



Leachate Treatment by Fenton Oxidation and Adsorption on Eggshell and Activated Carbon

E. Zamora-Villafranco¹, I. D. Barceló-Quintal^{1*}, A. Vega-Paz¹,
H. E. Solís-Correa¹, R. I. Méndez-Novelo² and G. Giacomán-Vallejos²

¹Basic and Engineering Division, Chemistry and Physical Chemistry of Environmental Area, University Autonomous Metropolitan-Azcapotzalco, Av. San Pablo 180, Col. Reynosa Tamaulipas, Azcapotzalco, Mexico DF, CP 02200, Mexico.

²Faculty of Engineering, Autonomous University of Yucatan, Av. Nonpolluting Industries Northern Beltway w/n, Merida, Yucatan, Mexico.

Authors' contributions

This work was carried out in collaboration between all authors. Author IDBQ designed the study, wrote the protocol and wrote the first draft of the manuscript. Author EZV performed the statistical analysis and analysis in general and the literature search. Authors AVP and RIMN supported in the interpretation of infrared analysis, gas chromatography-mass. Authors HESC and GGV supported in the development of kinetic studies. In general all authors supported in the review of the results, read and approved the final manuscript.

Article Information

DOI: 10.9734/BJAST/2016/28051

Editor(s):

(1) Aleksey Aleksandrovich Hlopitskiy, Department of Technology Inorganic Substances, Ukrainian State University of Chemical Technology, Ukraine.

Reviewers:

(1) Peter Anca, Technical University of Cluj Napoca, Romania.

(2) P. N. Palanisamy, Kongu Engineering College, Perundurai, Tamilnadu, India.

Complete Peer review History: <http://www.sciencedomain.org/review-history/15973>

Original Research Article

Received 30th June 2016
Accepted 3rd August 2016
Published 27th August 2016

ABSTRACT

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-Azcapotzalco, 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 $[Fe^{2+}]/[H_2O_2]$ was optimized for oxidation treatment; followed by adsorption with eggshell by the technique of batch. ES particle size was selected by

*Corresponding author: E-mail: ibarceloq@gmail.com;

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.

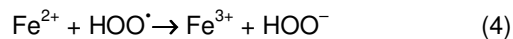
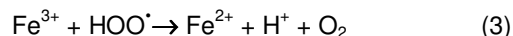
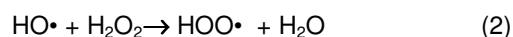
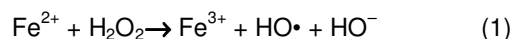
1. INTRODUCTION

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 (H₂O₂) is used in presence of ferrous salts such as FeSO₄ 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 HO• radicals. Ferric ion (Fe³⁺) and a set of oxidizing species (HO•, HOO•, HOO⁻ and H₂O₂) will be present. In addition ferric ions (Fe³⁺) will react with hydro peroxides radicals (HOO•) and will be reduced to Fe²⁺. By the other hand, Fe²⁺ will react with HOO• in excess to produce Fe³⁺. 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 [Fe²⁺/H₂O₂] 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 adsorbent is activated carbon (AC), which has a high removal efficiency (20%), but its cost is high [26]. Other adsorbents 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% CaCO_3 , small amounts of 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 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 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. Other characterization analyzes were by infrared spectroscopy (IR) in a model Nicolet iS10 Thermo Scientific and by

chromatography in a gas chromatograph coupled to mass Agilent Technologies, model 7820A GC System and 5975 Series MSD, using one HP5MS column with 30 m long by 0.25 mm, which withstands temperatures from -60 to 325°C.

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 μL of H_2SO_4 concentrated (Baker, USA) for each mL of RL; naming the adjusted leached (AL). Where oxidized leached by Fenton will be represented by (OL). Relationship $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ was optimized testing several relations (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 H_2O_2 (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 $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ 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 Fe^{2+} and Fe^{3+} determination from sludge of Fenton process

In order to identify and quantify the amount of Fe^{3+} in the sludge resulting from Fenton process, which served for determining the oxidation efficiency of leached RL, a solution of NH_4SCN (JT Baker, USA) reacted with Fe^{3+} producing a red complex ($[\text{Fe}(\text{SCN})_6]^{3-}$). One calibration curve was constructed using standard solutions of Fe^{3+} 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 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 μm). 15 mL of OL were adsorbed on each ES weights: 2.03 ± 0.045 g, 3.01 ± 0.043 g, 4.01 ± 0.053 g, 5.03 ± 0.049 g, 6.00 ± 0.047 g, 6.99 ± 0.064 g, 8.08 ± 0.61 g, 9.02 ± 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 EGL.

