

REMOVAL OF BPA FROM LANDFILL LEACHATES USING FENTON-ADSORPTION PROCESS

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The objective of this investigation was to identify and quantify the presence of Bisphenol-A (BPA) in raw and treated leachates with the Fenton-adsorption process. BPA is used as a monomer to produce epoxy resins and it is a compound classified as endocrine disruptor. For this reason, it is important to quantify its presence in effluents that will be disposed to the environment to avoid damage to human health and other organisms. The Fenton-adsorption process consisted in the implementation of an advanced oxidation using H₂O₂ and FeSO₄ applied to the raw leachate and subsequently the application of the adsorption process through a column packed with activated carbon. The quantification of BPA was carried out by gas chromatography coupled to mass spectrometry, using liquid-liquid and liquid-solid extraction methods. A recovery percentage study was carried out to validate the extraction methods. Finally, it was found that the leached evaluated contained >12 mg L⁻¹ and at the end of the treatment its concentration was <0.0174 mg L⁻¹.

Keywords: leachate; Fenton; adsorption; BPA; activated carbon.

INTRODUCTION

The compounds classified as endocrine disruptors (EDCs) have been detected in water bodies such as rivers, groundwater and lakes, as well as in domestic wastewater and leachate from landfills.^{1,2} Substances such as bisphenols, dioxins, pesticides, phthalates, alkyl phenolics, furans and synthetic steroids are considered EDCs since they have the potential to modify the metabolic process at the hormonal level and produce adverse biological effects.^{3,4} Bisphenol-A (better known as BPA) is widely used today in the production of plastics,^{5,6} therefore human exposure occurs mainly via hydrolysis of polycarbonate plastics and epoxy resins, resulting in low concentrations in food and liquids originally free of this compound.

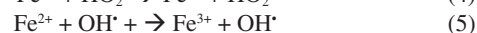
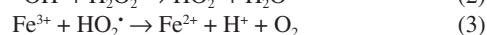
BPA is not found naturally in the environment, its presence is due to the production, consumption and subsequent disposal of the materials that contain it; the sources can be classified as “pre-consumption” (all activities of plastic manufacture) and “post-consumption” (wastes released through waste).⁷ BPA is released to the environment through the effluents of treated wastewater (human intake eliminated in wastewater), leachate from landfills (via hydrolysis of BPA from plastics), or natural degradation of polycarbonate plastics. The highest concentration reported has been found in landfill leachates, which is higher than 17 mg L⁻¹,⁸ and the lowest concentration has been found in clear waters, in units of µg L⁻¹ (for example: 0.002 µg L⁻¹ in drinking water).⁹ BPA can be leached from polycarbonate plastics when exposed to heat, which is the reason that the landfill leachate can contain high concentrations.

BPA is very common in the human daily diet due to the high use of plastic containers; however, humans can excrete it in their feces, but in aquatic animals it has been observed an accumulation in the population which could have a negative impact on such organisms. The main effects of BPA on vertebrate aquatic species are mainly in the definition of sex and the reproduction process, gonad functionality and development, thyroid system, metabolism, immune functions, among others.¹⁰

BPA is highly resistant to biological and chemical degradation. However, some specific microorganisms like *C. mexicana* can degrade this compound,¹¹⁻¹³ whose effectiveness depend on the nature of the water in which they are found and advanced oxidation technologies, physicochemical methods such as catalytic oxidation, Fenton oxidation and ozonation,^{4,14} have been reported as effectively methods for BPA degradation.

