The aim of this study was to evaluate the treatment of leachate from landfill through to Fenton advanced oxidation process with subsequent adsorption on the eggshell (ES) and activated carbon (AC). The project was carried out in laboratories of the Area of Chemistry and Physical Chemistry in Environmental of the University Autonomous Metropolitan-Acapotzalco, between January 2012 and October 2014. The raw leached was chemically characterized by different techniques, some organic compounds by IR and chromatography coupled to mass gases were identified in the crude leached, pH was adjusted and relationship $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ was optimized for oxidation treatment; followed by adsorption with eggshell by the technique of batch. ES particle size was selected by
adsorption. The adsorbent treatment was completed with activated carbon, therefore the surface area of both adsorbents was measured and leached oxidized was characterized after each adsorption. Finally adsorption kinetics of pseudo-first-order and pseudo-second-order were obtained, where both kinetics were fulfilled. Freundlich and Temkin isotherms were calculated where the latter presented the best fit. With ES as adsorbent there was good COD removal, saving the use of activated carbon in all adsorption processes. Also to use ES as this investigation, contributes to environment as it is a residue. The liquid finally obtained with all complete treatment satisfied the NOM-001-SEMARNAT-1996 Mexican Standard.

**Keywords:** Eggshell; activated carbon; advanced oxidation; isotherms.

1. INTRODUCTION

Anthropogenic activities generate solid wastes that threaten the environment and public health, so that solid waste disposal is a key activity to protect the environment [1-3]. In Mexico, in 2011 it was estimated that 72% of the volume of solid waste generated in the country was placed in landfills, 23% is deposited in uncontrolled sites and the remaining 5% is recycled. The number of landfills in the country had grown significantly, between 1995 and 2011 the number increased from 30 to 196 [4]. Solid waste disposal produces liquids.

With very high organic load and potentially toxic substances called leachates [5], of which their volume, quality and concentration depend on many factors such as population size, lifestyle, eating habits, and climate, industrial and agricultural activities, among others. Therefore, it is necessary to establish appropriate control measures to minimize harmful effects on environment [1,6,7]. Also waste stabilization degree has an effect on leachate composition thus leading to their classification as: New, intermediate and stabilized leachates [8,9].

Leachate treatment is difficult because they contain complex materials such as polycyclic aromatic hydrocarbons, alkenes, ketone, esters, alcohols, phthalates, phenols carboxylic acids, amines, amides, aldehydes and carbohydrates, which could be difficult to degrade, toxic and even carcinogenic to humans [10,3]. Among the treatments applied to leachates, can be found advanced oxidation processes (AOP’s), occur where free radicals, these are oxidizing species highly reactive capable of degrading to the chemical compounds found in leachates [11-15].

Fenton reaction has shown good results to treat chemical compounds difficult to degrade. This reaction where hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) is used in presence of ferrous salts such as FeSO\textsubscript{4} has been used successfully for leachates [16-20]. Barbusinski [21], proposed the following set of Fenton reactions:

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{3+} + \text{HO}^\bullet + \text{HO}^\bullet^- \quad (1) \\
\text{HO}^\bullet + \text{H}_2\text{O}_2 &\rightarrow \text{HOO}^\bullet^\bullet + \text{H}_2\text{O} \quad (2) \\
\text{Fe}^{3+} + \text{HOO}^\bullet^- &\rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2 \quad (3) \\
\text{Fe}^{2+} + \text{HOO}^\bullet^- &\rightarrow \text{Fe}^{3+} + \text{HO}^\bullet^- \quad (4)
\end{align*}
\]

The first reaction is general Fenton reaction; the chain initiation should be optimized in order to achieve the presence of important amounts of HO\textsuperscript{•} radicals. Ferric ion (Fe\textsuperscript{3+}) and a set of oxidizing species (HO\textsuperscript{•}, HOO\textsuperscript{••}, HOO and H\textsubscript{2}O\textsubscript{2}) will be present. In addition ferric ions (Fe\textsuperscript{3+}) will react with hydro peroxides radicals (HOO\textsuperscript{•}) and will be reduced to Fe\textsuperscript{2+}. By the other hand, Fe\textsuperscript{2+} will react with HOO\textsuperscript{•} in excess to produce Fe\textsuperscript{3+}.

Finally, ferric oxide hydrated will be formed which is observed during Fenton reaction. An important aspect for Fenton reaction efficiency is to look after the pH adjustment and control which must be adjusted between 2 and 4 [22-24], on the other hand the relationship [Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2}] must be optimized [16,22]. Finally, the sludge produced should be coagulated and sediment [16,22,25].

After advanced oxidation reaction, one adsorption process it can be applied in order to achieve further contaminant removal. The most commonly used absorbent is activated carbon (AC), which has a high removal efficiency (20%), but its cost is high [26]. Other absorbents obtained from natural materials have been investigated, some of these materials are wastes or their derivatives, such as chitosan obtained from shrimp shells and other crustaceans [27,28], coconut fiber [29,30], water hyacinth fiber [31], soybean [32], orange peel [33], banana peel [34,35], and eggshell (ES). Eggshell (ES) has been used as adsorbent due to its structural characteristics; approximately 12% of egg weight...
is provided by its shell and consists of a 94% CaCO₃, small amounts of MgCO₃, Ca₃(PO₄)₂ and a polysaccharide protein [38].