2.4 Use of AC as Complement Treatment

For this step, AC lignitic was used to complete the treatment process, 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 ± 0.08 g of AC and 40 mL of ESL 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. 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

Parameter	First sampling	Second sampling
Temperature (°C)	19.52±0.67	16.30±0.35
pH	8.33±0.58	8.53±0.40
COD (mgO ₂ /L)	8040.08±381.00	790.11±25.80
BOD (mgO ₂ /L)	4780.00±174.00	4686.04±145.00
OC (mg/L)	3465.00±100.65	3001.21±71.09
IC (mg/L)	461.07±22.43	394.13±19.32
TC (mg/L)	3926.14±123.76	3395.12±176.55
Conductivity (µs/cm)	392.00±21.68	323.70±14.74
Turbidity (NTU)	46.99±2.13	55.72±3.01

Table 2. Metals concentrations in RL

Metal	First sampling	Second sampling	Permitted limit (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)	3.52±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 (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

Metal	First sampling (µg/L)	Second sampling (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)	1.13±0.03	0.77±0.04
Fe (mg/L)	2.4±0.04	1.33±0.05
Cu (mg/L)	0.24 ±0.06	0.19±0.05
Mn (mg/L)	1.4±0.07	1.03±0.04
Ni (mg/L)	0.14±0.03	0.17±0.04
Cd (mg/L)	N.D.	N.D.
Pb (mg/L)	N.D.	N.D.

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-methylethylidene)bis-phenol, Tricosane, Pentoxifylina, Ácido mono(2-ethylhexil) ester 1,2-benzendicarboxilic and Cholestanol. In Fig. 2b, in the leachate after oxidation (OL), appear several peaks, which propably 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 $[Fe^{2+}]/[H_2O_2]$ relationship

After pH adjustment of the RL with concentrated H_2SO_4 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 $[Fe^{2+}]/[H_2O_2]$ 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 $[Fe^{2+}]/[H_2O_2]$ relationship over 0.6 have a white color, which implies $Fe(OH)_2$ precipitation due to a Fe^{2+} excess. The reaction can be considered as follows:

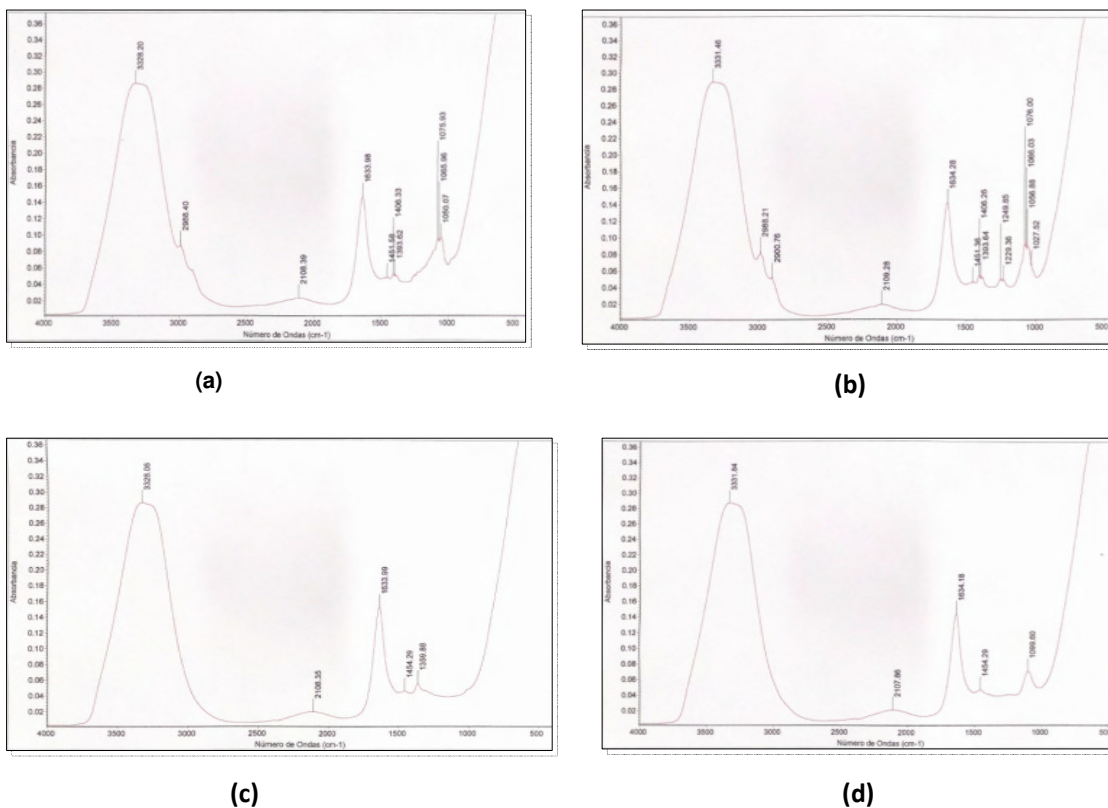
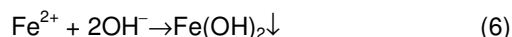
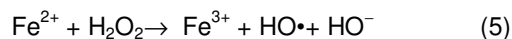


Fig. 1. 1a. RL, IR spectrum. 1b. OL, IR spectrum. 1c. ESL, IR spectrum. 1d. ACL, IR spectrum