Leachate is the result of liquid percolation through wastes in process of degradation; it is subject to successive filtration processes through the soil layers resulting in a high concentration of suspended solids. Treatments such as flotation or coagulation-flocculation, which consist of removing particles by the addition of chemicals, are inefficient. However, it has been probed that Fenton oxidation and the adsorption process together can efficiently remove suspended and dissolved particles.¹⁵

The general mechanism of Fenton oxidation includes the following steps:



This reaction starts in (1) and it becomes cyclical in (1), (2) and (3), while (4) and (5) are the end steps.¹⁶ The Fenton reagent is very effective for the elimination of organic contaminants since it can break macromolecules and transforming them into harmless compounds. The reaction causes the dissociation of the oxidant activating the hydroxyl radicals that degrade the organic.^{17,18} In previous studies the Fenton reaction has been used to treat waters and soils with the presence of BPA, obtaining removal efficiencies of 75-83% and diverse byproducts of Fe²⁺.¹⁹⁻²²

Contaminated waters have been treated with advanced oxidation processes and adsorption with activated carbon to remove estrogenic compounds, reaching 90% removals.²³ Activated carbon is one of the

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most used absorbent materials since it is very porous and has a large surface area, which gives it a good adsorption capacity to remove contaminants from water and gases, such as pesticides, metal ions, organic pollutants, etc.²⁴

The study area from this research has a karstic and highly permeable soil; leachates can filter very easily into groundwater (the only source of water for consumption in the area) and contaminate it, causing harmful effects in the population that is supplied from it and in the species that live there. In literature there are numerous treatments based only on advanced oxidation or adsorption process (among others) for the removal of organic matter, including the BPA compound, however no experiences are reported with both processes used consecutively in a treatment train for landfill leachate. This work shows the results of the analysis in each stage of the treatment, in addition, it is the first study in Mexico's southeastern on the quantification of BPA in leachates, an estrogenic substance that could be migrating to the highly vulnerable water table and causing contamination of fresh water and possibly reaching the sea. For this reason, the purpose of this study is to evaluate the Fenton-adsorption process for landfill leachate in order to remove the organic matter (measured as chemical oxygen demand -COD-) and, specifically, the BPA.

EXPERIMENTAL

The landfill in Mérida, Yucatán, is not young (more than 25 years in operation); *in situ*, the leachates in the evaporation ponds are recirculated and sent back to the landfill, where they have contact with the residues that are still stabilizing, which gives mixed characteristics to the effluent. In addition, the cover material of the filling (sahcab) is limestone type, which reduces porosity when compressed, which makes it act as a filter retaining larger particles and reacting dissolving carbonates, that gives the leachate high values of Na, K and hardness, which increases the pH and gives a buffering capacity.

The methodology of the treatment carried out with these leachates to reduce their organic load and the analysis of the presence of BPA compound in each stage of the process is described below.

Fenton-adsorption treatment for landfill leachate

Leachate samples were taken from the evaporation ponds of the sanitary landfill in the city of Merida, Yucatan, Mexico. Samples were stored in a dark room at 4 ° C until the analysis (time not exceeding 24 hours). These samples were treated with H₂SO₄ until reaching a pH = 4 (in previous investigations, this pH value was found to be optimal for Merida's leachate);¹⁸ then, an optimum dose of H₂O₂ and FeSO₄·7H₂O reagents was added (Fenton's oxidation), according to San Pedro *et al.*,¹⁵ corresponding to the relations $[\text{COD} / \text{H}_2\text{O}_2] = 9$ and $[\text{Fe}^{2+} / \text{H}_2\text{O}_2] = 0.6$ (with an average COD = 10193 mg L⁻¹, 3.4 g of FeSO₄·7H₂O and 3.3 mL de H₂O₂ were added to treat one liter of sample). After 5 minutes of rapid mixing (250 rpm), it was left to settle for one hour to later pass the sample through an Interfilter™ filter press, model 20-18, using a filter paper with a pore size of 20-25 μm to facilitate the separation of the sludge produced. The filtered leachate in this stage was called "Fenton effluent". The remaining solids were called "Fenton sludge".

Finally, the Fenton effluent was subjected to the adsorption process by passing it through a up flow column packed with macroporous granular activated carbon (GAC) of lignite type Gama L™, whose physical characteristics are: raw mineral material lignite, mesh count: 8 x 30, surface area: 348.61 m² g⁻¹, relative density: 0.38, cross-section of the adsorption area: 0.162 nm². The effluent obtained in this stage was called "adsorption effluent". The sample was passed

into the column until it was saturated (that is, when the final COD was close to the initial one). The saturated carbon in the adsorption column was named "saturated carbon". Figure 1 shows a diagram of the complete train treatment.

