



EVALUATION OF ADSORPTION AND FENTON-ADSORPTION PROCESSES FOR LANDFILL LEACHATE TREATMENT

EVALUACIÓN DE LOS PROCESOS DE ADSORCIÓN Y FENTON-ADSORCIÓN PARA EL TRATAMIENTO DE LIXIVIADOS DE RELLENO SANITARIO

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Abstract

The objective of this research was to compare the adsorption and Fenton-adsorption treatments for the removal of contaminants in leachate from landfills and thus determine the most efficient one. The adsorption process with granular activated carbon was tested in two types of samples: raw leachate and leachate treated by Fenton. The results showed color, chemical oxygen demand (COD), total nitrogen and total organic carbon (TOC) removal rates higher than 99% through the Fenton-adsorption process, while total nitrogen, COD, color and TOC removal rates of 81, 89, 92 and 93%, respectively, were obtained through the adsorption process on the raw leachate. Gas chromatography coupled to mass spectrometry (GS-MS) was used to found that the main organic compound in the leachate produced in the landfill from Mérida city, Yucatán, Mexico, is bisphenol-A, which was removed only during the adsorption stage of the Fenton-adsorption process. Furthermore, the biodegradability index (BI) increased from 0.084 to 0.476 through adsorption and up to 0.82 through the Fenton-adsorption treatment.

Keywords: activated carbon; adsorption; bisphenol-A; Fenton; leachate.

Resumen

El objetivo de esta investigación fue comparar los tratamientos de adsorción y Fenton-adsorción para la remoción de contaminantes en lixiviados de rellenos sanitarios y determinar el más eficiente. El proceso de adsorción con carbón activado granular fue probado en dos tipos de muestras: lixiviado crudo y lixiviado tratado con Fenton. Los resultados muestran que la remoción de color, demanda química de oxígeno (DQO), nitrógeno total y carbón orgánico total (COT) es superior a 99% con el proceso Fenton-adsorción, mientras que con el proceso de adsorción la remoción de nitrógeno total, DQO y COT fue de 81, 89 y 92%, respectivamente. Mediante el uso de cromatografía de gases acoplada a espectrometría de masas se encontró que el bisfenol-A es el principal compuesto orgánico presente en el lixiviado producido en el relleno sanitario de la ciudad de Mérida, Yucatán, México. Este compuesto fue removido sólo durante la etapa de adsorción del proceso Fenton-adsorción. Asimismo, el índice de biodegradabilidad (IB) se incrementó de 0.084 a 0.476 mediante el tratamiento del lixiviado con adsorción, y 0.82 con el tratamiento Fenton-adsorción.

Palabras clave: adsorción; bisfenol-A; carbón activado granular; Fenton; lixiviado.

1 Introduction

Currently the disposal of domestic solid waste is carried out mostly in landfills. Although some waste products may be used through recycling, reuse or

composting, per capita production along with poor culture in solid-waste management is beyond the capacity of waste reuse. Landfills are the most commonly used method for controlled management of municipal solid wastes (Renou *et al.*, 2008;

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Sharholy *et al.*, 2008; Visvanathan *et al.*, 2007). Chemical reactions -proper of biological activity- take place there, producing gases and leachate due to the moisture content of the residues (mainly the organic ones), compaction and water that inevitably pours into landfill.

According to the Mexican Standard NOM-083-SEMARNAT-2003 (SEMARNAT, 2004), a leachate is a liquid formed by the reaction, drain or filtering of materials constituting the residues. It may contain, either dissolved or suspended, substances that can infiltrate onto soils or drain from the sites where the residues are deposited. This can lead to contamination of soil and water bodies, causing their deterioration and posing a potential threat to human health and other living organisms. The leachate composition can vary considerably from one place to another, and even within the same site along the year (Yokoyama *et al.*, 2009). Depending on the landfill's age and composition, leachates are classified in young, medium-age or stabilized. Biological treatment processes (aerobic or anaerobic) are very effective on first-stage leachates of high biodegradability index (BI) (Calli *et al.*, 2005). However, they generally fail when the leachate's BI is low or when there are high concentrations of toxic metals (Deng and Englehardt, 2006).

In addition to large amounts of organic matter, the possible presence of heavy metals and high concentration of ammoniacal nitrogen, landfill leachates may contain contaminants originally from the present wastes. Yet, more contaminants may be produced during the residues' ripening process, thus making the matrix more complex by involving a large number of xenobiotic organic compounds (Banar *et al.*, 2006). These compounds' concentration is usually reported as $\mu\text{g/L}$; nevertheless, their inherent danger is that some may be severely toxic or carcinogenic even at trace levels. Therefore, leachate disposal with no previous treatment could cause a significant impact both on the environment and human health.

Adsorption is a widely used method for the removal of recalcitrant organic compounds in landfill leachates (Bashir *et al.*, 2009). Activated carbon is frequently used for the removal of organic matter, ammonium and toxic substances from the leachates (Xing *et al.*, 2008) and allows removing up to 70% of COD and ammoniacal nitrogen. Other adsorbent means have been tried, such as zeolite, vermiculite, illite, kaolinite, activated alumina, ash from a municipal solid waste incinerator (Abbas *et al.*, 2009; Wiszniowski *et al.*, 2006), and even peat and

compost (Shahriari *et al.*, 2008), with which removals similar to the aforementioned were obtained.

