

# LEACHATE TREATMENT BY FENTON OXIDATION AND ADSORPTION ON EGGSHELL AND ACTIVATED CARBON

## ABSTRACT:

The aim of this work was to evaluate leachate treatment through a Fenton advanced oxidation process with subsequent adsorption on eggshell (ES) and activated carbon (AC). Leachate from a landfill it treated by Fenton oxidation followed by adsorption with eggshell bioadsorbent and completed with activated carbon. Area of Environmental Chemistry and Physical Chemistry, University Autonomous Metropolitan-Azcapotzalco, between January 2012 and October 2014. Leaching crude previously characterized was oxidized by Fenton, optimizing the relation  $[Fe^{2+}]/[H_2O_2]$  with pH adjustment; followed by adsorption with eggshell by Batch technique with selection of particle size. The treatment was completed with activated carbon adsorbent, for both adsorbents surface area is measured and oxidized leached is characterized after each adsorption. Finally Freundlich and Temkin isotherms were obtained. During oxidation process an optimum relationship  $[Fe^{2+}]/[H_2O_2]$  of 0.125 was found. Adsorption on eggshell showed a profile close to Type II isotherm, which confirmed by scanning electron microscopy and X-ray diffraction. The Freundlich and Temkin isotherms were calculated, where the latter presented the best fit. With adsorption on eggshell, a good removal of COD was achieved, saving the use of activated carbon in all process of adsorption, also from the environmental point of view the reuse of eggshell is take advantage of a residue. The liquid finally obtained all treatment complied with Mexican Standard NOM-001-SEMARNAT-1996.

*Keywords: Eggshell, Activated Carbon, Advanced Oxidation, Isotherms*

## 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, 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 [10-13]. 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 [14,15].

Fenton reaction has shown good results to treat chemical compounds difficult to degrade. This reaction where hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is used in presence of ferrous salts such as  $\text{FeSO}_4$  has been used successfully for leachates [16-20]. Barbusinski [21], proposed the following set of Fenton reactions:



The first reaction is general Fenton reaction; the chain initiation should be optimized in order to achieve the presence of important amounts of  $\text{HO}\cdot$  radicals. Ferric ion ( $\text{Fe}^{3+}$ ) and a set of oxidizing species ( $\text{HO}\cdot$ ,  $\text{HOO}\cdot$ ,  $\text{HOO}^-$  and  $\text{H}_2\text{O}_2$ ) will be present. In addition ferric ions ( $\text{Fe}^{3+}$ ) will react with hydroperoxides radicals ( $\text{HOO}\cdot$ ) and will be reduced to  $\text{Fe}^{2+}$ . By the other hand,  $\text{Fe}^{2+}$  will react with  $\text{HOO}\cdot$  in excess to produce  $\text{Fe}^{3+}$ . 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 [ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ] must be optimized [16, 22]. Finally, the sludge produced should be coagulated and sedimented [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 [36, 37]. 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%  $\text{CaCO}_3$ , small amounts of  $\text{MgCO}_3$ ,  $\text{Ca}_3(\text{PO}_4)_2$  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 oxidated 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 bioadsorbent 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.

## 1. MATERIAL AND METHODS

### 2.1. Leachate Sampling and Characterization

Two raw leachate samples (RL), 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 N C 3000 (AnalytikJena, 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 spectrophotometer model SOLAAR M6 (Thermo Elemental, England) by flame and graphite furnace, previously processed by acid digestion in a microwave model 5 (MARS, USA). The COD determinate following steps: the first step was a sulfocromic oxidation using a reactor HANNA Instruments, model HI839800 (HANNA Instruments, USA) with the 5520 C Standard Methods technique; the second step was the color measurement, using the Portable Spectrophotometer HACH, model DR/2400, (Hach, USA), by 5520 D [43]. Each sample was measured in triplicate

## 2.2. Leachate Oxidation by Fenton Reaction

### 2.2.1. pH adjustment and optimization $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ratio

pH of the RL was adjusted to 3, with 8  $\mu\text{L}$  of  $\text{H}_2\text{SO}_4$  concentrated (Baker, USA) for each mL of RL; naming adjusted leachate (AL). For optimal oxidation of leachate (OL) by Fenton reaction, the relationship  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  was optimized testing several ratios (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9), using  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Baker, USA) and  $\text{H}_2\text{O}_2$  (30% v/v) (Baker, USA), followed by centrifugation for 15 minutes at 1500 rpm in a centrifuge model Allegra 21 (Beckman Coulter, USA). Using the optimized relationship  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  at different duration times: 15 min, 30 min, 45 min, 1 h, 2 h, 3 h and 5 h. The best results were found after 15 min of reaction: this time period was used in all experiments.