Egg consumption per capita per annum varies from country to country for example in Mexico was 321 in the 2002; this is because Mexican population consumes large quantities of eggs [39]. Barceló et al. [40] showed that leachate previously oxidized by Fenton reaction can be adsorbed on eggshell (ES), achieving a significant pollutant load reduction and leading simultaneously to relevant economic advantages since ES is much cheaper than AC. Using this bio-adsorbent also allows reduction in solid waste, supporting the Mexican regulations on waste disposal [41,42]. Thus, the aim of this work is to evaluate leachate treatment through an advanced oxidation process by Fenton reaction, followed by two adsorption consecutive processes with ES and AC in batch scale.

2. MATERIALS AND METHODS

2.1 Leachate Sampling and Characterization

Two raw leachate (RL) samples were obtained in a landfill located in a municipality of the State of Mexico, Mexico, in two different sampling moments: March, 2012 (dry season) and October, 2012 (after end of rainy season). The pH, conductivity and temperature were measured in situ with an interface Lab Quest (Vernier, USA), using the corresponding electrodes. Total carbon (TC), inorganic carbon (IC) and organic carbon (OC) were determined with a carbon analyzer multi NC 3000 (Analytik Jena, Germany). BOD was measured using an incubator model FOC225E Sensor System 10 (VELP, Italy). Al, Ca, Cd, Cu, Pb, Fe, K, and Mn were determined with atomic absorption spectrometry with an interface Lab Quest (Vernier, USA) reacted with FeSO₄·7H₂O (Baker, USA) and H₂O₂ (30% v/v) (Baker, USA), followed by centrifugation at 1500 rpm in a centrifuge model Allegra 21 (Beckman Coulter, USA) for each reaction time. Reaction times tested were: 15 min, 30 min, 45 min, 1 h, 2 h, 3 h and 5 h. The best reaction time, were after 15 min, this time period was used in all experiments and optimal [Fe²⁺]/[H₂O₂] relation was 0.1. Subsequently, a fine study was conducted with deviations of±0.025 for relations of 0.05, 0.075, 0.125 and 0.15 considering 0.1 ratio of the first relationships studied; this was in order to determine the ideal ratio to be used in adsorption process. Same conditions of centrifugation and time reaction were used.

One gram of chitosan by 100 mL of oxidized leached (OL) was added for purpose to coagulate, accelerate and improve the sedimentation, with this step a good separation of supernatant from sludge was achieved; since the separation of hydrated iron oxide as a colloid is difficult and incomplete. The supernatant was filtered through a 1 micron filter (Whatman GF/B grade).

2.2.2 Fe²⁺ and Fe³⁺ determination from sludge of Fenton process

In order to identify and quantify the amount of Fe²⁺ in the sludge resulting from Fenton process, which served for determining the oxidation efficiency of leached RL, a solution of NH₄SCN (JT Baker, USA) reacted with Fe⁷⁺ producing a red complex ([Fe(SCN)]₆)³⁻. One calibration curve was constructed using standard solutions of Fe²⁺ with a wavelength 460 nm [44] and measured by
UV-vis photo colorimetry, model UV-160A (Shimadzu, Japan). Total iron was measured by atomic absorption spectrophotometer, model SOLAAR M6 (Thermo Elemental, England) flame method, the sample was prepared prior microwave acid digestion in a model 5 (MARS, USA) and Fe$^{2+}$ concentration was determined by difference of total iron concentration minus the concentration of Fe$^{3+}$.

2.3 Adsorption of Leachate in Eggshell (ESL)

2.3.1 Eggshell (ES) characterization

The ES was donated by a food company. The structure and composition of ES was carried out with electron microscopy with JSM-6610 LV (JEOL, Ltd., USA) microscope. Surface area and porosity was calculated by isotherm Brunauer-Emmett-Teller (BET) in ASAP 2020 equipment (Micromeritics, USA).

2.3.2 ES particle size selection

ES washed with neutral Extran® (Merck, USA), dried at 60°C, ground and sieved in mesh Tyler type (WS Tyler Incorporated, USA). After this procedure, the +100 mesh particles (150 µm) and +325 (44 µm) were selected. With 2±0.076 g of each ES size, using 15 mL of leachate in each test, in a shaker, model Lab-line, USA, the samples stirred for 4 h at 25°C and 100 rpm. Tests were carried out in triplicate.

2.3.3 Using constant weight of ES

In order to obtain the ES saturation surface, tests with constant ES weight performed with the leachate obtained from second sampling. An ES weight of 2±0.74 g and an OL volume of 40 mL, were stirred at 200 rpm and 25°C with contact times of 2 h, 4 h, 7 h, 10 h, 24 h, 48 h, 72 h and 80 h. The tests performed in triplicate; Freundlich and Temkin isotherms were calculated. Liquid resulting after adsorption with AC it was called (ACL).