Advanced oxidation processes have been used to increase the biodegradability of recalcitrant and/or non-biodegradable organic substances (Wu *et al.*, 2010), since it is possible to fracture large molecules; smaller molecules can be removed afterwards by means of a biological process. The Fenton process consists of a mixture (under acid conditions) of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, producing $\cdot\text{OH}$ radicals in a very inexpensive way. This process produces large amounts of foam and sludge, characterized by their low density; this causes sedimentation to be difficult. However, effluent filtration instead settling prevents the sludge from being a problem.

The objective of this research was to prove that adsorption preceded by the Fenton process can efficiently remove organic matter from leachates as the raw leachate macromolecules have been degraded to smaller ones. This prevents clogging the activated carbon interstices, thus allowing better removal of organic matter and color.

2 Experimental

The methodology is divided into four stages: 1) leachate characterization, 2) Fenton process, 3) comparison of the Fenton-adsorption and adsorption processes and 4) qualification of leachates through GC-MS. Some stages included other processes described below.

2.1 Leachate characterization

Three sampling campaigns were conducted in the leachate's evaporation ponds at the landfill at Mérida city, Yucatán. The parameters analyzed were chemical oxygen demand (COD), chemical oxygen demand soluble fraction (COD_s), biological oxygen demand the fifth day (BOD_5), biological oxygen demand the fifth day soluble fraction (BOD_{5s}), total organic carbon (TOC), total solids (TS), total suspended solids (TSS), total dissolved solids (TDS), pH, color, turbidity, total nitrogen (TN) and ammonia nitrogen ($\text{NH}_3\text{-N}$), according to standard methods (APHA, 2005).

2.2 Fenton process

The content of carbonates and bicarbonates in the leachate from Merida city is high, this interferes

with the efficiency of Fenton oxidation. However, Pietrogiovanna *et al.* 2010 suggests a pH 4 or inferior to remove them and promote the reaction. For this experiment, pH was adjusted to 4 with concentrated H_2SO_4 ; the ratio tested was $(\text{Fe}^{2+}/\text{H}_2\text{O}_2) = 0.6$ from $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ and $(\text{COD}/\text{H}_2\text{O}_2) = 9$, from H_2O_2 30% w/w. Contact time was one hour. Subsequently, the Fenton process was modified in the sedimentation stage, optimized by using an InterfilterTM filter press, model 20-18 and filter paper of 20-25 μm pore size to facilitate the separation of the sludge produced (Mendez *et al.* 2010). For batch adsorption test were prepared 1 L of leachate with Fenton and for continuous adsorption were prepared 450 L.

2.3 Comparison of the Fenton-adsorption and adsorption processes

To compare the Fenton-adsorption and adsorption processes, the same granular activated carbon (GAC) was used for the adsorption process in both samples (raw leachate and Fenton effluent). It is a lignite-based macroporous Gama LTM GAC. Its physical characteristics are: raw material mineral lignite; mesh count: 8*30; surface area: 348.61 m^2/g ; relative density: 0.38; cross-section of the adsorption area: 0.162 nm^2 .

2.3.1 Adsorption in a batch reactor

Samples of 50 mL (raw leachate and Fenton effluent) were placed in a batch reactor and added doses of 1 to 10 g of GAC. The samples were stirred at 200 rpm for one hour using agitation plates. Subsequently, the sample was filtered and COD and color concentrations were measured before and after adsorption. The tests were performed in duplicated and at random.

2.3.2 Continuous adsorption

Two columns packed with GAC were used. Initial COD and color values of the influent were measured. The Fenton-process effluent and the raw leachate samples were passed through a 60-cm long and 20-cm diameter column and the contact time was set at 45 min; column characteristics were defined based on the pump (Cole Parmer Master Flex U.S. 77200-60) capacity, the porosity of CAG and the contact time necessary to perform the adsorption, whereby it is possible to obtain the height of packing, depending on the commercial column acquired (May, 2010). The

total sample volume in both cases was 450 L. The tests were performed in duplicated.

Effluent samples were taken from each column at different times to measure COD and color concentration. Progress charts for the two treatments were developed after these data to determine the carbon's removal efficiency in each case.

2.4 Leachate qualification by GC-MS

The liquid-liquid sample extraction method and conditions of the gas chromatograph (Agilent Technologies, model 6890N) coupled to mass spectrometer (Agilent Technologies, model 5973N) were the same used by Ramirez *et al.* 2013: the temperature program of the gas chromatograph oven was set at 15° C/min from 80° C (2 min) to 290° C (4min), run time: 20 min; volume of injection 1 μL , mode split 10:1 (automatic injector model 7683); the carrier gas was ultra-high purity Helium; and a capillary column Agilent HP5MS (30m*0.25mm*0.25 μm) was used. All reagents used were of HPLC grade.

2.5 Statistical analyses

Statgraphics Plus software, version 5.1 for Windows, analysis of variance via fixed effects and the method of least significant difference (LSD) to contrast the means of each treatment was used for all statistical analysis. The significance level was $\alpha = 0.05$. The samples were independent and random.

3 Results and discussion

Figures 1 and 2 show the ANOVA results from the adsorption tests in a batch reactor. Significant differences (P-value < 0.05) are observed between the two samples (raw leachate and Fenton effluent) in both COD and color removal; adsorption is more efficient in the Fenton effluent. This is possible because organic substances and dissolved heavy metals may be removed efficiently with Fenton oxidation process by breaking of long molecular chains by means of radical OH^- obtained in the reaction between H_2O_2 and Fe^{2+} ions (Salas and Ale, 2014). Therefore, broken molecules in Fenton effluent could adhere to the activated carbon interstices advantage over the surface area available, whereas macromolecules of raw leachate obturated such interstices.