One gram of chitosan by 100mL 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. $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ determination from sludge of Fenton process

In order to identify and quantify the amount of  $\text{Fe}^{3+}$  in the sludge resulting from Fenton process, which served for determining the oxidation efficiency of leached RL, a solution of  $\text{NH}_4\text{SCN}$  (JT Baker, USA) reacted with  $\text{Fe}^{3+}$  producing a red complex  $[\text{Fe}(\text{SCN})_6]^{3-}$ . One calibration curve was constructed using standard solutions of  $\text{Fe}^{3+}$  with a wavelength 460 nm [44] and measured by UV-vis photocolormetry, 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  $\text{Fe}^{2+}$  concentration was determined by difference of total iron concentration minus the concentration of  $\text{Fe}^{3+}$ .

## 2.3. Adsorption of Leachate in Eggshell(EL)

### 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  $\mu\text{m}$ ) and +325 (44  $\mu\text{m}$ ) were selected. With  $2 \pm 0.076$  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  $2 \pm 0.74$  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 and 72 h.

### 2.3.4. Usage of variable ES weight

ES washed, dried at 60 °C, ground and sieved, using the +60 mesh particles (250  $\mu\text{m}$ ). 15 mL of OL were adsorbed on each ES weights:  $2.03 \pm 0.045$  g,  $3.01 \pm 0.043$  g,  $4.01 \pm 0.053$  g,  $5.03 \pm 0.049$  g,  $6.00 \pm 0.047$  g,  $6.99 \pm 0.064$  g,  $8.08 \pm 0.61$  g,  $9.02 \pm 0.077$  g, 10.23 g and  $11.33 \pm 0.057 \pm 0.101$  g, and determined from BP 221S analytical balance (Sartorius, Germany). The samples were shaken at 200 rpm on shaker, model orbit (Lab-Line, USA) for 24 hours at 25 °C. Tests carried out in triplicate at batch system. After, each sample filtered in paper Whatman GF/B grade. COD removal measured in each sample. The Freundlich and Temkin isotherms were calculated. After oxidation with Fenton and adsorption on ES, the liquid obtained was named EL.

## 2.4 Use of AC as Complement Treatment

For this step, lignitic AC was used to complete the treatment process (polish), (ALC) since it is considered a good adsorbent with a high mesopores and macropores content, according to the manufacturer Carbotecnia, Mexico. Surface area determined with isotherm Brunauer-Emmett-Teller (BET) in ASAP 2020 equipment (Micromeritics, USA). AC experiments carried out using  $2 \pm 0.08$  g of AC and 40 mL of EL leachate. Samples stirred at 150 rpm and 25 °C. Several contact times were tested: 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.

## 2. 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], 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 [45].

Table 1:Untreated leachate (RL) characterization

| Parameter                 | First sampling     | Second sampling    |
|---------------------------|--------------------|--------------------|
| Temperature (°C)          | $19.52 \pm 0.67$   | $16.3 \pm 0.35$    |
| pH                        | $8.33 \pm 0.584$   | $8.53 \pm 0.403$   |
| COD (mgO <sub>2</sub> /L) | $8040 \pm 381$     | $7903 \pm 258$     |
| BOD (mgO <sub>2</sub> /L) | $4780 \pm 174$     | $4686 \pm 145$     |
| OC (mg/L)                 | $3465 \pm 100.65$  | $3001 \pm 71.09$   |
| IC (mg/L)                 | $461 \pm 22.43$    | $394 \pm 19.32$    |
| TC (mg/L)                 | $3926 \pm 123.76$  | $3395 \pm 176.55$  |
| Conductivity (µs/cm)      | $392.6 \pm 21.678$ | $323.7 \pm 14.742$ |
| Turbidity (NTU)           | $46.99 \pm 2.128$  | $55.7 \pm 3.012$   |

While, in leachates treated by Fenton-adsorption[46], existing compounds Mono (2-ethylhexyl) ester, 1,2-benzenedicarboxylic acid and 2-chlorocyclohexanol, and none showed signs of high toxicity. RL had an average pH of  $8.43 \pm 0.34$ ; both samples are considered; this value is characteristic of mature leachate [47]. In the landfill, where the samples collected, only one leachate pond, the different cells discharged into the pond, regardless of the 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].