3. RESULTS AND DISCUSSION

3.1 Leachate Characterization

In Table 1, it is shows the result of characterization untreated leachate (RL) for two sampling. According to Ramírez-Sosa et al. [13] and Baun et al. [45], leachates contain a great number of compounds, many of which are persistent, such as: (4-methyl-phenol, 2,4-bis(1,1-dimethylethyl)-phenol, 4,4’-(1-methylethylidene) bis-phenol, ketones (pentoxifylline), alcohols (benzyl alcohol), terpenoids (terpinhydrate) and pyridines (3-(1-methyl-2-pyrrolidinyl)-(S)-pyridine). These compounds are considered potentially toxic according to Mexican Standard NOM-052-SEMARNAT-2005 [46].

Leachate treated by Fenton adsorption RL had an average pH of 8.43±0.34; this value is characteristic of mature leachate [47]. In the landfill, where the samples were collected, only is used a big leachate pond where they unload leachate of all cells regardless age of leachate.

Table 2 shows metals concentrations in RL; it can be noted that none of the metals analyzed exceeded the established Mexican Standard for wastewater discharges or reuse [41].
Table 1. Untreated leachate (RL) characterization

<table>
<thead>
<tr>
<th>Parameter</th>
<th>First sampling</th>
<th>Second sampling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>19.52±0.67</td>
<td>16.30±0.35</td>
</tr>
<tr>
<td>pH</td>
<td>8.33±0.58</td>
<td>8.53±0.40</td>
</tr>
<tr>
<td>COD (mgO₂/L)</td>
<td>8040.08±381.00</td>
<td>790.11±25.80</td>
</tr>
<tr>
<td>BOD (mgO₂/L)</td>
<td>4780.00±174.00</td>
<td>4686.04±145.00</td>
</tr>
<tr>
<td>OC (mg/L)</td>
<td>3465.00±100.65</td>
<td>3001.21±71.09</td>
</tr>
<tr>
<td>IC (mg/L)</td>
<td>461.07±22.43</td>
<td>394.13±19.32</td>
</tr>
<tr>
<td>TC (mg/L)</td>
<td>3926.14±123.76</td>
<td>3395.12±176.55</td>
</tr>
<tr>
<td>Conductivity (µs/cm)</td>
<td>392.00±21.68</td>
<td>323.70±14.74</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>46.99±2.13</td>
<td>55.72±3.01</td>
</tr>
</tbody>
</table>

Table 2. Metals concentrations in RL

<table>
<thead>
<tr>
<th>Metal</th>
<th>First sampling (mg/L)</th>
<th>Second sampling (mg/L)</th>
<th>Permitted limit (mg/L)</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca (mg/L)</td>
<td>32.78±1.127</td>
<td>20.64±1.028</td>
<td>400</td>
<td>FAO[48]</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>16.46±0.31</td>
<td>10.84±0.27</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>4.08±0.065</td>
<td>3.65±0.075</td>
<td>5.0</td>
<td>Canadian water quality guidelines for the protection of agriculture [49]</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>3.52±0.076</td>
<td>2.48±0.098</td>
<td>5</td>
<td>Canadian water quality guidelines for the protection of agriculture [49]</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>0.85±0.003</td>
<td>0.73±0.002</td>
<td>4</td>
<td>Mexican water quality guidelines for agriculture [49]</td>
</tr>
<tr>
<td>Mn (mg/L)</td>
<td>0.18±0.009</td>
<td>0.16±0.006</td>
<td>0.2</td>
<td>Mexican water quality guidelines for the protection of agriculture [49]</td>
</tr>
<tr>
<td>Ni (mg/L)</td>
<td>0.48±0.025</td>
<td>0.51±0.022</td>
<td>2</td>
<td>Mexican water quality guidelines for agriculture [49]</td>
</tr>
<tr>
<td>Cd (mg/L)</td>
<td>N.D.</td>
<td>N.D.</td>
<td>0.2</td>
<td>Mexican water quality guidelines for the protection of agriculture [49]</td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>N.D.</td>
<td>N.D.</td>
<td>0.5</td>
<td>Mexican water quality guidelines for the protection of agriculture [49]</td>
</tr>
</tbody>
</table>

*ND: Not detected by flame method; detection limit 0.04 mg/L for Cd and 0.07 mg/L for Pb

For liquid obtained after adsorption (ESL) on ES, the metals analysis performed by atomic absorption using a graphite furnace, the results are given in Table 3.

Table 3. Metals concentration in the liquid leachate after adsorption in ES

<table>
<thead>
<tr>
<th>Metal</th>
<th>First sampling (µg/L)</th>
<th>Second sampling (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca (mg/L)</td>
<td>20.02±0.62</td>
<td>17.21±0.74</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>11.16±0.56</td>
<td>22.04±0.84</td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>1.13±0.03</td>
<td>0.77±0.04</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>2.4±0.04</td>
<td>1.33±0.05</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>0.24±0.06</td>
<td>0.19±0.05</td>
</tr>
<tr>
<td>Mn (mg/L)</td>
<td>1.4±0.07</td>
<td>1.03±0.04</td>
</tr>
<tr>
<td>Ni (mg/L)</td>
<td>0.14±0.03</td>
<td>0.17±0.04</td>
</tr>
<tr>
<td>Cd (mg/L)</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

Concentrations of Ca, K, Al and Fe were lower in ESL than in RL, which indicates that a part of these metals could remain in the sludge and the other could be adsorbed on the ES.