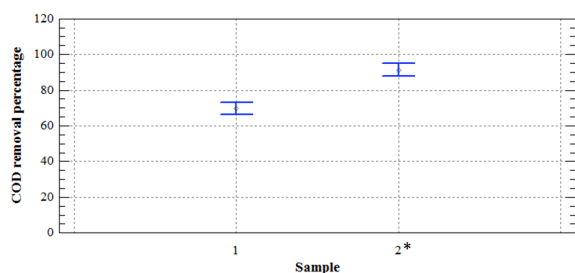


Fig. 1. ANOVA results according to the type of sample: raw leachate (1) vs. Fenton effluent (2*), regarding COD removal percentage. P-value=0.0000.

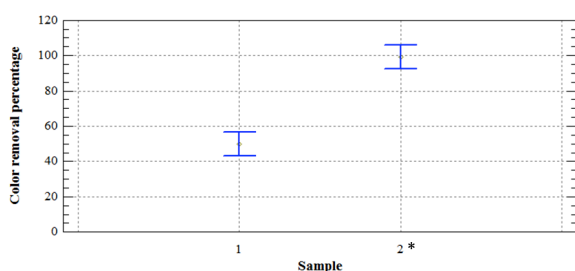


Fig. 2. ANOVA results according to the type of sample: raw leachate (1) vs. Fenton effluent (2*), regarding color removal percentage. P-value=0.0000.

Table 1 shows the analysis results for the raw leachate and the effluents from the two treatments (continuous adsorption). In the “Raw leachate” column, the sample’s COD concentration (10,193 mg/L) corresponds in theory to a young landfill leachate (Bodzek *et al.*, 2006; Renou *et al.*, 2008); yet, pH is 8.31, proper of a mature leachate (Bashir *et al.*, 2009). Since the Mérida, Yucatán, landfill is not young, the leachate’s COD concentration is explained by the landfill’s local operation: the leachates in the evaporation ponds are recirculated and sent back to the landfill. There they get in contact with residues yet stabilizing, that give the effluent mixed characteristics. Furthermore, the landfill’s cover material (sascab) is limestone, which reduces its porosity when compressed and thus acts as a filter. It retains large particles and dissolves carbonates, which gives the leachate high Na, K and hardness values, as well as high pH due to the presence of carbonates and bicarbonates. Overall, the leachate gets a buffering capacity (Méndez *et al.*, 2010).

According to Kang *et al.* (2002), the organic concentration (measured as COD, BOD₅ and TOC) decreases as the landfill’s age increases. The organic load -measured as BOD_{5T} and reported in Table 1- represents about 12% of the total COD concentration; this is because BOD decreases more rapidly than COD, which remains in the leachate due to the presence of refractory organic material. This leachate’s BI (biodegradability index) is < 1 and most nitrogen is ammoniacal (85%). Furthermore, the color concentration is high and indicates that there is a large amount of dissolved particles since dissolved solids represent nearly 98% of total solids.

Fenton process has many advantages for the treatment of leachate and wastewater in general as well as being economical, does not involve energy in the process, is not toxic and there are no limitations on the transfer of matter because it is a homogeneous process (Cueto, 2012). The “Fenton” column in Table 1 shows the decrease in BOD_{5T} and BOD concentrations, as well as a change in pH, which is natural since the leachate was acidified in order to carry out the Fenton process. The increase of solids content is explained by the advanced oxidation process: after breaking the macromolecules, it acts as a coagulant, forming sparse flocs (mainly iron hydroxides) that do not precipitate easily. In this study, Fenton process only reaches 54% removal of COD, which is typical for such treatment in mature landfill leachate. Cortez *et al.* (2011), achieved a 46% COD removal with conditions of pH=3 and a molar ratio of H₂O₂/Fe²⁺=3, for mature leachate, while Yilmaz *et al.* (2012), achieved a 56% removal of COD with optimum initial pH = 3, 2000 mg/L Fe²⁺, 5000 mg/L H₂O₂, for a young leachate.

To remove toxic organic compounds present in water, activated carbon is often used because of its high surface area, pore structure, high adsorption capacity, and chemical nature. It has been considered to porosity and surface area parameters defining the quality of activated carbon. At present it has been shown that the activated carbon surface chemistry plays an important role in the adsorption process. For this reason it was decided to use the adsorption process preceded by Fenton to ensure greater removal of contaminants from leachate (Valdés y Saror, 2010). The “Fenton-adsorption” column (Table 1) shows that the parameter values decrease markedly.