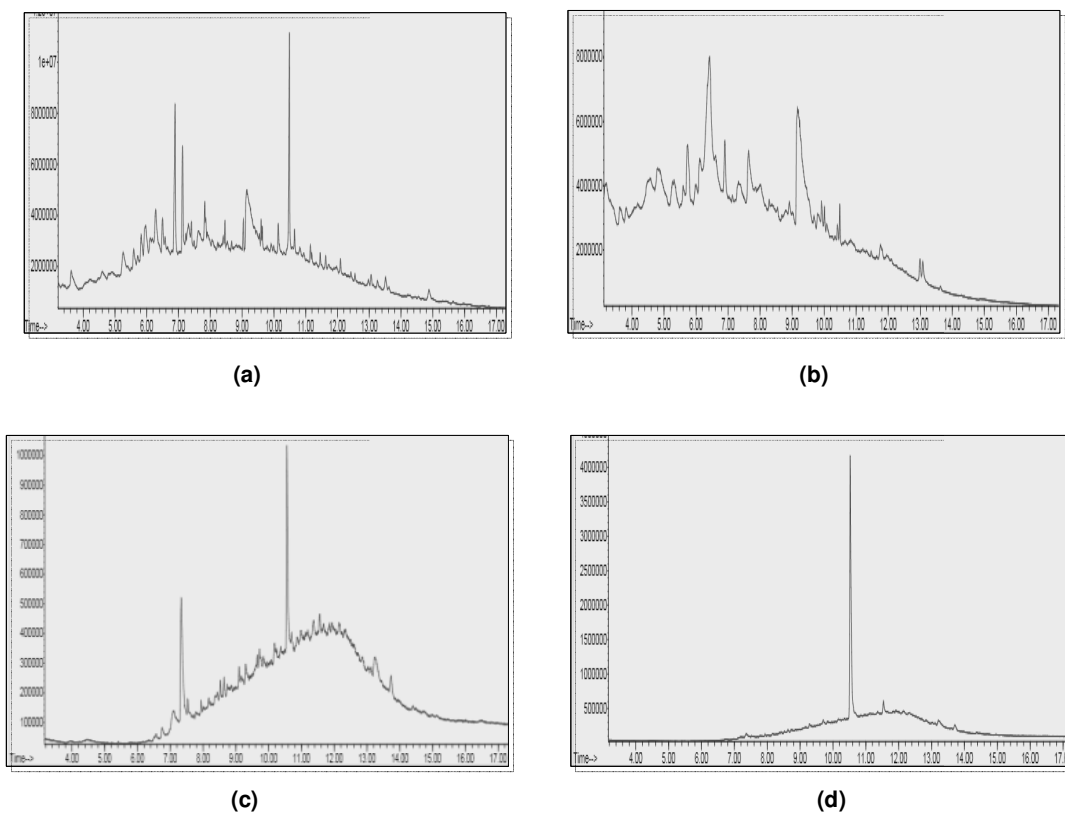


Fig. 2. 2a. RL chromatogram, 2b OL chromatogram, 2c. EGL chromatogram. 2d. ACL chromatogram

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 $\text{Fe}(\text{OH})_2$, 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_2O_2 (30%) respectively and one equivalent of 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 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_2O_2 amount was 2.0384 mg/L of OC per 1 mL of H_2O_2 .

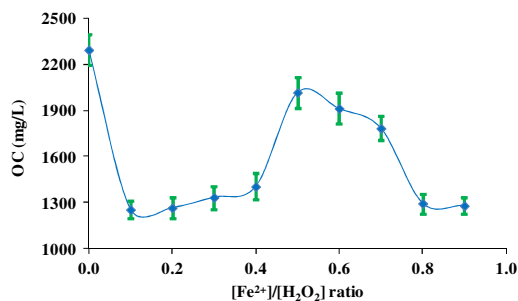


Fig. 3. Determination of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ relationship

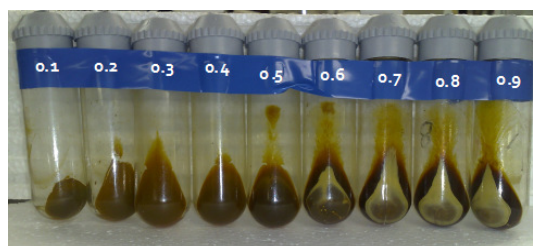


Fig. 4. Sludge obtained by centrifugation of different $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ relationship

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 $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ 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, 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 colloid 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%.

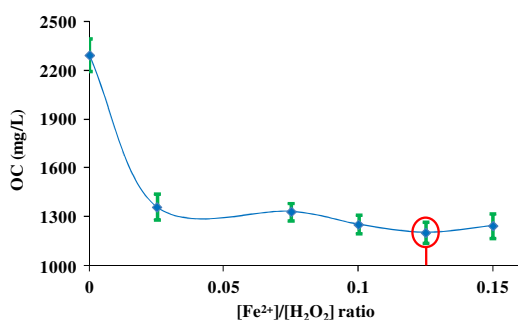


Fig. 5. Determination of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ relationship finer

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 $2.96 \pm 0.124 \text{ m}^2/\text{g}$.