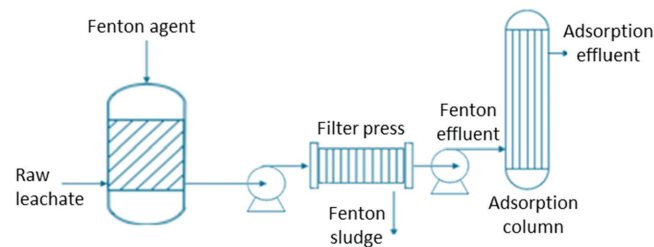


Figure 1. Schematic of the leachate treatment train

The solid and liquid samples obtained in each stage of the treatment were characterized using the standard methods,²⁵ for the parameters analyzed: chemical oxygen demand (COD), chemical oxygen demand soluble fraction (COD_s), biological oxygen demand the fifth day (BOD₅), 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 nitrogen ammonia (NH₃-N).

Extraction of organic compounds

For the extraction of the organic compounds contained in the liquid samples (raw leachate, Fenton and adsorption effluents) and solid samples (Fenton sludge and saturated carbon) the following procedures were carried out (all reagents used were HPLC grade -high purity liquid chromatography-):

a) Liquid samples

The extraction of organic compounds in the liquid samples were carried out with the procedure used by Ramírez-Sosa *et al.*,²⁶ and consisted in adjusting the pH to 12 with NaOH 10 M and adding 50 mL of CH₂Cl₂ to aliquot of 500 mL, shaking and recovering the lower phase. This procedure was performed for triplicate. The recovered sample was adjusting to pH 2 with H₂SO₄ 5.26 M and the extraction was repeated for triplicate (in the same way as in the alkaline phase). The recovered extract (approximately 300 mL) was taken to a rotavapor apparatus to concentrate the sample to 5 mL. Then, anhydrous Na₂SO₄ was added to remove the humidity and filtered with glass fiber. Finally, the sample obtained was evaporated using a gentle stream of nitrogen up to 1 mL.

b) Solid samples

The Fenton sludge and saturated carbon samples recently obtained from the leachate treatment were left at room temperature (25 °C) for 24 hours in order to remove the humidity excess. Subsequently, 5 g of sample was weighed on a filter paper and it was placed into a Teflon tube, 25 mL of CH₂Cl₂ was added and taken to the microwave (power 400 W, 70 ° C for 15 min, ramp 2 min). After the extraction, the tube was cooled at room temperature. The supernatant was filtered using glass fiber (a little Na₂SO₄ was used to remove the humidity that it might still contain) and was taken to the rotavapor apparatus to evaporate it to approximately 5 mL. Subsequently, a gentle stream of nitrogen was passed to concentrate 1 mL.

Identification and quantification of organic compounds

EPA Method 524.2²⁷ was modified and adapted to the samples. For the identification of the organic compounds a gas chromatograph

(Thermo Scientific), Trace GC Ultra model, coupled to a mass spectrometer ITQ900 was employed; software Xcalibur was used for data acquisition and interpretation; for comparison of the experimental mass spectra, the NIST 2008 database was used. The run method was: temperature of injector: 270 °C; transfer line: 270 °C; ramp: 50 °C, 2 min, increasing 10 °C min⁻¹ to 300 °C, 3 min; split flow 60 mL min⁻¹; split time: 1; flow 1 mL min⁻¹; volume of injection: 1 µL; column: Thermo TR-SQC (30 m*0.25 mm*0.25 µm) and run time: 30 min.

