiency to 8.7%, which strongly suggests a refractory behavior even to the photo-Fenton process. The global efficiencies attained at the end of this stage correspond to 83.6% for Pb, 64.9% for As, and 9.1% for Hg. The removal mechanism that reduces the concentration of heavy metals involves their adsorption onto solid iron (III) hydroxide, which is concomitant with the generation of OH$^-$ ions by the photo-Fenton reaction and which increases the pH of the effluent [53].

The slurry phase that forms during the photo-Fenton process is able to remove heavy metals by adsorption if they are present in the effluent as soluble species. Telles-Benatti et al. [53] have demonstrated that when treating polluted effluents in which heavy metals such as Cd, Pb, Hg, or Cr are present with the photo-Fenton

Table 3
Removal percentages and concentrations of the treated leachate [mg/L].

Parameter	Final concentration [mg/L]	Removal percentage (%)
COD	6384 ± 759	56.50
Total carbon (TC)	290 ± 50	94.96
Ammonium (NH_4^+)	84 ± 1	63.83
Hardness ($CaCO_3$)	1929 ± 704	78.08
Arsenic (As)	0.124 ± 0.169	46.66
Lead (Pb)	3.22 ± 16.86	85.51
Mercury (Hg)	30.25 ± 9.6	9.09

process, the generated sludge is able to retain and remove them from the effluent by precipitation. The ferric precipitate generated by these means can effectively bind and immobilize hazardous metals such as Pb. If the effluent contains silicates and aluminum oxides, these co-precipitate so that their crystalline structure is retained and their release into the environment is avoided. Mercury, on the contrary, is weakly adsorbed onto the surface of the solid and is likely to be released again into the effluent, which explains its weak removal at the end of this stage [53].

Arsenic behaves similarly, being effectively adsorbed onto the iron (III) hydroxide. Because it may be present as As^{3+}, the photo-Fenton reaction (Eq. (1)) is responsible for its oxidation to As^{5+}, which exhibits higher affinities for the iron (III) hydroxide, leading to its final uptake [6,54].

As can be observed from Table 3, the combined coagulation–flocculation/photo-Fenton treatment is quite efficient at the removal of carbon, with a removal efficiency of 94.96%, and at the removal of Pb (85.5%). The removal of pollutants such as COD, NH_4^+, and As was good yet incomplete, thus special precautions are still needed if the treated leachate is to undergo further biological treatment. Mercury registered only 9.09% removal (most of it during the photo-Fenton treatment).

According to Mexican law regarding effluent limits, the treated leachate cannot be discharged into natural water bodies without further treatment due to its high Hg and COD concentrations and its pH [55]. In general, the proposed combined treatment for the studied landfill leachate did achieve a deep decontamination level compared to each of the individual treatments [11,33]. Additional advantages of the combined treatment are the removal of heavy metals with the mineralization of organic matter and its ease of use. One of the main disadvantages of this treatment is the generation of a large volume of sludge with high pollution potential [56].

4. Conclusions

The sampled leachate corresponds to a mature landfill, based on its BOD_5/COD, SO_4^{2-}/S^{2-} ratios, as well as its pH value. For the leachate's initial treatment, a dose of 300 mg/L of $FeCl_3$ at pH 3 was considered adequate to remove up to 81.9% of the TC, 17.8% of the COD, 36.1% of NH_4^+, 27.5% of Pb, 7.7% of As, and 0.3% of Hg. The high removal efficiencies of TC are attributed to the leachate's high content of humic substances, which, in the presence of colloidal particles from clayey soil, settle easily out of solution. The photo-Fenton treatment was mediated by a $[H_2O_2]/[Fe^{2+}]$ ratio = 114, and after a total irradiation of 90 kJ/L, it achieved 96.5% removal efficiency for TC, 63.0% for COD, and 75.9% for NH_4^+. The efficiency of the oxidative process was 47%, considering the dosed H_2O_2 concentration. This stage of the treatment enhanced the removal of metals such as Pb and As through their adsorption on a self-generated mass of ferric hydroxide, the product of the ferrous/ferric catalyst sacrifice, which was also able to remove Hg, although to a limited extent.

The proposed treatment is a good option for the removal of COD and TC, as well as NH_4^+. The removal of Pb and As is, in general, efficient, considering that treatability efficiencies of 85% and 95% for

As (100–1000 µg/L) and Pb (1–100 mg/L), were reported by the US EPA [31] for the most efficient treatment (chemical precipitation).

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