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 $\text{pH} = 6.9 \pm 0.34$, 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 (q_e) 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 $2 \pm 0.74 \text{ g}$ 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

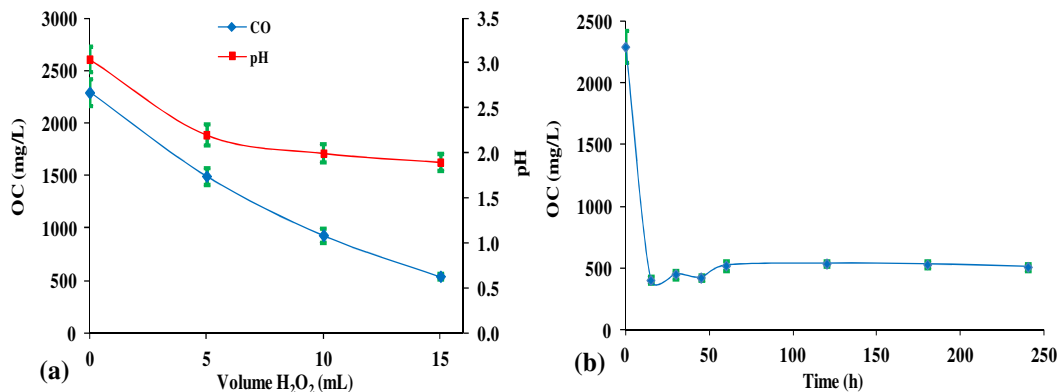


Fig. 6. 6a. OC reduction and pH values with various amounts of H₂O₂ reacting with 20 mL of AL. 6b. Different times of reactions for OC removal

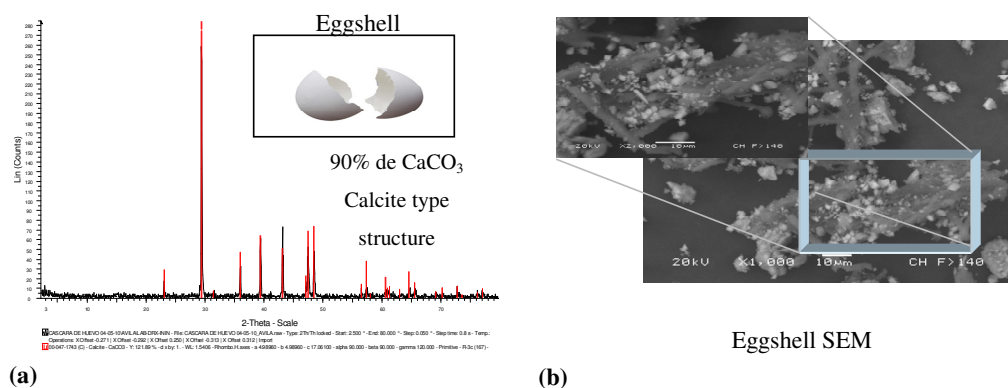


Fig. 7. 7a. Eggshell x-ray diffraction, 7b. Eggshell scanning electron microscopy (SEM)

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

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

amount (q_e) in mg/g against adsorption equilibrium concentration (C_{eq}) is plotted, see Fig. 9. The curve obtained showed a trend of the type II, which is possibly due to the small surface area of adsorbent [53].

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

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 .

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

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.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

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°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].

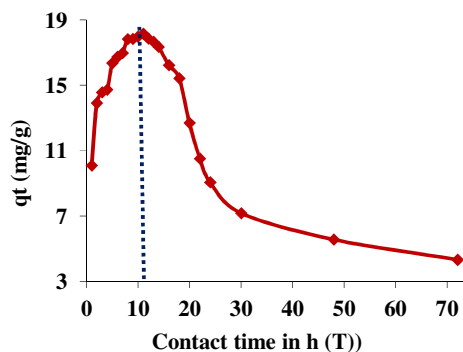


Fig. 8. COD adsorbed on ES to constant weight

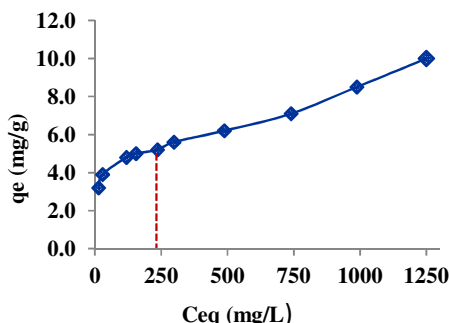


Fig. 9. q_e (COD) adsorbed on ES to variable weight

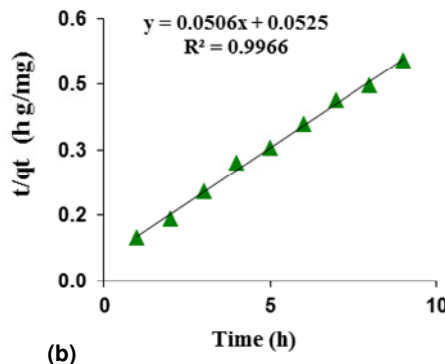
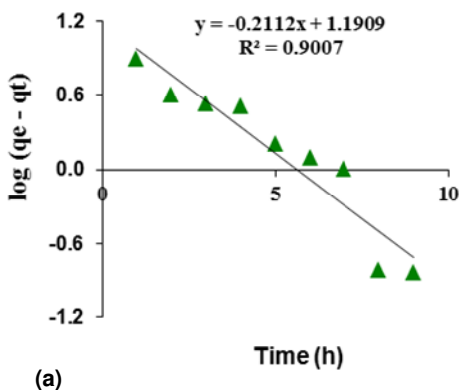