IR spectrum results are presented in Fig. 1 and chromatograms results in Fig. 2 of: RL (1a and 2a), OL (1b and 2b), ESL (1c and 2c) and ACL (1d and 2b) respectively. In IR spectra is shown appearance and disappearance of peaks that represent functional groups. Three peaks remained all time throughout treatment process, whose values are 3331.38, 2108.00 and 1633.99 cm⁻¹. In the oxidation step more peaks appeared, probably due to fragmentation of large molecules, where some of them were adsorbed by ES and adsorption was continued by AC.
In Fig. 2 are represented chromatograms of leachate throughout the treatment process. In Fig. 2a is shown chromatogram of RL, where could be identified by mass spectroscopy, compounds in aromatic region for nonpolar compounds. Some of these compounds identified in RL were: 3-(1-methyl-2-pyrrolidinyl)-(S)-pyridine, 2,4-bis(1,1-dimethylethyl)-phenol, 4,4’-(1-methylethyliden)bis-phenol, Tricosane, Pentoxifyllina, Ácido mono(2-ethylhexil) ester 1,2-benzendicarboxilic and Cholestanol. In Fig. 2b, in the leachate after oxidation (OL), appear several peaks, which probably are aromatic molecules broken. In Fig. 2c, chromatogram of EGL is presented, after adsorption in ES, one can observe as decrease the amount of compounds contained on leachate. Finally in Fig. 2d, chromatogram ACL is showed, which is the liquid obtained after adsorption on activated carbon. One can observe the presence of a single peak which apparently represents a compound that was not degraded, but final solution is transparent, see Fig. 14e.

3.2 Leachate Oxidation by the Fenton Reaction

3.2.1 Optimization of the [Fe²⁺]/[H₂O₂] relationship

After pH adjustment of the RL with concentrated H₂SO₄ to a value of 3, organic matter (measured as TOC) decreased from 3465±101 mg/L to 2292±98 mg/L and COD decreased 49%. Fig. 3 shows the profile of the resulting curve by plotting the different [Fe²⁺]/[H₂O₂] relationships versus OC concentration. According to data in Fig. 3, the best TOC degradation was obtained when this relation was about 0.1.

Fig. 4 shows that [Fe²⁺]/[H₂O₂] relationship over 0.6 have a white color, which implies Fe(OH)₂ precipitation due to a Fe²⁺ excess. The reaction can be considered as follows:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^+ + \text{HO}^- \quad (5)
\]

\[
\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \downarrow \quad (6)
\]

Fig. 1. 1a. RL, IR spectrum. 1b. OL, IR spectrum. 1c. ESL, IR spectrum. 1d. ACL, IR spectrum
When used 0.125 for \([\text{Fe}^{2+}] / [\text{H}_2\text{O}_2]\) relation, greatest removal of organic carbon (OC) was obtained, since there was no excess of Fe\(^{2+}\), thereby avoiding the formation of Fe(OH)$_2$. Fig. 5. In order to determine the conversion degree of Fe\(^{2+}\) to Fe\(^{3+}\), the sludge was analyzed at each ratio tested of \([\text{Fe}^{2+}] / [\text{H}_2\text{O}_2]\). The results of these analyzes indicated that 0.125 relation showed the highest conversion of Fe\(^{2+}\) to Fe\(^{3+}\) (96.48%). Considering this ratio and knowing the amount of TOC present in the leachate, three tests more were effected: 5 mL, 10 mL and 15 mL of H$_2$O$_2$ (30%) respectively and one equivalent of Fe\(^{2+}\) of 0.399 g, 0.799 g and 1.198 g (using FeSO$_4$·7H$_2$O), respectively, in order to maintain this relationship in oxidation of leached. A volume of 20 mL of pH adjusted leachate (AL) was used and reaction occurred during one hour.

During Fenton oxidation reaction, the pH decreased to 2 (Fig. 6a), where optimum H$_2$O$_2$ amount was 2.0384 mg/L of OC per 1 mL of H$_2$O$_2$. 

![Fig. 2. 2a. RL chromatogram, 2b OL chromatogram, 2c. EGL chromatogram. 2d. ACL chromatogram](image)

![Fig. 3. Determination of \([\text{Fe}^{2+}] / [\text{H}_2\text{O}_2]\)](image)

![Fig. 4. Sludge obtained by centrifugation of different \([\text{Fe}^{2+}] / [\text{H}_2\text{O}_2]\) relationship](image)
With higher reaction rate, was possible to reduce the time for high organic matter degradation. In this experiment the OC removal increased at 15 min and remained nearly constant after 60 min, Fig. 6b.