171 Table 2: Metals concentrations in RL

| Metal     | Firstsampling | Secondsampling | Permittedlimit (mg/L) | Standard                                                                                                               |
|-----------|---------------|----------------|-----------------------|------------------------------------------------------------------------------------------------------------------------|
| Ca (mg/L) | 32.78 ±1.127  | 20.64±1.028    | 400                   | FAO[48]                                                                                                                |
| K (mg/L)  | 16.46 ± 0.31  | 10.84 ± 0.27   | -                     | -                                                                                                                      |
| Al (mg/L) | 4.08 ± 0.065  | 3.65 ± 0.075   | 5.0                   | Canadian water quality guidelines for the protection of agriculture [49]                                               |
| Fe (mg/L) | 3 ± 0.076     | 2.48 ± 0.098   | 5                     | Canadian water quality guidelines for the protection of agriculture [49]                                               |
| Cu (mg/L) | 0.85 ±0.003   | 0.73 ± 0.002   | 4                     | Mexican standard NOM-001-SEMARNAT-1996 [41]                                                                            |
| Mn (mg/L) | 0.18 ± 0.009  | 0.16 ± 0.006   | 0.2                   | Canadian water quality guidelines for the protection of agriculture [49]                                               |
| Ni (mg/L) | 0.48 ± 0.025  | 0.51 ± 0.022   | 2                     | Mexican standard NOM-001-SEMARNAT-1996 [41]                                                                            |
| Cd (mg/L) | N.D.          | N.D.           | 0.2                   | Mexican standard NOM-001-SEMARNAT-1996 [41]                                                                            |
| Pb (mg/L) | N.D.          | N.D.           | 0.5                   | Mexican standard NOM-001-SEMARNAT-1996 and Canadian water quality guidelines for the protection of agriculture[41, 49] |

\*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 (EL) on ES, the metals analysis performed by atomic absorption using a graphite furnace, the results are given in Table 3. Concentrations of Ca, K, Al and Fe were lower in EL 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.

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

| Metal     | Firstsampling (µg/L) | Secondsampling (µg/L) |
|-----------|----------------------|-----------------------|
| Ca (mg/L) | 20.02± 0.62          | 17.21 ± 0.74          |
| K (mg/L)  | 11.16 ± 0.56         | 22.04 ± 0.84          |
| Al (mg/L) | 1.1 ± 0.030          | 0.77 ± 0.041          |
| Fe (mg/L) | 2 ± 0.044            | 1.33 ± 0.052          |
| Cu (mg/L) | 1.2 ±0.061           | 0.98 ± 0.046          |
| Mn (mg/L) | 1.4 ± 0.07           | 1.03 ± 0.040          |
| Ni (mg/L) | 1.1 ± 0.034          | 0.87 ± 0.037          |
| Cd (mg/L) | N.D.                 | N.D.                  |
| Pb (mg/L) | N.D.                 | N.D.                  |

## 3.2. Oxidation of Leachate by the Fenton Reaction

### 3.2.1. Optimization of the $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ratio

After pH adjustment of the RL with concentrated  $\text{H}_2\text{SO}_4$  to a value of 3, organic matter (measured as TOC) decreased from  $3465 \pm 101$  mg/L to  $2292 \pm 98$  mg/L and COD decreased 49%. Figure 1 shows the profile of the resulting curve by plotting the different relationships  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  versus OC concentration. According to data in Figure 1, the best TOC degradation was obtained when the ratio  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  was about 0.1.

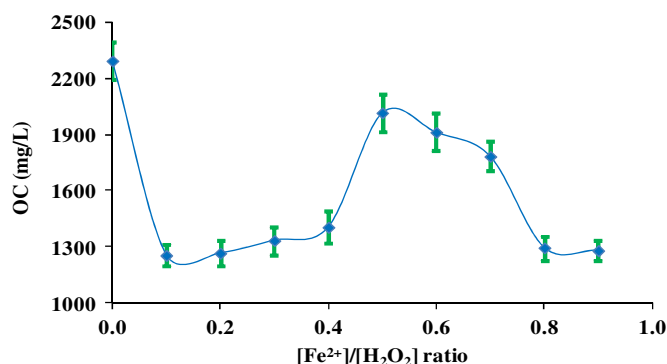


Figure 1: Determination of relationship  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ .

Figure 2 shows that relationship  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  over 0.6 have a white color, which implies  $\text{Fe}(\text{OH})_2$  precipitation due to a  $\text{Fe}^{2+}$  excess. The reaction can be considered as follows:

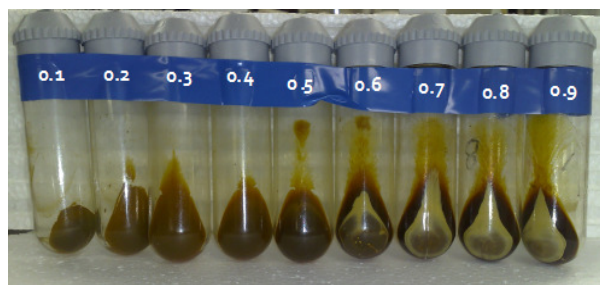


Figure 2: Sludge obtained by centrifugation of different relationships  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$

In order to get a more precise  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  ratio, values of 0.05, 0.075, 0.15 and 0.125 were evaluated. Figure 3 reveals that the greatest OC removal was obtained with a ratio  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  of 0.125, since there was no excess of  $\text{Fe}^{2+}$ , thereby avoiding the formation of  $\text{Fe}(\text{OH})_2$ . This result shows that  $\text{Fe}^{2+}$  was the limiting reagent rather than  $\text{H}_2\text{O}_2$  in this reaction.

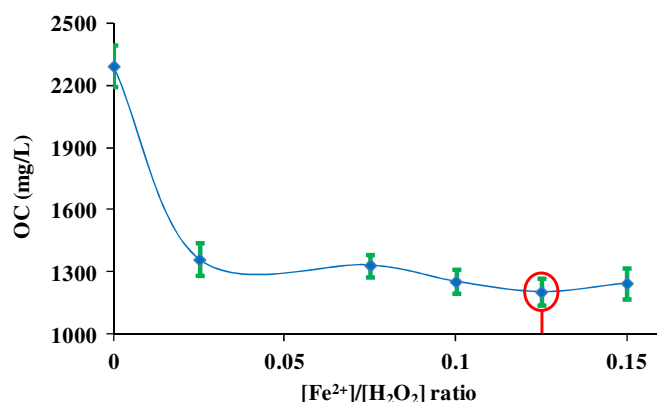


Figure 3: Determination of the ratio  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  finer.

In order to determine the conversion degree of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , 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 the 0.125 ratio showed the highest conversion (76.48%). Considering the latter  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  ratio and knowing the amount of TOC present in the leachate, three tests were added: 5 mL, 10 mL and 15 mL of  $\text{H}_2\text{O}_2$  (30%) respectively and one equivalent of  $\text{Fe}^{2+}$  of 0.399 g, 0.799 g and 1.198 g (using  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), respectively, in order to maintain this relationship. A volume of 20 ml of AL was used and the reaction occurred during one hour.

During the Fenton oxidation reaction, the pH decreased to 2 (Figure 4a), where the optimum  $\text{H}_2\text{O}_2$  amount was 2.0384 mg/L of OC per 1 mL of  $\text{H}_2\text{O}_2$ .

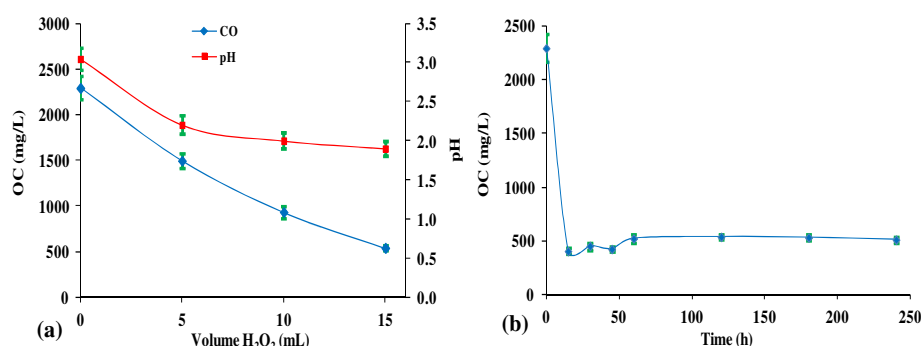


Figure 4: 4a. Reduction of OC and pH values when various amounts of  $\text{H}_2\text{O}_2$  react with 20 mL of LA. 4b. OC removal at different reaction times.