Fig. 10. 10a. Pseudo-first-order kinetics, 10b. Pseudo-second-order kinetics

Table 5. Constantes de la cinética de adsorción de la CH

Pseudo-primer-orden		Pseudo-segundo-orden	
R ²	0.9007	R ²	0.9966
q _e (mg/g)	15.5203	q _e (mg/g)	19.7628
k ₁ (h ⁻¹)	0.4864	k ₂ (g/mgh)	0.0488

Furthermore q_e 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:

$$\frac{X}{M} = k_F Ceq^{1/n} \quad (5)$$

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).
- Ceq: Equilibrium concentration of the adsorbate in solution after adsorption (mg/L).
- 1/n: Parameter related to adsorption intensity.

Freundlich linearized equation:

$$\log\left(\frac{X}{M}\right) = \log k_F + \frac{1}{n} \log Ceq \quad (6)$$

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 R² 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 (b_t) 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:

$$\theta = \frac{RT}{b_t} \ln(ACeq) \quad (7)$$

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:

$$\theta = B \ln A + B \ln Ceq \quad (8)$$

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_i : 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 R^2 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 Fe^{3+} and 302.60 mg/g of Ca^{2+} . Further, in view that ES contains $CaCO_3$, 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

B	A	bt (joule/mole)
$B_1 = 1.220$	$A_1 = 0.896$	$bt_1 = 2026.17$
$B_2 = 1.122$	$A_2 = 1.481$	$bt_2 = 2203.02$
$B_3 = 1.140$	$A_3 = 1.043$	$bt_3 = 2168.50$

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]:

$$\frac{m}{v} = \frac{C_o - C_e}{k_F * C_e^{1/n}} \tag{9}$$

Where:

- m : Support mass
- v : 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.

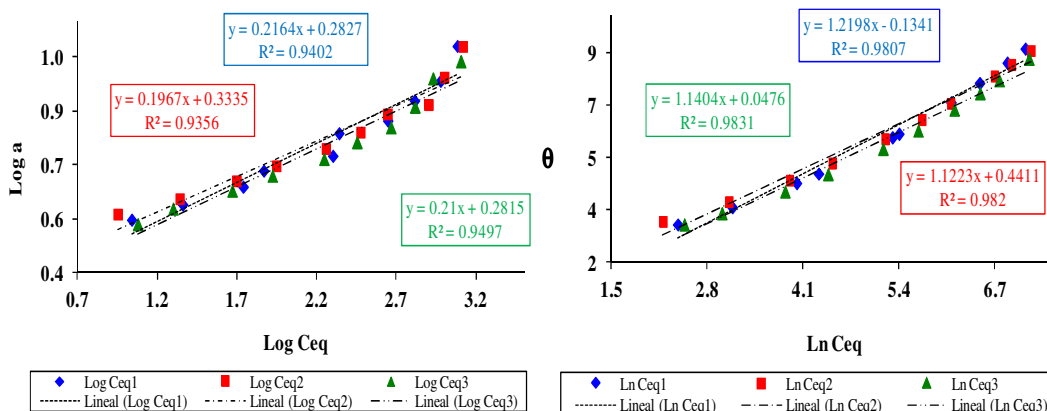


Fig. 11. 11a. Freundlich isotherms, 11b. Temkin isotherms

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.

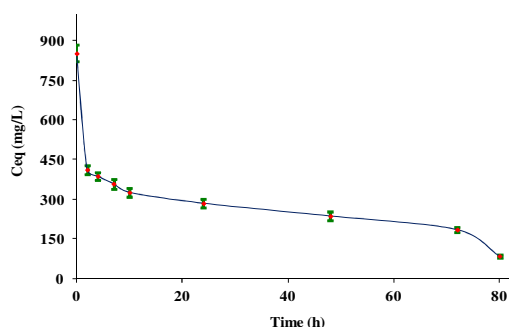


Fig. 12. Time versus Ceq for EL, after being treatment with AC

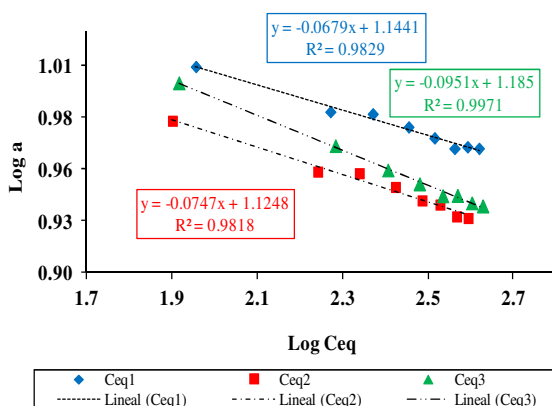
B, A and bt values are shown in Table 6, where the latter's absolute values obtained for AC are much higher than those obtained in experiments with ES (Table 7), showing that AC has a large area of adsorption.