For the quantification of the compound of interest, it was employed a flame ionizer detector. The chromatographic conditions were: oven initial temperature: 100 °C, during 1 min, increasing 10 °C min⁻¹ to reach 270 °C, 1 min; run time: 19 min; splitless flow: 50 mL min⁻¹ with 1 min splitless time saver 20 mL min⁻¹; gas He, ratio 1.5 mL min⁻¹; volume of injection: 2 µL; column: Thermo TR-SQC (30 m*0.25 mm*0.25 µm); base temperature 300 °C, Air/H₂ ratio: 10 (350 and 35 mL min⁻¹) and signal state: 1 mV.

Recovery percentage study

The standard compound Bisphenol-A (CAS 80-05-7), Sigma Aldrich 99% purity, and solutions with known concentrations (using CH₂Cl₂ as solvent) were prepared to carry out calibration curves. Using the intercept method, detection and quantification limits were calculated.

To standardize the extraction technique of organic compounds from the leachate, tests of accuracy and precision were carried out. For liquid samples, a matrix was prepared with 6 L of distilled water and 2 L of each of the following samples: raw leachate, Fenton effluent and adsorption effluent. It was added 800, 2750 and 600 mg L⁻¹ of BPA to samples of the matrix and a white of distilled water was used. For the solid waste, samples of 5 g were taken (both for carbon and sludge and a witness was used for each one); and added 160, 550 and 1200 mg of BPA. Dilutions of the analyzed samples were made to be placed in the range of the calibration curve.

Finally, the compounds were quantified, and the corresponding data analysis was made to establish the recovery percentages, the limits of detection and quantification, the accuracy and the correlation coefficient.

RESULTS AND DISCUSSION

Fenton-adsorption

The composition of the leachates depends on many factors, for example, the nature of the waste, chemical and biochemical processes of degradation, and water content in the wastes, among others.²⁸ This means that the type and quantity of contaminants vary from one place to another. Table 1 shows the results of the parameters analyzed in the samples of raw leachate, Fenton effluent and adsorption effluent. In the last column, the global percentage of contaminants removal is observed, which is greater than 99% in the parameters of COD, color, ammonia nitrogen, total carbon and total organic carbon. Also, in the last row of the Table 1, the biodegradability index (BI) is observed, which is the BOD₅/COD ratio and indicates the state of degradation of the leachates. A BI value between 0.4 and 0.8 is usual for municipal wastewater.²⁹ A low BI value means that biological treatments will be inefficient to decontaminate the leachates, for this reason the Fenton-adsorption process was used, since the leachate from the Mérida sanitary landfill has a BI value of 0.084. It is worth mentioning that the standard deviation presented for the TOC_T is high, this is due the fact that the concentration in the samples was variable (three samples were taken on different days).

The efficiency of the treatment of leachates with Fenton-adsorption for the removal of measured contaminants such as COD, BOD or TC is high, but does not provide information about the substances that contain the organic load. Therefore, it is necessary to trace these compounds. Previous studies have characterized leachates from different regions,³⁰⁻³² the species found and their concentrations being highly variable.

Identification and quantification of BPA

Figure 2 shows the total ion chromatogram (TIC) obtained from the analysis of the raw leachate; according to the intensity of the ions detected (area under the curve), the major compound is 4,4'-(propane-2,2-diyl) diphenol, CAS number 80-05-7, known as BPA, which appears in the minute 21.47. BPA (molecular formula C₁₅H₁₆O₂) is a white solid, with molecular weight equal to 228.29 g mol⁻¹

Table 1. Results of the parameters analyzed in the leachate samples through the treatment