The experiments showed that the Fenton reaction is extremely exothermic, which allowed to reach a higher reaction rate thereby reducing the time needed to obtain high organic matter degradation. In this experiment the OC removal increased at 15 min and remained nearly constant after 60 min, figure 4b.

To improve the sedimentation of sludge produced was added 1g of chitosan for each 100 mL of LF. During the Fenton oxidation step, the COD removal achieved was 77%, with a  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  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  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  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  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  ratio optimized of 0.8 at pH 5. The importance of relationship  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  in RL oxidation by Fenton reaction; is confirmed with the results obtained.

An important observation is that relationship  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  to 0.125 and pH 2, allowing complete oxidation of RL and  $\text{Fe}^{2+}$ , where practically passed to  $\text{Fe}^{3+}$ , without appearance of white colloid  $\text{Fe}^{2+}$ ,

as seen in figure 2. COD removal done in this research was similar to that obtained by Hermosilla et al. [19], who treated leachate by Fenton and photo-Fenton, with a removal of approximately 80% in each treatment; however when using photo-Fenton process there are spending of electrical energy. In order to reduce costs, authors like [52] investigated the process of solar photo-Fenton, however in this research was not applied because its efficiency is affected by acidification of the leachate, as well as weather conditions, especially the incidence of sunlight.

### 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 SEM and X-ray spectroscopy, the X-ray results are shown in Figure 5a, where the main component of ES is  $\text{CaCO}_3$  calcite type. SEM in Figure 5b shows ES with porous structures joined by proteins. Surface area of ES bioadsorbent was  $2.9623 \pm 0.124 \text{ m}^2/\text{g}$ .

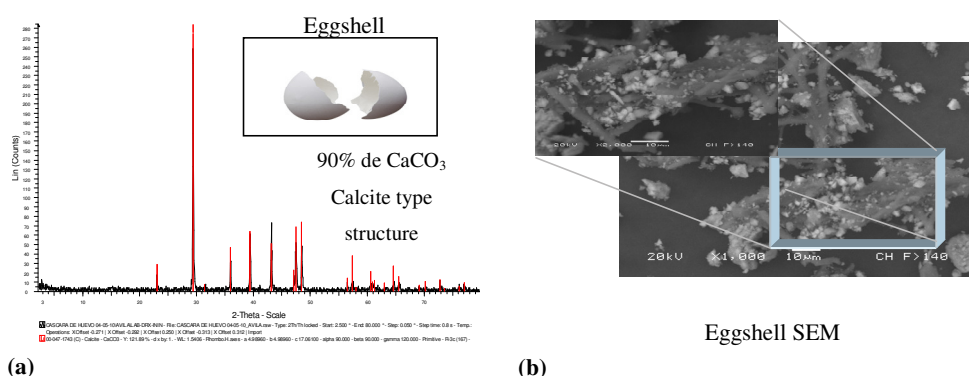


Figure 5: 5a. X-ray diffraction 5b. ES Scanning electron microscopy (SEM)

#### 3.3.2. Selection of the particle size of ES

Table 4 shows the concentrations of COD, OC, IC and TC obtained using different particle sizes of ES as adsorbent of leachate LC. 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, it is recommended prior Fenton oxidation for to eliminate most of these compounds. To directly use the eggshell without previous oxidation process of leachate, could be transformed into highly dangerous solid waste and is not the purpose of their use.

Table 4. Concentrations of COD, OC, IC and TC obtained with the ES retained on +100 mesh and +325 mesh

| Material                                     | COD (mg/L)      | OC (mg/L)       | IC (mg/L)    | TC (mg/L)       |
|----------------------------------------------|-----------------|-----------------|--------------|-----------------|
| RL                                           | 8 040 $\pm$ 381 | 3 465 $\pm$ 101 | 461 $\pm$ 22 | 3 926 $\pm$ 124 |
| ES retained in 100<br>(> 150 $\mu\text{m}$ ) | 5 058 $\pm$ 273 | 1 836 $\pm$ 84  | 238 $\pm$ 10 | 2 074 $\pm$ 88  |
| ES retained in 325<br>(> 44 $\mu\text{m}$ )  | 4 245 $\pm$ 178 | 1 640 $\pm$ 80  | 227 $\pm$ 11 | 1 867 $\pm$ 93  |

It is worth to note that at the end of the adsorption process, pH in EL was  $6.9 \pm 0.34$ ; thus adsorption step with ES had the advantage of increasing in situ the pH without adding any basic reagent.