Table 1. Average values of the parameters measured at each treatment stage

Parameter	Raw leachate	Fenton	Fenton-adsorption	Adsorption
COD (mg/L)	10,193 (263)	4,658 (813)	44 (37)	1,135 (428)
COD _s (mg/L)	9,958 (151)	3,840 (189)	36 (42)	1,031 (316)
BOD ₅ (mg/L)	861 (46)	387 (64)	36 (28)	540 (0)
BOD _{5s} (mg/L)	748 (6)	321 (19)	33 (25)	531 (41)
pH	8.31 (0.1)	3.96 (0.4)	7.11 (0.4)	8.33 (0.9)
Color 455 nm (Pt-Co units)	13,667 (870)	6,940 (6078)	20 (19)	1,030 (156)
TS (mg/L)	19,050 (685)	23,533 (804)	1,338 (790)	5,738 (380)
TSS (mg/L)	360 (47)	2,056 (1993)	110 (9)	216 (60)
TDS (mg/L)	18,690 (671)	21,477 (1677)	1,228 (799)	5,522 (440)
TN (mg/L)	2,113 (210)	1,813 (300)	58 (25)	320 (226)
NH ₃ -N (mg/L)	1,797 (479)	1,653 (391)	15 (12)	256 (204)
TC (mg/L)	5,112 (507)	1,388 (153)	24 (8)	412 (146)
IC (mg/L)	162 (6)	7 (3)	14 (14)	306 (131)
TOC (mg/L)	4,950 (513)	1,380 (150)	9 (6)	106 (15)
BI	0.084	0.083	0.82	0.476

s=soluble fraction; () standard deviation

Table 2. Removal percentages of the parameters analyzed in the effluents, Fenton-adsorption and adsorption, during the three sampling campaign

Parameter	Fenton-adsorption	Adsorption
Color 455 nm (Pt-Co units)	99.83 (0.14)	92.46 (1.56)
TS (mg)	97.95 (3.98)	71.13 (0.62)
TSS (mg)	79.65 (4.14)	42.12 (24.12)
TDS (mg)	98.36 (4.12)	71.87 (1.33)
COD (mg/L)	99.96 (0.37)	89.74 (3.78)
COD _s (mg/L)	99.96 (0.42)	90.41 (2.84)
TN (mg/L)	99.96 (1.34)	81.95 (3.98)
NH ₃ -N (mg/L)	99.97 (1.07)	80.47 (3.46)
BOD ₅ (mg/L)	96.89 (3.48)	30.34 (0.4)
BOD _{5s} (mg/L)	96.88 (3.37)	22.08 (8.35)
TC (mg/L)	98.3 (0.08)	92.07 (3.95)
IC (mg/L)	95.0 (7.14)	28.69 (7.36)
TOC (mg/L)	99.3 (0.12)	93.88 (3.51)

s=soluble fraction; () standard deviation

The BOD₅ concentration in the final effluent is within the limits allowed by the NOM-001-SEMARNAT-1996 for discharge into natural and artificial reservoirs, as well as urban use -60mg/L- (SEMARNAT, 2003). However, although the TN and TSS removals are high, they remain off the maximum allowed limits therein stated -25 and 60 mg/L, respectively-. On this regard, since the BI is increased from 0.084 to 0.82, it is feasible to use a subsequent biological treatment to ensure that discharges fall within the limits allowed by the standard.

In the literature is possible to find results of other treatments that have been employed to treat mature

leachate and its efficiency in terms of removal COD, for example: ozone with hydrogen peroxide, 72% COD removal (Cortez *et al.* 2011); coagulation-flocculation-anodic oxidation 90% COD removal (Ubaldo *et al.* 2014); air stripping-Fenton-sequencing batch reactor (SBR)-coagulation, 83% COD removal, (Guo *et al.* 2010); powdered activated carbon augmented SBR process, 64% removal of COD, (Aziz *et al.* 2011). However, removal efficiencies achieved with this treatment train (Fenton-adsorption) are higher.

Finally, the "Adsorption" column in Table 1 shows the results of this treatment, with a decrease in all parameters compared to initial values. Although the

effluent's characteristics are far from being within the standards' permissible limits, the BI increases from 0.084 to 0.476, thus making a biological treatment viable to improve it. Because the activated carbon is a material with high internal surface adsorptivity and a lot of very different compounds, it is a common choice in the treatment of leachate. Activated carbon possesses high capacity and low retention selectivity. Moreover, the activated carbon has low specificity to a retention process, is a universal adsorbent. However, because of its non-polar nature and the type of forces involved in the adsorption process preferably retain apolar molecules and high molecular weight (hydrocarbons, phenols, colorants.) while substances such as nitrogen, oxygen and water are retained virtually no carbon at room temperature (Halim *et al.* 2010). In literature it states that removal of COD and nitrogen do not exceed 50-70%, however in this study over 89% for color and COD and 80% nitrogen removal were achieved.

Table 2 shows the removal percentages according to the measured parameter. In all parameters, removal with the Fenton-adsorption treatment is higher, particularly color, COD, total and ammoniacal nitrogen and TOC, which reached percentages higher than 99%. Some authors suggest that the COD and ammoniacal nitrogen removal percentages during the leachate treatment by adsorption ranges from 50-85% (Abbas *et al.*, 2009; Renou *et al.*, 2008). However, according to Kurniawan *et al.* (2006), COD removals up to 90% may be achieved through the same treatment as long as the initial concentration is relatively low (940 to 7,000 mg/L). Results in Table 2 show that the color, CODS, IC and TOC removal percentages are higher than 90%, due to the material used in the adsorption process (lignite-based macroporous GAC).

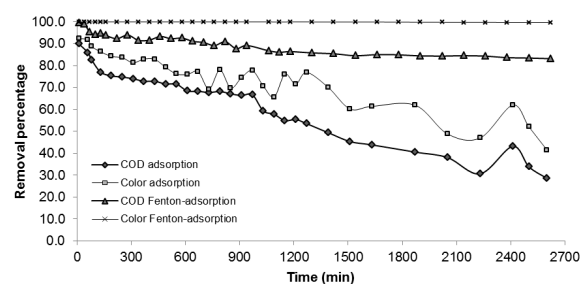


Fig. 3. Progress chart for leachate treated by adsorption and Fenton-adsorption.