The added chitosan accelerated sedimentation of sludge produced in oxidation of adjusted leached (AL). During the Fenton oxidation step, the COD removal achieved was 77%, with a [Fe^{2+}]/[\text{H}_2\text{O}_2] ratio of 0.125 at pH 2. This removal was greater than that obtained by Cortez et al. [50], which was 60.9% with a relationship [Fe^{2+}]/[\text{H}_2\text{O}_2] of 0.3. Moreover, the removal obtained in this study was similar to that obtained by Mahmud et al. [51], whose removal was 78.7%, with an [Fe^{2+}]/[\text{H}_2\text{O}_2] ratio optimized of 0.8 at pH 5, but with the advantage that relationship 0.125 and pH=2 the oxidation of Fe^{2+} to Fe^{3+} is optimized and allowing complete oxidation of AL and Fe^{2+}, without appearance of white colloidal Fe^{2+}, as seen in Fig. 4. Hermosilla et al. [19] made a leachate treatment by Fenton and photo-Fenton, with a removal of approximately 80%, but there are spending of electrical energy. In order to reduce costs, authors like [52] investigated the process by solar photo-Fenton, however in our research was not applied because its efficiency is affected by acidification of the leachate, as well as weather conditions, especially the incidence of sunlight. The authors of this paper instead use photo-Fenton or solar photo-Fenton, completed this treatment by adsorption on eggshells and activated carbon, achieving a total removal of 96.61%.

3.3 Adsorption of Leachate after Oxidation by the Fenton Reaction

3.3.1 ES characterization

Structure and composition of ES, it has been determined by means of X-ray and SEM spectroscopy, the X-ray results are shown in Fig. 7a, where the main component of ES is CaCO_3 calcite type. SEM in Fig. 7b shows ES with porous structures joined by proteins. Surface area of ES bio-adsorbent was 2.96±0.124 m²/g.

3.3.2 Selection of the particle size of ES

Table 4 shows concentrations of COD, OC, IC and TC obtained in liquid before adsorption, using different particle sizes of ES as adsorbent of leachate OL. The results in Table 4 indicate that ES is a residue capable of adsorbing contaminants present in leachate pretreated by Fenton and pH adjusted. The best COD, OC, IC and TC concentrations decreased with +325 mesh particle size used; It is important to note that the components of the raw leachate contain highly toxic compounds, determined as COD, it is recommended prior Fenton oxidation for to eliminate most of these compounds. To directly use ES without previous oxidation process of leachate could be transformed into highly dangerous solid waste and is not the purpose of their use.

It is important to note that at final with eggshell adsorption, result a solution, (ESL) with pH= 6.9±0.34, thus adsorption step with ES has advantage of increasing in situ the pH without adding any basic reagent.

3.3.3 Use of constant ES weight

In order to measure the removal rate of organic matter (OM) and inorganic matter (IM) measured as COD and the time at which equilibrium is reached, studies of the adsorption kinetics with adsorbent ES, were conducted. In Fig. 8, it presents the ratio of adsorbate at equilibrium (qe) against the contact time, where variation of the adsorptivity to different contact times is observed. The COD adsorption was very fast in the first 10 hours, subsequently equilibrium was reached and maintained until the 14 hours; finally a phase without COD removal is presented, decreasing with a contact time prolonged, reaching the saturation of ES surface, until that desorption is presented. For this experimental phase were used 2±0.74 g of ES and 40 mL of OL.

3.3.4 Usage of variable ES weight

In order to obtain the ES adsorption isotherms, experiments with variable ES weight were carried out as indicated in section 2.3.3, thus, adsorbent
Fig. 6. 6a. OC reduction and pH values with various amounts of $H_2O_2$ reacting with 20 mL of AL. 6b. Different times of reactions for OC removal

Fig. 7. 7a. Eggshell x-ray diffraction, 7b. Eggshell scanning electron microscopy (SEM)

Table 4. Concentrations of COD, OC, IC and TC obtained in liquid after adsorption with ES using +100 mesh and +325 mesh

<table>
<thead>
<tr>
<th>Material</th>
<th>COD (mg/L)</th>
<th>OC (mg/L)</th>
<th>IC (mg/L)</th>
<th>TC (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RL</td>
<td>8 04±381</td>
<td>3 47±101</td>
<td>46±22</td>
<td>3 926±124</td>
</tr>
<tr>
<td>ES particle size: &gt;150 µm (100 mesh)</td>
<td>5 06±273</td>
<td>1 84±84</td>
<td>238±10</td>
<td>2 074±88</td>
</tr>
<tr>
<td>ES particle size: &gt;44 µm (325 mesh)</td>
<td>4 25±178</td>
<td>1 64±80</td>
<td>227±11</td>
<td>1 867±93</td>
</tr>
</tbody>
</table>

pseudo-second-order, where the equilibrium time was reached. Figs. 10a and 10b show the linearity which was presented in each of adsorption kinetics. For kinetics pseudo first order is assumed that the adsorption rate is proportional to the number of free sites [54]. It is based on the difference between concentration of the adsorbate at equilibrium and at time t.