3.4.1 Isotermas de adsorción de Freundlich y Temkin para AC

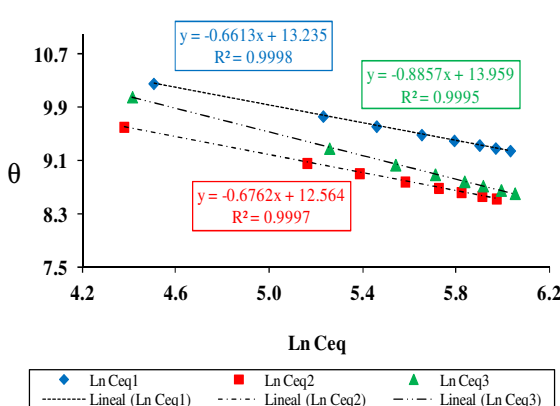
For the adsorption on AC, Freundlich isotherms and Temkin isotherms were determined. Figs. 13a and 13b show the results of behavior each isotherm. The R² values were appropriate for Freundlich isotherms (Fig. 13a); indicating that adsorption process is not limited to monolayer formation. Furthermore, 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 7. Values of the constants Temkin isotherms using a constant weight of the adsorbent AC

B	A	bt (joule/mol)
B ₁ = - 0.661	A ₁ = 2.0333 E-09	bt ₁ = -3746.51
B ₂ = - 0.676	A ₂ = 8.5247 E-09	bt ₂ = -3664.21
B ₃ = - 0.886	A ₃ = 1.4300 E-07	bt ₃ = -2797.20



(a)



(b)

Fig. 13. 13a. Freundlich isotherms, 13b. Temkin isotherms



Fig. 14. 14a. Raw leachate (RL), 14b. Leachate pH 3 (AL), 14c. Leachate Fenton oxidized (OL), 14d. Adsorbed leachate OL on eggshell (ESL), 14e. Adsorbed ESL on Active Carbon (ACL), final liquid product

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-AC 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

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

**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 $[Fe^{2+}]/[H_2O_2]$ 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

1. Johari A, Ahmed SI, Hashim H, Alkali H, Ramli M. Economic and environmental benefits of landfill gas from municipal solid waste in Malaysia. *Renew Sust Energ Rev*. 2012;16:2907-2912.
2. Armijo C, Taboada P, Aguilar Q, Ojeda B. Solid waste generation and composition in Mexico: A comparison between rural and urban communities. *J Environ Sci Eng*. 2010;4(11):71-78.
3. Li W, Zhou Q, Hua T. Removal of organic matter from landfill leachate by advanced oxidation processes: A review. *International Journal of Chemical Engineering*. 2010;10.
4. SEDESOL. Dirección general de equipamiento e infraestructura en zonas urbano-marginadas. México; 2012.
5. Alcántara II, Buenrostro O, Carrillo A. Geological characterization and environmental implications of the placement of the Morelia Dump, Michoacán, Central Mexico. *JAWMA*. 2005;55(6):755-764.
6. Gabska D, Wolski K. Use of turfgrasses in landfill leachate treatment. *Journal of Environmental Studies*. 2011;20(5):1161-1165.
7. Kumar U, Kumar M, Chauhan R, Kumar P, Ramanathan AI, Subramanian V. Assessment of the impact of landfill on groundwater quality: A case study of the Pirana site in western India. *Environ Monit Assess*. 2008;141:309-321.
8. Ehrig HJ. Treatment of sanitary landfill leachate: Biological treatment. *Waste Manage Res*. 1984;2:131-152.
9. Tatsi AA, Zouboulis AI. A field investigation of the quantity and quality of leachate from a municipal solid waste landfill in a Mediterranean climate (Thessaloniki, Greece). *Adv Environ Res*. 2002;6:207-219.
10. Marttinen S, Kettunen R, Rintala J. Occurrence and removal of organic pollutants in sewages and landfill leachates. *Sci. Total Environ*. 2003;301: 1-12.
11. Monje I, Orta M. Removal and transformation of recalcitrant organic matter from stabilized saline landfill leachates by coagulation-ozonation coupling processes. *Water Res*. 2004;38: 2359-2366.
12. Sang YM, Gu QB, Sun TC, Li FS. Color and organic compounds removal from secondary effluent of landfill leachate with a novel inorganic polymer coagulant. *Water Sci Technol*. 2008;58:1423-1432.
13. Ramírez-Sosa D, Castillo-Borges E, Méndez-Novelo R, Sauri-Riancho M, Barceló-Quintal M, Marrufo-Gómez JM. Determination of organic compounds in landfill leachates treated by Fenton-Adsorption. *Waste Manage*. 2013;33(2): 390-395.
14. Neyens E, Baeyens J. A review of classic Fenton's peroxidation as an advanced oxidation technique. *J. Hazard Mater B*. 2003;98:33-50.
15. Choi H, Al-Abed SR, Dionysiou DD, Stathatos E, Lianos P. TiO₂ based advanced oxidation nanotechnologies for water purification and reuse. *Sustainability Sci. Eng*. 2010;2:229-254.
16. Zamora-Villafranco E, Barceló-Quintal ID, Gómez-Salazar S, Barceló-Quintal M, Solís-Correa HE, Soriano-Rodríguez JM. Adsorption kinetics of matter contained in a leachate using eggshell and activated carbón. *J Environmental Protection*. 2014; 5:608-619.
17. Singh SK, Tang WZ. Statistical analysis of optimum Fenton oxidation conditions for landfill leachate treatment. *Waste Manage*. 2013;33:81-88.
18. Deng Y. Physical and oxidative removal of organics during fenton treatment of mature municipal landfill leachate. *J Hazard Mater*. 2007;146:334-340.
19. Hermosilla D, Cortijo M, Huang CP. Optimizing the treatment of landfill leachate by conventional Fenton and photo-fenton processes. *Sci. Total Environ*. 2009;407:3473-3481.
20. Yoon J, Lee Y, Kim S. Investigation of the reaction pathways of HO· radicals produced by Fenton oxidation in the condition of wastewater treatment. *Water Sci Technol. International Conference on oxidation technology for water and wastewater treatment No. 2*. 2001;44(5): 15-21.