Figure 3 shows progress chart for each sample treated in the adsorption columns. In the case of the raw leachate treated with adsorption, it is observed that the COD and color removal decay takes place almost at the same time. However, COD removal in the leachate treated with Fenton-adsorption decays after a time in as the fluid goes through column; yet, color removal remained above 99%. This is because macromolecules coloring the leachate degraded in the Fenton process; the remaining ones were easily retained in the interstices of the activated carbon. In the case of COD, given the nature of the organic molecules recalcitrant to intensive oxidation (mainly humic and fulvic acids; Wang *et al.*, 2004), the column is saturated more rapidly. Still, it has a great advantage over the raw leachate treated by adsorption: according to Figure 3, better quality effluents are obtained by a long time when leachates are pretreated by the Fenton process.

Table 3 presents the organic compounds found according to the above methodology (see process 2.4). The results correspond to samples taken from raw leachate, Fenton effluent, Fenton-adsorption effluent and adsorption effluent. Due to the matrix's complexity, not all ions found by the gas chromatograph coupled to mass spectrometer could be identified in the database. The compounds reported in Table 3 are the ions identified with quality higher than 90%. Previous studies have identified more than 200 organic compounds in landfill leachates (Slack *et al.*, 2005), some of which belong to the list of priority compounds due to their high toxicity.

Several compounds were found in the leachate from the Mérida city landfill, most of them have been located in other landfill leachate in the world (Renou *et al.* 2008; Eggen *et al.* 2010), among which Phenol, 4,4'-(1-methylethylidene)bis-, Bisphenol A (CAS 80-05-7), stands out. It is used as a monomer to produce epoxy resins and polycarbonates, and as stabilizer or antioxidant for plastics materials. Bisphenol A levels found in landfill leachates depend directly on the type of residues disposed (Yamamoto *et al.*, 2001). Although not environmentally toxic, studies have reported that Bisphenol A presents estrogenicity (Markey *et al.*, 2001; Pérez *et al.*, 1998; Schafer *et al.*, 1999). Therefore, it is a contaminant undesirable for human health. Other compounds of interest found in the raw leachate are aniline and 4-methylphenol, since they are toxic.

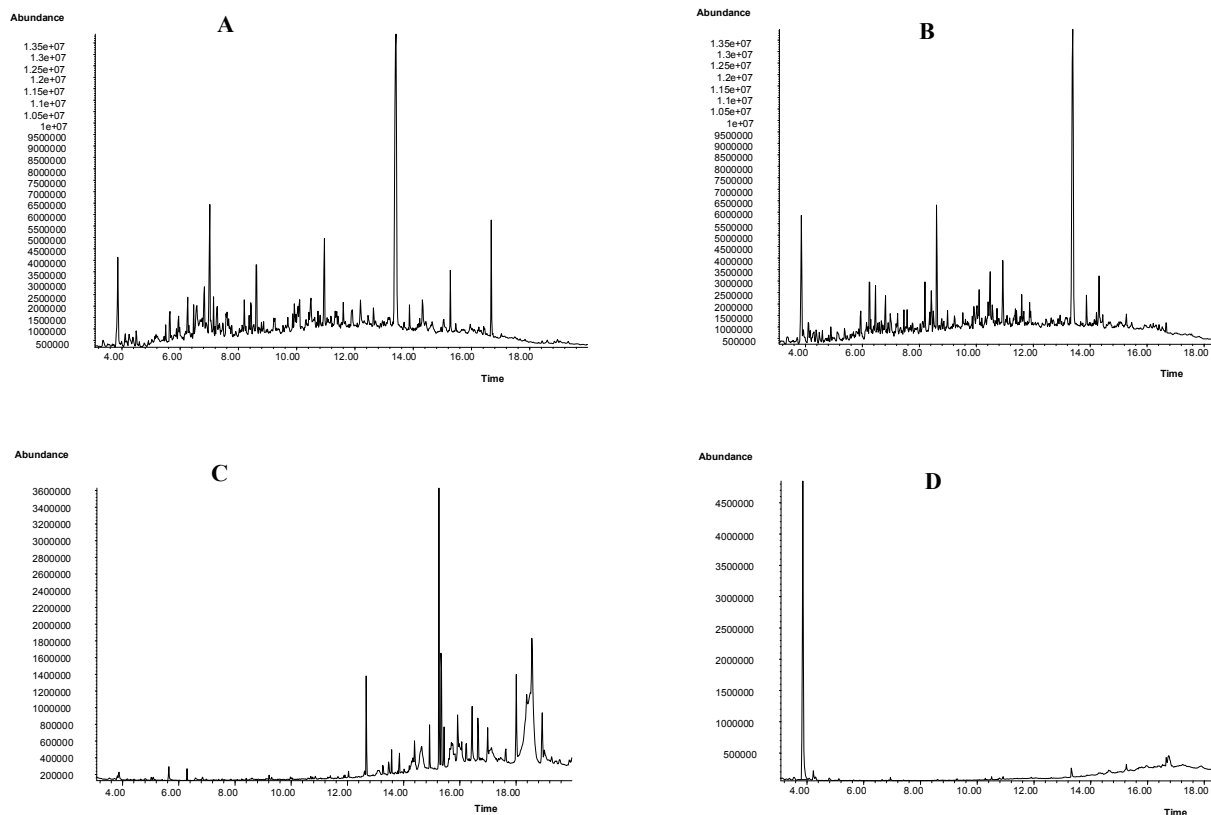


Fig. 4. Total ion chromatogram of the samples taken: A = Raw leachate; B = Fenton effluent; C = adsorption effluent; D = Fenton-adsorption effluent.