3.3.5 Kinetics of pseudo first order and pseudo second order in ES adsorption

Zamora, [22] Obtained, two kinetic adsorption for first 10 hours, a pseudo-first-order and other

\[
\frac{dq}{dt} = k_1(q_e - q)
\]
\[ \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \]  

(2)

Where \( k_1 \) (h\(^{-1}\)) is the adsorption constant kinetics of pseudo-first-order, \( q_e \) and \( q_t \) (mg/g) are the amount of adsorbate at equilibrium and at time \( t \) respectively.

For pseudo-second-order kinetics is assumed that adsorption mechanism follows a second order, where adsorption rate is proportional to square of the number of unoccupied sites [54]. This kinetic can be represented in equation 3, according Ho and McKay [55], whose linearization is indicated in equation 4.

\[ \frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \]  

(3)

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \]  

(4)

Where \( k_2 \) (hg/mg) is the adsorption constant kinetics of pseudo-second-order, \( q_e \) and \( q_t \) (mg/g) are amount of adsorbate at equilibrium and at time \( t \) respectively.

Indicated in Fig. 10 the graphs for kinetic pseudo-first-order (10a) and pseudo-second-order (10b).

Table 5 shows results of adsorption kinetics for ES adsorbent, at controlled temperature of 25\(^\circ\)C. Factor linear correlation was higher for pseudo-second-order kinetic equal to 0.9966, with \( q_e \) equal to 19.7628, so that adsorption process with CH will be better adjusted to this kinetics; the adsorption system is apparently chemisorption [56].
Table 5. Constantes de la cinética de adsorción de la CH

<table>
<thead>
<tr>
<th>Pseudo-primer-orden</th>
<th>Pseudo-segundo-orden</th>
</tr>
</thead>
<tbody>
<tr>
<td>R²</td>
<td>R²</td>
</tr>
<tr>
<td>qₑ (mg/g)</td>
<td>qₑ (mg/g)</td>
</tr>
<tr>
<td>k₁ (h⁻¹)</td>
<td>k₂ (g/mgh)</td>
</tr>
<tr>
<td>0.9007</td>
<td>0.9966</td>
</tr>
<tr>
<td>15.5203</td>
<td>19.7628</td>
</tr>
<tr>
<td>0.4864</td>
<td>0.0488</td>
</tr>
</tbody>
</table>

Furthermore qₑ value for pseudo-first-order kinetic was 15.5203, with factor linear correlation of 0.9007; see Table 5. Although it’s value less than pseudo-second-order could be acceptable, indicating that entire adsorption process also this kinetics could happen. This could be explained considering that leachate are constituted by a mixture of molecules with different nature and sizes, where in Fenton oxidation process may form substances of different sizes, for example, molecules break may occur and compete for active sites of this adsorbent, where most follow a pseudo second order kinetics and other in lesser extent follow pseudo-first-order.

3.3.6 Adsorption isotherms Freundlich and Temkin for ES

Three average Freundlich isotherms were obtained (Fig. 11a). The Freundlich expression is described as:

\[
\frac{X}{M} = k_F C_{eq}^{1/n}
\]  

(5)

Where:

- \(X\): Difference between initial concentration and equilibrium concentration at each time multiplied by volume in liters LF.
- \(M\): Adsorbent weight in grams.
- \(k_F\): Constant related to adsorption capacity (mg/g).
- \(C_{eq}\): Equilibrium concentration of the adsorbate in solution after adsorption (mg/L).
- \(1/n\): Parameter related to adsorption intensity.

Freundlich linearized equation:

\[
\log \left( \frac{X}{M} \right) = \log k_F + \frac{1}{n} \log C_{eq}
\]  

(6)

The values found for Freundlich isotherms were: for first isotherm, \(n = 4.621\) and \(k_F = 1.917\); for second isotherm, \(n = 5.084\) and \(k_F = 2.155\); and for third isotherm, \(n = 4.762\) and \(k_F = 1.912\). The \(R^2\) values obtained for each Freundlich isotherm are acceptable.

According to Namasivayam et al. [57], for \(n\) values higher than 1 indicate that the adsorption process is heterogeneous and is not limited to monolayer formation; this means that in this experiment occurred a multilayer adsorption and the application the model Langmuir was not efficient, hence, it was not considered for this paper. El Nemr et al. [58] consider when \(n=1\), adsorption is linear, if \(n<1\) the adsorption process is chemisorption and if \(n>1\), is physisorption; in this case, \(n\) is greater than 1 then ES is an adsorbent which allows physisorption predominantly.

Considering the values of \(1/n\) and \(k_F\) obtained from the Freundlich isotherms; then Temkin isotherms were determined (Fig. 11b). The Temkin isotherm contains a factor that takes into account explicitly the adsorbent-adsorbate interactions. This model assumes, on the one hand, that heat of adsorption (bt) of molecules present on adsorbent surface decreases linearly with coverage due to adsorbent-adsorbate interactions which maintain a close relationship with temperature, and, on the other hand, indicates that adsorption is characterized by a uniform distribution of binding energies related to affinity adsorbate-adsorbent [59,60].