### 3.3.3. Use of constant ES weight

Figure 6 shows that adsorption maximum time is reached at 24 h by adsorption tests performed at this time, also shows that compounds through measures COD from leachate are adsorbed into ES surface during the first 10 h with fast adsorption thereby saturating the ES surface, which may subsequently generate multilayer formation and subsequent desorption at longer times.

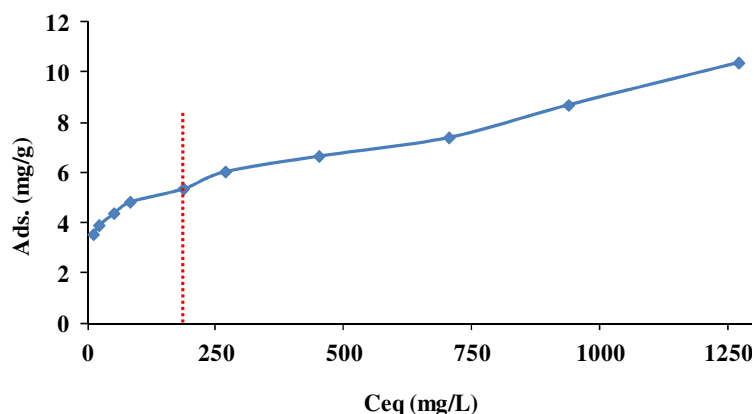


Figure 6: COD adsorbed on ES constant weight

### 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 amount (mg/g) against adsorption equilibrium concentration (Ceq) is plotted, see Figure 7. The curve obtained showed a trend of the type II, which is possibly due to the small surface area of adsorbent[53].

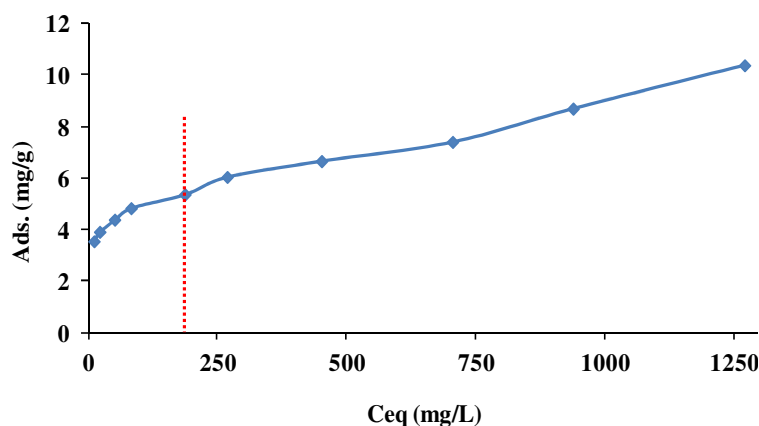


Figure 7: ES isotherm for variable weight

Three average Freundlich isotherms were obtained (Figure 8a). The Freundlich expression is described as:

$$a = \frac{X}{M} = K_F Ceq^{1/n}$$

Equation (1)

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)

Ceq: equilibrium concentration of the adsorbate in solution after adsorption (mg/L)

1/n: parameter related to adsorption intensity

Freundlich linearized equation:

$$\log \left( \frac{X}{M} \right) = \log K_F + \frac{1}{n} \log Ceq \quad \text{Equation (2)}$$

The values found for the Freundlich isotherms were: for the first isotherm,  $n = 4.621$  and  $K_F = 1.917$ ; for the second isotherm,  $n = 5.084$  and  $K_F = 2.155$ ; and for the 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. [54], 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 of the model Langmuir was not efficient, hence, it was not considered for this paper. El Nemr et al. [55] 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 (Figure 8b). 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 ( $\theta$ ) 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 [56, 57]

The Temkin equation is described as:

$$\theta = \frac{RT}{b_T} \ln (A Ceq) \quad \text{Equation (3)}$$

Where:

$T$ : Absolute temperature in Kelvin degrees

$R$ : Ideal gas constant, 8.314 J/mol $^{\circ}$ 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:

$$\theta = B \ln A + B \ln Ceq \quad \text{Equation (4)}$$

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 $^{\circ}$ K

$b_T$ : Constant related to adsorption heat.