According to Martínez and López (2001), aniline is a compound susceptible to oxidation by the Fenton process; as shown in Table 3, it is not present in its effluent. High molecular weight molecules such as Cholestan-3-ol, (3 β ,5 β)- and cholestanol are removed as well by intensive oxidation. However, complex aromatic compounds such as Benzene, 1,3-bis(1,1-dimethylethyl)-, p-cresol (4-methylphenol) and Phenol, 2,4-bis (1,1-dimethylethyl) were refractory to the Fenton process.

Figure 4 shows the chromatograms for the four samples tested. Compared with Figure 4-A (raw leachate), the adsorption process (Fig. 4-C) removed only the first ions (low molecular weight). The only remaining compound in the Fenton-adsorption effluent is 2-chlorocyclohexanol (Fig. 4-D), which is not toxic. This means that the complete treatment is effective in removing organic contaminant species present in the raw leachate.

Conclusions

Fenton process has many environmental advantages plus it is economical, but it alone is not enough for obtaining adequate effluent quality when it comes to mature leachate. Hence, the use of a second treatment is necessary.

On the other hand, in this study it was found that although the removal efficiency of COD is high (>89%) with the adsorption treatment, even could not be arranged in a body water without causing any negative impact (a subsequent biological treatment could be used, as BI is suitable for it -0.476-). Try raw leachate only with adsorption process causes quickly saturate of the GAP packing the column, and therefore, the useful life is shortened.

Adsorption preceded by the Fenton process with granular activated carbon is more efficient in removing contaminants from landfill leachate than if treated only by adsorption (with GAC).

Table 3. Organic compounds found in the leachate samples analyzed and their possible sources

Compound	Synonym	Source
Raw leachate		
Aniline	1-Aminobenzene	Polyurethane foam manufacturing, agricultural chemicals, synthetic paint, antioxidants, stabilizers for the rubber industry, herbicides, varnish and explosives
Benzene, 1-methyl-2-(1-methylethyl)-	o-cymene	Solvents, manufacture of synthetic resins, metal polish, organic compounds synthesis
2-chlorocyclohexanol	Cyclohexanol 2-chloro-	-
4-methylphenol	p-cresol	Dissolution of chemicals (disinfectants and deodorants), pesticides manufacturing; naturally found in foods and in wood smoke, tobacco and coal tar
Bicyclo[2.2.1]heptan-2-one, 1,7,7-trimethyl-, (1S)-	1(S) camphor	Nitrocellulose plasticizer, moth repellent, antimicrobial, embalming, fireworks, anesthetic, flavoring
Cyclohexanecarboxylic acid	Hexahydrobenzoic acid	Cosmetics, perfumes (taste and odor), food
3-cyclohexene-1-methanol, $\alpha,\alpha,4$ -trimethyl-	(S) α -terpineol	Perfumes, cosmetics, flavors, sanitizers, cleaners
Benzene, 1,3-bis(1,1-dimethylethyl)-	Benzene, m-di-tert-butyl-	-
Phenol 2,4-bis (1,1-dimethylethyl)	2,4-di-tert-butylphenol	Antioxidant used in soaps, plastics, food and oils
2 (3H)-benzothiazolinone	Benzothiazolinone	-
3,5-di-tert-butyl-4-hydroxyphenylpropionic acid	Fenozan	-
Phenol, 4,4'-(1-methylethylidene)bis-	Bisphenol A	Plastics, food and beverage can coating, fungicide, water pipe coating
Pentoxifylline	Trental	Medication, blood flow activator
Cholestan-3-ol, (3 β ,5 β)-	Coprostanol	Biomarker for the presence of fecal contamination, feces odor
Cholestanol	Cholesterol	Found in vertebrates' body tissues and plasma
Fenton effluent		
2-chlorocyclohexanol	Cyclohexanol 2-chloro-	-
Benzyl alcohol	Phenylmethanol	Solvent, found in many fruits and teas
4-methylphenol	p-cresol	Dissolution of chemicals (disinfectants and deodorants), pesticides manufacturing; naturally found in foods and in wood smoke, tobacco and coal tar
Benzene, 1,3-bis(1,1-dimethylethyl)-	Benzene, m-di-tert-butyl-	-
Terpin hydrate	Terpinol	Medication, expectorant
3-(1-methyl-2-pyrrolidinyl)-(S)-pyridine	Nicotine	Cigarettes, insecticides
Phenol 2,4-bis (1,1-dimethylethyl)	2,4-di-tert-butylphenol	Antioxidant used in soaps, plastics, food and oils
2 (3H)-benzothiazolinone	Benzothiazolinone	-
Phenol, 4,4'-(1-methylethylidene)bis-	Bisphenol A	Plastics, food and beverage can coating, fungicide, water pipe coating
Fenton-adsorption effluent ¹		
2-chlorocyclohexanol	Cyclohexanol 2-chloro-	-
1,3, 5-Trimethylbenzene	Benzene, m-di-tert-butyl-	-
Cholestan-3-ol, (3 β ,5 β)-	Coprostanol	Biomarker for the presence of fecal contamination, feces odor
Eicosane	-	-
Benzene, 1-methyl-2-(1-methylethyl)-	o-cymene	Solvents, manufacture of synthetic resins, metal polish, organic compounds synthesis
Phenol, 4,4'-(1-methylethylidene)bis-	Bisphenol A	Plastics, food and beverage can coating, fungicide, water pipe coating