The Temkin equation is described as:

\[
\theta = \frac{RT}{b_t} \ln(AC_{eq})
\]  

(7)

Where:

- \(T\): Absolute temperature in Kelvin degrees
- \(R\): Ideal gas constant, 8.314 J/mol° K.
- \(b_t\): Constant related to adsorption heat.
- \(A\): Equilibrium constant (L/min) corresponding to maximum energy of system.

The Temkin equation can be written in linear way to determine the constants:

\[
\theta = B L_n A + B L_n C_{eq}
\]  

(8)

Where:

- \(B\): \((RT)/b_t\) and is related to temperature and heat of adsorption
- \(T\): Absolute temperature in Kelvin degrees.
- \(R\): Ideal gas constant, 8.314 J/mol° K
*b*: Constant related to adsorption heat.
*A*: Equilibrium constant (L/min) corresponding to maximum energy required.

Fig. 11 are Freundlich Isotherms (Fig. 11a) and Temkin Isotherms (Fig. 11b) to three replicates in each case, varying in both the mass of adsorbent. Fig. 11b indicates that Temkin isotherm describes the ES adsorption a bit better than Freundlich isotherm; according to results of R² correlations, which were closer to 1 with Temkin isotherm that with Freundlich isotherm, Fig. 11a.

Table 6 lists the values of constants B, A and bt, for three Temkin isotherms, where the values are similar for each constant. The bt values for leachate adsorptions are greater than in the case of those obtained by Hameed et al. [59] with coconut bunch waste. This may be due that components of leached already oxidized are less in number or sizes smaller due to degradation by strong oxidation Fenton and they have more affinity to the bio-adsorbent on the one hand by varying weight there are greater surface area and greater adsorption because there is greater number of active sites.

Despite that ES has a small surface area is to suitable bio-adsorbent for the species contained in the oxidized leachate. This is confirmed by the adsorption percentage of 51%, and isotherm Type II, characteristic of little superficial area of ES.

To final ES adsorption process, eggshell was analyzed, getting 929.20 mg/g of Fe³⁺ and 302.60 mg/g of Ca²⁺. Further, in view that ES contains CaCO₃, residue resulting can be applied to soils deficient in Fe and Ca as well as to acid soils, for example for floriculture, no for food agriculture, according to the specifications in the Mexican Standard NOM-021-SEMARNAT-2000 [61].

### Table 6. Values of constants Temkin isotherms

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>A</th>
<th>bt (joule/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₁</td>
<td>1.220</td>
<td>A₁ = 0.896</td>
<td>bt₁ = 2026.17</td>
</tr>
<tr>
<td>B₂</td>
<td>1.122</td>
<td>A₂ = 1.481</td>
<td>bt₂ = 2203.02</td>
</tr>
<tr>
<td>B₃</td>
<td>1.140</td>
<td>A₃ = 1.043</td>
<td>bt₃ = 2168.50</td>
</tr>
</tbody>
</table>

### 3.3.7 ES amount required for leachate treatment

In order to calculate the amount of ES as adsorbent for oxidized leachate, is used the following equation [62]:

\[
m = \frac{C_o - C_e}{k_F C_o^{1/n}}
\]

Where:

- \(m\): Support mass
- \(n\): Treated liquid volume
- \(C_o\): Initial concentration
- \(C_e\): Final concentration
- \(k_F\): Constant related to adsorption capacity (mg/g)
- \(1/n\): Parameter related to adsorption intensity

The values obtained for \(1/n\) and \(k_F\) of Freundlich isotherm for ES adsorption were 0.207 and 1.995, respectively; with these values the required amount of ES was calculated. According to equation 9, 108 g of ES per liter of OL was necessary.
3.4 Using AC as Complementary Treatment

For complying with Mexican Standard NOM-001-SEMARNAT-1996 [41], additional treatment was necessary. As stated in the methodology, lignitic AC was selected because it contains macropores and mesopores. Fig. 12 depicts the time versus Ceq for EL adsorbed on AC; also, it can be inferred that lignitic AC is a good adsorbent, because at 24 hours the 67% COD was adsorbed. It becomes plain that the AC comprises macropores and mesopores, thus adsorption curve displayed two stages: During the first, that lasted approximately 4 hours, adsorption is fast, indicating the saturation of active centers with determined pore size. In the second step, the adsorption becomes slower thus indicating the saturation of active centers different from those of the first stage.

B, A and bt values are shown in Table 6, where the latter’s absolute values obtained for AC are much higher than those obtained in experiments with ES (Table 7), showing that AC has a large area of adsorption.