Parameter	Raw leachate	Standard deviation	Fenton effluent	Standard deviation	Adsorption effluent	Standard deviation	% of global removal
TOC _T (mg L ⁻¹)	10193	263	4658	813	44	37	99.5
TOC _S (mg L ⁻¹)	9958	151	3840	189	36	42	99.6
BOD _{5T} (mg L ⁻¹)	861	46	387	64	36	28	95.8
BOD _{5S} (mg L ⁻¹)	748	6	321	19	33	25	95.6
pH	8.31	0.1	3.96	0.2	7.11	0.1	-
Color 455 nm (u Pt-Co)	13667	870	6940	6078	20	19	99.8
TS (mg L ⁻¹)	19050	685	23533	804	1338	790	92.9
TSS (mg L ⁻¹)	360	47	2056	1993	110	9	69.5
TSD (mg L ⁻¹)	18690	671	21477	1677	1228	799	93.4
TN (mg L ⁻¹)	2113	210	1813	300	58	25	97.2
N-NH ₃ (mg L ⁻¹)	1797	479	1653	391	15	12	99.2
TC (mg L ⁻¹)	5112	507	1388	153	24	8	99.5
IC (mg L ⁻¹)	162	6	7	3	14	14	91.3
TOC (mg L ⁻¹)	4950	513	1380	150	9	6	99.8
BI	0.084	-	0.083	-	0.820	-	-

and melting and boiling points of 158 and 220 °C, respectively. Its solubility in water is 120-300 mg L⁻¹ at room temperature.⁵ Since BPA is the most abundant organic specie in the leachate, qualitative and quantitative monitoring of this compound was carried out throughout the treatment.

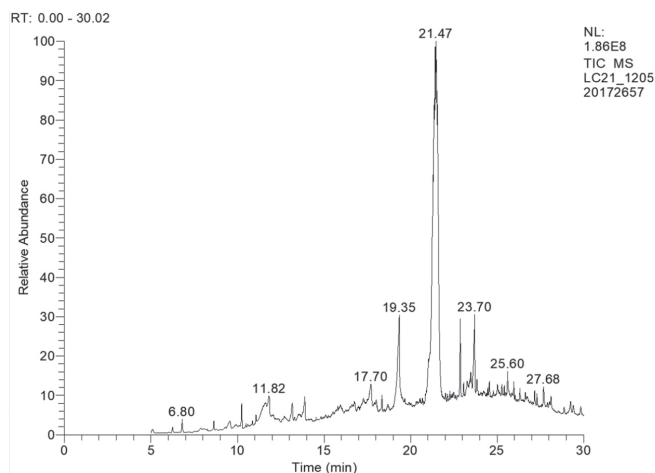


Figure 2. TIC of the raw leachate sample

The first step of Fenton oxidation is the acidification of the sample. For the treatment of the leachate from the Merida city landfill, the pH was adjusted to 4 with H₂SO₄. This change in the sample generates the first step in the degradation of the BPA molecule, since a decrease in the particle size is observed. The effect of pH with respect to the particle size of BPA was analyzed in the study of Zhao *et al.*,³³ the smallest size was found at pH 5, decreasing by about 23%, while at pH 9 it was only minimized by 11%. Once the sample was acidulated, the Fenton reagent was added to later pass to the filtering stage.

TIC of the Fenton effluent is shown in Figure 3, where the BPA is the compound with the greatest area under the curve (21.35 min). Figure 4 shows the TIC of the residue of this stage where the presence of BPA is observed (minute 21.06). Although, qualitatively the presence of BPA is still intense in Figures 3 and 4, the quantitative analysis revealed that there is a decrease of almost 65% in the Fenton effluent (in the literature,^{34,35} experiences of BPA removal are reported in the range of 16-78% using H₂O₂ as degradation agent). This high degradation percentage achieved is probably due to the increase of OH[•] radicals during the intensive oxidation. In the study of Zhang *et al.*,² the degradation of the BPA molecule oxidized with CuFeO₂/H₂O₂ was monitored and the following intermediate