21. Barbusinski K. Fenton reaction. Controversy concerning the chemistry. *Ecol Chem Eng S.* 2009;16(3):347–359.
22. Zamora-Villafranco E. Treatment of leachate from a landfill through advanced oxidation processes Fenton-adsorption using eggshells and activated carbon. (Tratamiento de un lixiviado proveniente de un relleno sanitario por medio de los procesos de oxidación avanzada Fenton-Adsorción utilizando cascara de huevo y carbón activado). UAM-A, México D.F.; 2014.
23. Zhang H, Choi HJ, Canazo P, Huang C. Multivariate approach to the Fenton process for the treatment of landfill leachate. *J Hazard Mater.* 2009;161:1306-1312.
24. Kang YW, Hwang K. Effects of reaction conditions on the oxidation efficiency in the Fenton process. *Water Res.* 2000;34(10): 2786-2790.
25. Wang F, Smith D, Gamal El-Din M. Application of advanced oxidation methods for landfill leachate treatment – A review. *J Environ Sci.* 2003;2:413-427.
26. Maranon E, Castrillon L, Fernandez-Nava Y, Fernandez-Mendez A, Fernandez-Sanchez A. Tertiary treatment of landfill leachates by adsorption. *Waste Manage Res.* 2009;27:527–533.
27. Xu Y, Gallert C, Winter J. Chitin purification from shrimp wastes by microbial deproteination and decalcification. *Appl Microbiol Biotechnol.* 2008;79:687-697.
28. Hargono, Djaeni M. Utilization of chitosan prepared from shrimp shell as fat diluent. *Journal of Coastal Development.* 2003;7: 31- 37.
29. Parab H, Joshi S, Shenoy N, Lali A, Sarma US, Sudersanan M. Determination of kinetic and equilibrium parameters of the batch adsorption of Co(II), Cr(III) and Ni(II) onto coir pith. *Process Biochem.* 2006;41: 609-615.
30. Kavitha D, Namasivayam C. Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. *Bio Resource Technol.* 2007;98:14-21.
31. El-Khaiary MI. Kinetics and mechanism of adsorption of methylene blue from aqueous solution by nitric acid treated water hyacinth. *J. Hazard Mater.* 2007;147:28-36.
32. Arami M, Limaee YN, Mahmoodi NM, Tabrizi SN. Equilibrium and kinetics studies for the adsorption of direct and acid dyes from aqueous solution by soy meal hull. *J Hazard Mater B.* 2006;135(1–3): 171–179.
33. Arami M, Limaee NY, Mahmoodi NM, Tabrizi SN. Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetics studies. *J Colloid Interface Sci.* 2005;288:371–376.
34. Annadurai G, Juang RS, Lee DJ. Factorial design analysis for adsorption of dye on activated carbon beads incorporated with calcium alginate. *Adv Environ Res.* 2002a;6:191–198.
35. Annadurai G, Juang RS, Lee DJ. Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. *J Hazard Mater B.* 2002b;92:263–274.
36. Arami M, Limaee YN, Mahmoodi NM, Tabrizi SN. Investigation on the adsorption capability of egg shell membrane towards textile dyes. *Chemosphere.* 2008;65:1999–2008.
37. Arunlertaree C, Kaewsomboon W, Kumsopa A, Pokethitiyook P, Panyawathanakit P. Removal of lead from battery manufacturing wastewater by eggshell, Songklanakarin. *J Sci Technol.* 2007;29(3):857-868.
38. Kalyani G, Babu G, Vijaya B, Prasanna Y. Equilibrium and kinetic studies on biosorption of zinc onto gallusdomesticus shell powder. *J Eng Appl Sci ARPN.* 2009;4(1):39-49.
39. ICE. International Egg Commission; 2014. Available:<https://www.internationalegg.com/corporate/eggindustry/details.asp?id=18> (Accessed January, 2014)
40. Barceló I, Solís H, Aceves H, López E, Méndez R, García J, Guzmán R. In Optimización de la relación Fe^{2+}/H_2O_2 en el proceso de oxidación de lixiviados de un relleno sanitario y posterior adsorción. *Proceedings of X Congreso Internacional y XVI Congreso Nacional de Ciencias Ambientales, Querétaro, México, Aug 17-19, 2011; Universidad Autónoma de Querétaro: Querétaro; 2011.*
41. SEMARNAT. Secretaría de medio ambiente y recursos naturales, Mexican standard NOM-001-SEMARNAT-1996: máximo permisible limits of pollutants in