3.4.1 Isothermas de adsorción de Freundlich y Temkin para AC

For the adsorption on AC, Freundlich isotherms and Temkin isotherms were determined. Figs. 13a and 13b show the results of behavior each isotherm. The R² values were appropriate for Freundlich isotherms (Fig. 13a); indicating that adsorption process is not limited to monolayer formation. Furthermore, it predicts that the adsorbate concentration on the adsorbent increases when the latter’s concentration increases. The values of n greater than 1 (14.7, 13.4, 10.5) indicate that the adsorption was favorable [63]. When Temkin isotherms were calculated (Fig. 13b), they had a better fit than Freundlich isotherms.

<table>
<thead>
<tr>
<th>B</th>
<th>A</th>
<th>bt (joule/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B_1 )</td>
<td>( A_1 )</td>
<td>( bt_1 )</td>
</tr>
<tr>
<td>(-0.661)</td>
<td>(2.0333 \times 10^{-9})</td>
<td>(-3746.51)</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>( A_2 )</td>
<td>( bt_2 )</td>
</tr>
<tr>
<td>(-0.676)</td>
<td>(8.5247 \times 10^{-9})</td>
<td>(-3664.21)</td>
</tr>
<tr>
<td>( B_3 )</td>
<td>( A_3 )</td>
<td>( bt_3 )</td>
</tr>
<tr>
<td>(-0.886)</td>
<td>(1.4300 \times 10^{-7})</td>
<td>(-2797.20)</td>
</tr>
</tbody>
</table>

Table 7. Values of the constants Temkin isotherms using a constant weight of the adsorbent AC

Fig. 13. 13a. Freundlich isotherms, 13b. Temkin isotherms
3.4.2 AC amount required for treatment

To justify the active carbon savings, the OL adsorption tests were conducted directly with this adsorbent, starting with 1727 mg/L of COD, resulting finally 852 mg/L of COD with 708 g of AC. However when ES was used (ESL) and subsequent treatment with AC, it was possible to reach the 284 mg/L of COD value, indicating the Mexican Standard NOM-001-SEMARNAT-1996 and Mexican Federal Law of Rights [41,42]. Using only 62.6 g of AC represents a saving of 92% of AC.

3.5 Efficiency of the Treatment by Fenton Oxidation-ES Adsorption

Table 8 shows the percentages of COD removal in each treatment and overall COD removal. It observed that the highest removal was obtained during the oxidation step. The complete treatment (Fenton oxidation + adsorption on eggshell + adsorption on activated carbon) allows removal 96% total COD.

Table 8. Removal of COD in the treatment

<table>
<thead>
<tr>
<th>Stage</th>
<th>COD (mg/L)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw leachate (RL)</td>
<td>7903±258</td>
<td>-</td>
</tr>
<tr>
<td>Fenton oxidized leached (OL)</td>
<td>1798±73</td>
<td>77.25±3.1</td>
</tr>
<tr>
<td>Fenton oxidized leached/ES (ESL)</td>
<td>852±31</td>
<td>52.61±2.3</td>
</tr>
<tr>
<td>Fenton oxidized leached/ES /AC (ACL)</td>
<td>284±18</td>
<td>66.67±1.6</td>
</tr>
<tr>
<td>Global removal</td>
<td>-</td>
<td>96.41</td>
</tr>
</tbody>
</table>

*Percentage removal is taken with reference to the raw leachate

Fig. 14 shows that leachate's color and turbidity decreased through the different treatment stages. Fig. 14e shows that the liquid obtained at end of treatment is completely clear. Final COD concentration and pH were 284 mg/L and 6.9 respectively. The final product obtained with the proposed treatment complies with Mexican Standard NOM-001-SEMARNAT-1996 and Mexican Federal Law of Rights [41,42], thus final liquid product can be discharged in a receptor body type A (rivers, coastal waters, soil) or reused for example in landscape irrigation.

4. CONCLUSIONS

Due to the characteristics of leachate, it selected a high capacity process of oxidation like Fenton and it allowed the presence of highly oxidative radicals (HO•, HOO•); for this reason was necessary a pH adjustment and also of relationship [Fe$^{2+}$]/[H$_2$O$_2$] to prevent a Fe$^{2+}$ excess; at this stage the highest COD removal was reached. The adsorption process as continuation of leachate treatment, allowed a more complete removal of COD. Within this process, eggshell used as adsorbent provides several advantages: the first is the reuse of a waste material, also its composition allowed in situ pH adjustment without using additional reagents for this purpose.

Finally, it obtained savings associated with utilization of AC, which used only as a complementary treatment and not as the main adsorbent. ES adsorption profile presented a type II isotherm and the values obtained better adjusted to the Temkin isotherm. With the treatment proposed, in this research an important COD removal obtained enabling compliance with the Mexican Standard NOM-001-SEMARNAT-1996 and Mexican Federal Law of Rights for discharges in natural water bodies.
COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES


41. SEMARNAT. Secretaría de medio ambiente y recursos naturales, Mexican standard NOM-001-SEMARNAT-1996: maximum permissible limits of pollutants in


59. Hameed BH, Mahmoud DK, Ahmad AL. Equilibrium modeling and kinetic studies on the absorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste; 2008.

60. Senthil P, Ramalingam S, Senthamarai C, Niranjanaa M, Vijayalakshmi P, Sivanesan S. Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and