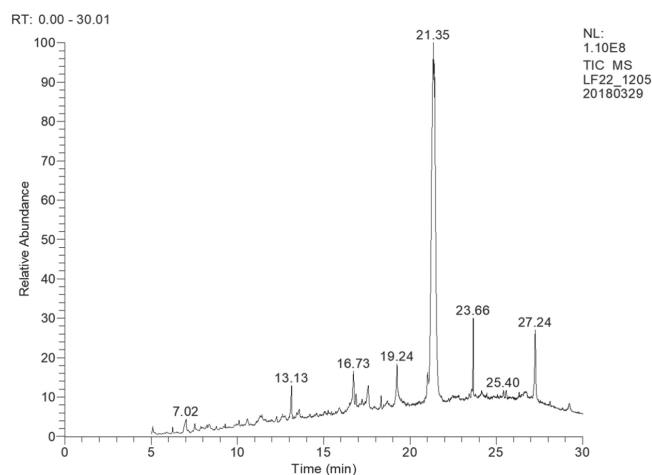


Figure 3. TIC of the Fenton effluent sample

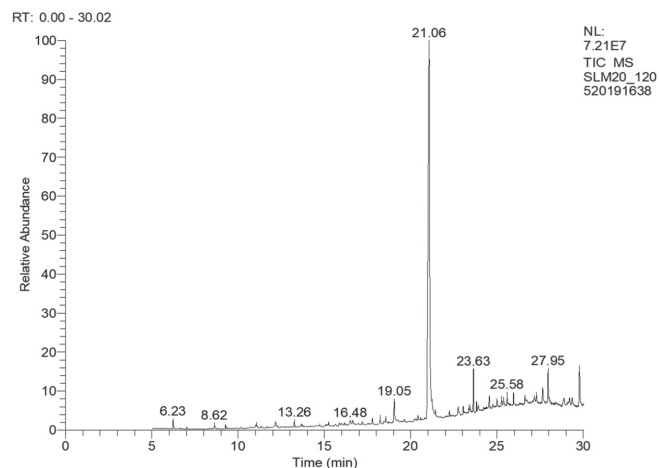


Figure 4. TIC of the Fenton sludge sample

species were found: phenol, p-hydroquinone, 4-isopropenylphenol, 4-hydroxyacetophenone and BPA-o-catechol, the latter was found as a predominant compound in other studies.³⁶⁻³⁸

Under the presence of certain substances, such as hydroxyl radicals or sulfates,⁴ the intermediates of the BPA degradation reaction eventually become CO₂ and water. Degradation follows two possible paths,³⁸ the first is the transformation to BPA-o-catechol (by hydroxylation); the second is by partitioning the molecule because of the oxidizing agent, to form the molecules 4-isopropenylphenol and phenol. Both routes coincide in the formation of 4-hydroxyacetophenone and hydroquinone to subsequently break the aromatic rings and become lactic and glycolic acids. Finally, these compounds are transformed into water and CO₂. The BPA mineralization reaction,² in the presence of H₂O₂ is as follows:



For the adsorption of BPA in liquid solvents, activated carbon is an alternative due to its large surface area and adsorptive capacity. Lazim *et al.*,⁵ compared different adsorbent materials showing the best efficiencies for almond shell (188.9 mg g⁻¹), activated rice straw (181.19 mg g⁻¹) and two commercial activated carbons (129.6 and 78.13 mg g⁻¹, respectively). Figure 5 shows the TIC of the adsorption effluent, where the representative peak of BPA has vanished (since it should be reflected at 21-22 min). The peaks observed in the chromatogram correspond to siloxanes from the column used in the