$A$ : Equilibrium constant (L/min) corresponding to maximum energy required.

Figures 8 are Freundlich Isotherms (figure 8a) and Temkin Isotherms (figure 8b) to three replicates in each case. Figure 8b indicates that Temkin isotherm describes the ES adsorption a bit better than Freundlich isotherm; according to results of  $R^2$  correlations, which were closer to 1 with Temkin isotherm than with Freundlich isotherm, figure 8a.

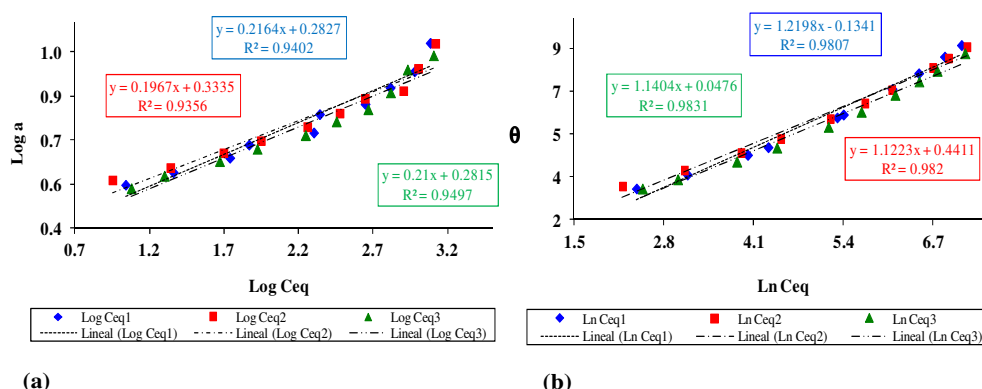


Figure 8: 8a. Freundlich isotherms. 8b. Temkin isotherms varying the mass of adsorbent ES

Table 5 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. [56] with coconutbunch 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 bioadsorbent on the one hand by varying weight there are greater surface area and greater adsorption because there is greater number of active sites.

Table 5. Values of constants Temkin isotherms

| B                      | A                      | bt (joule/mole)           |
|------------------------|------------------------|---------------------------|
| B <sub>1</sub> = 1.220 | A <sub>1</sub> = 0.896 | bt <sub>1</sub> = 2026.17 |
| B <sub>2</sub> = 1.122 | A <sub>2</sub> = 1.481 | bt <sub>2</sub> = 2203.02 |
| B <sub>3</sub> = 1.140 | A <sub>3</sub> = 1.043 | bt <sub>3</sub> = 2168.50 |

Despite that ES has a small surface area is to suitable bioadsorbent 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 929.2 mg/g of Fe<sup>3+</sup> and 302.6 mg/g of Ca<sup>2+</sup>. Further, in view that ES contains CaCO<sub>3</sub>, 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 [58].

### 3.3.5 ES amount required for leachate treatment.

In order to calculate the amount of ES as adsorbent for oxidized leachate, is used the following equation [59]:

$$\frac{m}{v} = \frac{C_o - C_e}{K_F * C_e^{1/n}} \quad \text{Equation (5)}$$

Where:

m: Support mass

v: Treated liquid volume

C<sub>o</sub>: Initial concentration

C<sub>e</sub>: Final concentration

K<sub>F</sub>: 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 5, 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. Figure 9 depicts the time versus  $C_{eq}$  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 h, 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.