- waste water discharges into national waters; (Norma Oficial Mexicana NOM-001-SEMARNAT-1996: límites máximos permisibles de contaminantes en las descargas de aguas residuales en aguas y bienes nacionales). Diario Oficial de la Federación. México City. 1996;1997:1-11.
42. SEMARNAT. Secretaría de medio ambiente y recursos naturales, Mexican federal law of rights: Provisions in national waters (Ley federal de derechos: Disposiciones aplicables en materia de aguas nacionales). Diario Oficial de la Federación. México City. 2009;2010: 21-30.
 43. Standard Methods. Standard methods 5520 C, Standard methods for the examination of water and wastewater. American Public Health Association, Washington, USA; 1997.
 44. Kolthoff IM, Sandell ED. Textbook of quantitative inorganic analysis. 3rd ed. The Mac Millan Company, New York. 1956; 225-228.
 45. Baun A, Ledin A, Reitzel LA, Bjerg PL, Christensen TH. Xenobiotic organic compounds in leachates from ten Danish MSW landfills—chemical analysis and toxicity tests. *Water Res.* 2004;38:3845–3858.
 46. SEMARNAT. Secretaría de Medio Ambiente y Recursos Naturales, Mexican Standard NOM-052-SEMARNAT-2005: which establish the features, the process of identification, classification and listing of hazardous waste (Norma Oficial Mexicana NOM-052-SEMARNAT-2005: que establece las características, el procedimiento de identificación, clasificación y los listados de los residuos peligrosos). Diario Oficial de la Federación. México City. 2005;2006:15-26.
 47. Amokrane A, Comel C, Veron J. Landfill leachates pretreatment by coagulation-flocculation. *Water Research.* 1997;31: 2775-2782.
 48. FAO. FAO irrigation and drainage papers. Available:<http://www.fao.Org/DOCREP/003/T023E/T0234E00.HTM> (Accessed May 2013)
 49. Canadian Council of Ministers of the Environment. Canadian Water Quality Guidelines for the Protection of Agricultural Water Uses: Canada; 1999.
 50. Cortez S, Teixeira P, Oliveira R, Mota M. Fenton's oxidation as post-treatment of a mature municipal landfill leachate. *IJCEE.* 2010;2(1):40-43.
 51. Mahmud K, Hossain Md. D, Shams S. Different treatment strategies for highly polluted landfill leachate in developing countries. *Waste Manage.* 2012;32:2096-2105.
 52. Silva TFCV, Silva MEF, Cunha-Queda AC, Fonseca A, Saraiva I, Boaventura RAR, Vilar VJP. Sanitary landfill leachate treatment using combined solar photo-Fenton and biological oxidation processes at pre-industrial scale. *Chem Eng J.* 2013; 228:850-866.
 53. Maron SH, Prutton CF. Principles of physical chemistry. MacMillan Editorial: USA. 1958;214-225.
 54. Lasheen MR, Ammar NS, Ibrahim HS. Adsorption/desorption of Cd(II), Cu(II) and Pb(II) using chemically modified orange peel: Equilibrium and kinetic studies. *Solid State Sciences.* 2012;14:202-21.
 55. Ho YS, Huang CT, Huang HW. Equilibrium sorption isotherm for metal ions on tree fern. *Process Biochem.* 2002;37:1421-1430.
 56. Rauf N, Tahir SS, Kang J, Chang Y. Equilibrium, thermodynamics and kinetics studies for the removal of alpha and beta endosulfan by adsorption onto bentonite clay. *Chemical Engineering Journal.* 2012;192:369-376.
 57. Namasivayam C, Jeyakumar R, Yamuna RT. Day removal from wastewater by adsorption on 'waste' Fe (III)/Cr (III) hydroxide. *Waste Manage.* 1994;14: 643-648.
 58. El Nemr A, Khaled A, Abdelwahab O, El-Sikaily A. Treatment of wastewater containing toxic chromium using new activated carbon developed from date palm seed. *J Hazard Mater.* 2008; 152(1):263-275.
 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

- thermodynamics of interactions. Desalination. 2010;261:52-60.
61. SEMARNAT. Secretaría de Medio Ambiente y Recursos Naturales, Mexican Standard NOM-021-SEMARNAT-2000: which establish the specifications for fertility, salinity oil classification, survey, sampling and analysis (Norma Oficial Mexicana NOM-021-SEMARNAT-2000: que establece las especificaciones de fertilidad, salinidad clasificación de suelos, estudio, muestreo y análisis). Diario Oficial de la Federación, México City. 2000;2002:13-26.
62. Metcalf and Eddy. Wastewater engineering treatment and reuse. 4th Ed. International Edition: USA. 2003;1161.
63. Hameed BH, Ahmad AA, Aziz N. Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash. Chem Eng J. 2007;133: 195–203.

© 2016 Zamora-Villafranco et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
<http://sciencedomain.org/review-history/15973>