2-methylpent-1-en-3-ol- 2,6,10,15,19,23- Hexamethyl-6,10,14,18,22- tetracosahexaene	- - -	Vaccines	-
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¹Final effluent of the leachate treated by the Fenton-adsorption process.

²Final effluent of the leachate treated only by the adsorption process.

Color, COD, total nitrogen, ammoniacal nitrogen and TOC removals over 99% are achieved with the Fenton-adsorption treatment train, and removals over 95% are achieved for TDS and BOD₅. The BI was improved in both treatments.

The most abundant organic compound in the raw leachate was Bisphenol A. It is not degraded by Fenton oxidation, but is retained by the carbon in the adsorption process (preceded by Fenton).

It was found that the Fenton-adsorption process is effective for the treatment of landfill leachates. However, it is costly due to the adsorption material, which should undertake studies designed to optimize the use of GAP, for example heterogeneous Fenton treatment (Méndez *et al.* 2015) in which GAP is used as the support Fe²⁺ to prevent sludge formation and improve the efficiency of carbon adsorption.

References

- Abbas, A., Jingsong, G., Ping, L., Ya, P., Al-Rekabi W. (2009), Review on landfill leachate treatments. *American Journal of Applied Sciences Research* 6, 672-684.
- APHA-AWWA-WPCF (2005). *Standard Methods for the Examination of Water and Wastewater*, 18th ed. American Public Health Association, Washington DC.
- Aziz, S. Q., Aziz, H. A., Yusoff, M. S., Bashir, M. J., (2011). Landfill leachate treatment using powdered activated carbon augmented sequencing batch reactor (SBR) process: Optimization by response surface methodology. *Journal of Hazardous Materials* 189, 404-413.
- Banar, M., Özkan, A., Kürkcüoğlu M. (2006). Characterization of the leachate in an urban landfill by physicochemical analysis and solid phase microextraction-GC/MS. *Environmental Monitoring and Assessment* 121, 437-457.
- Bashir, M.J., Isa, M.H., Kutty S.R., Awang Z.B., Aziz H.A., Mohajeri S., Farooqi I.H. (2009), Landfill leachate treatment by electrochemical oxidation. *Waste Management* 29, 2534-2541.
- Bodzek, M., Lobos-Moysa, E., Zamorowska, M. (2006). Removal of organic compounds from municipal landfill leachate in a membrane bioreactor. *Desalination* 198, 16-23.
- Calli, B., Mertoglu, B., Inanc, B. (2005). Landfill leachate management in Istanbul: applications and alternatives. *Chemosphere* 59, 819-829.
- Cortez, S., Teixeira, P., Oliveira, R., Mota, M. (2011). Evaluation of Fenton and ozone-based advanced oxidation processes as mature landfill leachate pre-treatments. *Journal of Environmental Management* 92, 749-755.
- Cueto C. R. (2012). *Study of the degradation and mineralization of Bisphenol a (BPA) by Fenton oxidation* (in Spanish). Degree thesis, Universidad de Cantabria, España.
- Deng, Y., Englehardt, J. (2006). Electrochemical oxidation for landfill leachate treatment. *Waste Management* 27, 380-388.
- Eggen, T., Moeder, M., Arukwe, A. (2010). Municipal landfill leachates: a significant source for new and emerging pollutants. *Science of the Total Environment* 408, 5147-5157.
- Guo, J. S., Abbas, A. A., Chen, Y. P., Liu, Z. P., Fang, F., Chen, P. (2010). Treatment of landfill leachate using a combined stripping, Fenton, SBR, and coagulation process. *Journal of Hazardous Materials* 178, 699-705.
- Halim, A. A., Aziz, H. A., Johari, M. A. M., Ariffin, K.S. (2010). Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment. *Desalination* 262, 31-35.