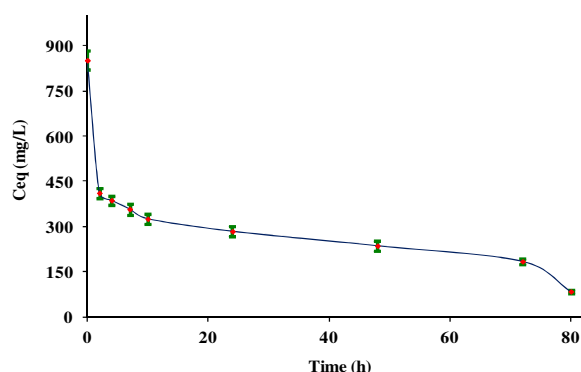


Figure 9: Time versus  $C_{eq}$  for EL, after being treatment with AC

For the adsorption on AC, Freundlich isotherm and Temkin isotherm were determined. Figures 10a and 10b show the results of behavior each isotherm. The  $R^2$  values were appropriate for Freundlich isotherm (figure 10a); 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 [60]. When the Temkin isotherms were calculated (Figure 10b), they had a better fit than the Freundlich isotherms.

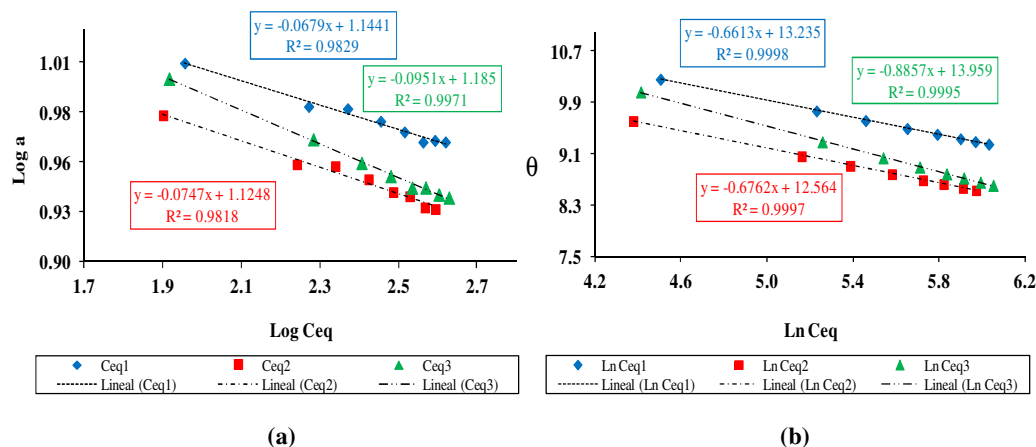


Figure 10: 10a. Freundlich isotherms. 10b. Temkin isotherms for adsorbent AC to constant weight

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 5), showing that AC has a large area of adsorption.

Table 6. Values of the constants Temkin isotherms using a constant weight of the adsorbent AC

| B               | A                   | bt (joule/mol)    |
|-----------------|---------------------|-------------------|
| $B_1 = -0.6613$ | $A_1 = 2.03329E-09$ | $bt_1 = -3746.51$ |
| $B_2 = -0.6762$ | $A_2 = 8.52467E-09$ | $bt_2 = -3664.21$ |
| $B_3 = -0.8857$ | $A_3 = 1.43001E-07$ | $bt_3 = -2797.20$ |

### 3.4.1. AC amount required for treatment.

To justify the activated 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 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-AC Adsorption

Table 7 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 7. Removal of COD in the treatment

| Stage                                     | COD (mg/L)     | Removal (%)    |
|-------------------------------------------|----------------|----------------|
| Rawleachate                               | $7903 \pm 258$ | -              |
| Fentonoxidizedleached                     | $1798 \pm 73$  | $77 \pm 3.1$   |
| Fentonoxidizedleached +chitosan           | $1727 \pm 93$  | $78^* \pm 0.6$ |
| Fenton oxidized leached +chitosan /ES     | $852 \pm 31$   | $51 \pm 2.3$   |
| Fenton oxidized leached +chitosan /ES /AC | $284 \pm 18$   | $67 \pm 1.6$   |
| Global Removal                            | -              | 96             |

\*Percentage removal is taken with reference to the raw leachate

Figure 11 shows that leachate's color and turbidity decreased through the different treatment stages. Figure 11e 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.



Figure 11: 11a. Raw leachate (RL). 11b. Leachate pH 3 (AL). 11c. Leachate Fenton oxidized (OL). 11d. Adsorbed leachate on eggshell(EL). 11e. Adsorbed EL on Active Carbon (ALC), final liquid product.

### 3. 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 ( $\text{HO}\cdot$ ,  $\text{HOO}\cdot$ ); for this reason was necessary a pH adjustment and also of relationship  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  to prevent a  $\text{Fe}^{2+}$  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.

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