- Kang, K.H., Shin, S., Park H. (2002). Characterization of humic substances present in landfill leachates with different landfill ages and its implications. *Water Research* 36, 4023-4032.
- Kurniawan, T.A., Lo, W., Chan, G. (2006). Physicochemical treatments for removal of recalcitrant contaminants from landfill leachate. *Waste Management* 129, 80-100.
- Markey, C., Luque, E., Muñoz de Toro, M., Sonnenschein, C., Soto, A. (2001). In utero exposure to bisphenol A alters the development and tissue organization of the mouse mammary gland. *Biology of Reproduction* 65, 1215-1223.
- Martínez, E., López, G. (2001). Chemical treatment of organic pollutants: Fenton process, (in Spanish). *Ingeniería Química* 375, 149-151.
- May A. (2010). *Optimization of the adsorption process of a leachate treatment Fenton-filtration-adsorption* (in Spanish). Master's thesis, Universidad Autónoma de Yucatán, México.
- Méndez, R., Castillo, E., Sauri, M., Barceló, I., Ramírez R. (2010). *Development of a technology for the treatment of leachate*, (in Spanish), Proceedings of the Third National Meeting of Experts on Solid Residues, Mexico City.
- Méndez R., May A., Barceló I., Giacomán G., Zetina C. (2015) *Leachate treatment by heterogeneous Fenton* (In Spanish). 3rd Network forum quality, systems development treatment, recovery and sustainability of water bodies: water technology. UAM Azcapotzalco, México D.F.
- Pérez, P., Pulgar, R., Olea-Serrano, F., Villalobos, M., Rivas, A., Metzler, M., Pedraza, V., Olea, N. (1998). The estrogenicity of bisphenol A-related diphenylalkanes with various substituents at the central carbon and the hydroxy groups. *Environmental Health Perspectives* 106, 167-174.
- Ramírez, D., Castillo. E., Méndez, R., Sauri, M., Barceló. M., Marrufo J. (2013). Determination of organic compounds in landfill leachates treated by Fenton-Adsorption. *Waste Management* 2, 390-395.
- Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F., Moulin, P., (2008), Landfill leachate treatment: review and opportunity. *Journal of Hazardous Materials* 150, 468-493.
- Salas G. and Ale N. (2014). Treatment of wastewater from an oil refinery by advanced oxidation process (AOP) using Fenton's reagent (H_2O_2/Fe^{2+}) (in Spanish). *Revista Peruana de Química e Ingeniería Química* 11, 12-18.
- Sang, Y., Gu, Q., Sun, T., Li, F. (2008). Color and organic compounds removal from secondary effluent of landfill leachate with a novel inorganic polymer coagulant. *Water Science Technology* 58, 1423-1432.
- Schafer, T., Lapp, C., Hanes, M., Lewis, J., Wataha, J., Schuster, G. (1999). Estrogenicity of bisphenol A and bisphenol A dimethacrylate *in vitro*. *Journal of Biomedical Materials Research* 45, 192-197.
- SEMARNAT, (2003), Mexican Official Norm NOM-001-SEMARNAT-1996, that establishes the maximum allowable pollutant in wastewater discharges in national waters (in Spanish), Official Journal of the Federation, Mexico.
- SEMARNAT, (2004), Mexican Official Norm NOM-083-SEMARNAT-2003, environmental protection specifications for site selection, design, construction, operation, monitoring, closure and additional works of a final disposal site for solid waste and special handling (in Spanish), Official Journal of the Federation, Mexico.
- Shahriari, H., Fernandes, L., Tezel, F. (2008). Investigation of organic, inorganic and synthetic adsorbents for the pretreatment of landfill leachate. *Environmental Technology* 29, 543-552.
- Sharholly, M., Ahmad, K., Mahmood, G., Trivedi, R. (2008). Municipal solid waste management in Indian cities: a review. *Waste Management* 28, 459-467.
- Slack, R., Gronow, J., Voulvoulis, N. (2005). Household hazardous waste in municipal landfills: contaminants in leachate. *Science of the Total Environment* 337, 119-137.

- Ubaldo V. E. D. C., Nájera A. H. A., Gutiérrez H. R. F. (2014). Evaluation of the removal of organic load by mature leachate a coupled system: coagulation-flocculation-anodic oxidation (in Spanish) *Revista AIDIS de Ingeniería y Ciencias Ambientales: Investigación, Desarrollo y Práctica* 7, 170-178.
- Valdés, H., y Zaror, C. A. (2010). Influence of surface chemical composition of the activated carbon adsorption benzothiazoles (in Spanish). *Ingeniare. Revista Chilena de Ingeniería* 18, 38-43.
- Visvanathan, C., Choudhary, M., Montalbo, M., Jegatheesan, V. (2007). Landfill leachate treatment using thermophilic membrane bioreactor. *Desalination* 204, 8-16.
- Wang F., El-Din, M., Smith, D. (2004). Oxidation of aged raw landfill leachate with O₃ only and O₃/H₂O₂: treatment efficiency and molecular size distribution analysis. *Ozone: Science and Engineering* 26, 287-298.
- Wiszniewski, J., Robert, D., Surmacz-Gorska, J., Miksch, K., Weber J. (2006). Landfill leachate treatment methods: a review. *Environmental Chemistry Letters* 4, 51-61.
- Wu, Y., Zhou, S., Qin, F., Peng, H., Lai, Y., Lin, Y. (2010). Removal of humic substances from landfill leachate by Fenton oxidation and coagulation. *Process Safety and Environmental Protection* 88, 276-284
- Xing, W., Ngo, H., Kim, H., Guo, W., Hagare, P. (2008). Physicochemical processes for landfill leachate treatment: experiments and mathematical models. *Separation Science and Technology* 43, 347-361.
- Yamamoto, T., Yasuhara, A., Shiraishi, H., Nakasugi, O. (2001). Bisphenol A in hazardous waste landfill leachates. *Chemosphere* 42, 415-418.
- Yilmaz, T., Aygün, A., Berktaş, A., Nas, B. (2010). Removal of COD and colour from young municipal landfill leachate by Fenton process. *Environmental Technology* 31, 1635-1640.
- Yokoyama, L., Campos, J.C., Moura, D.A.G., Costa, A.P.M., Cardillo, L. (2009). *Ammonia removal from landfill leachates by air stripping*, Twelfth International Waste Management and Landfill Symposium, Cagliari, Italy, October 5-9.