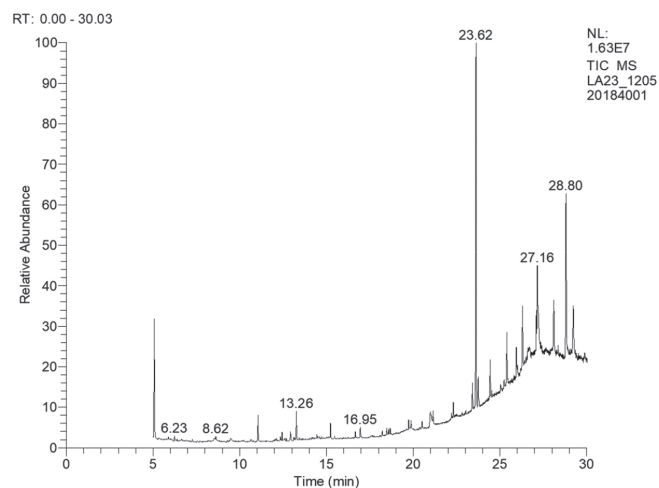


Figure 5. TIC of the adsorption effluent sample

gas chromatograph. On the other hand, in Figure 6 the TIC of the saturated carbon sample is observed, where at minute 21.2 the peak of BPA appears. In relation to the total amount of BPA in the sample of raw leachate, 8% is retained in the Fenton sludge, while a 1.63% is adsorbed on the activated carbon at the end of the treatment.

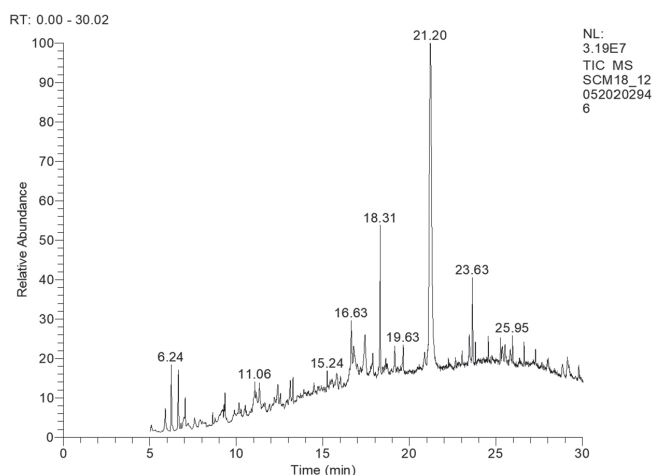


Figure 6. TIC of the saturated carbon sample

Table 2 shows the results of the quantification, the overall percentage of BPA removal in leachates treated with Fenton-adsorption is >99% (according to the recovery percentage study, whose limit of quantification is 0.0174 mg L⁻¹). Therefore, it can be concluded that the granular activated carbon used in the adsorption process acted as a receptor for the particles previously degraded in the Fenton process and completed the removal of almost all the substance. The responsibility for this fact is strongly related to the nature of carbon and its interstitial availability,^{39,40} before the molecules previously degraded in the Fenton stage. It is worthwhile mention, although the removal of BPA is high, the degradation is not yet complete, since the remainder in the solid samples is 0.25 mg g⁻¹ (Fenton sludge + saturated carbon). Since the degradation is an infinite process, it is possible that the compound continues to oxidize over time in the solid samples, because the pH and the possible OH⁻ remaining favor this process.^{4,5,41}

Table 3 shows the results of different studies on the removal of BPA in samples of clear and residual water, as well as landfill

Table 2. Results of the quantitative analysis of BPA in all samples

Sample	Concentration	Standard deviation
Raw leachate	12.66 mg L ⁻¹	7.02
Fenton effluent	4.49 mg L ⁻¹	2.93
Adsorption effluent	Nd	--
Fenton sludge	0.21 mg g ⁻¹	0.12
Saturated carbon	0.04 mg g ⁻¹	0.02

leachate, where it is observed that the efficiency of the presented treatment is superior.

Validation of organic compound extraction method

Before quantification, a percentage recovery study was conducted to standardize the organic compound extraction technique. The percentages of recovery were calculated following equation:

$$R = \frac{y - x_i}{x_a} \quad (7)$$

where y is the sample plus the added analyte concentration, x_i the initial sample concentration and x_a is the added analyte concentration.

The concentration levels 800, 2750 and 6000 mg L⁻¹ (160, 550, 1200 mg g⁻¹) were analyzed; in order to measure these concentrations, dilutions were made so that the results were within the range of the calibration curve of Figure 7 (3.25-50 mg L⁻¹). The percentages of average recovery that were obtained are shown in Table 4. The percentage of acceptable recovery according to the Manual of Policies and Procedures of the International Association of Official Agricultural Chemists (AOAC) is between 60 and 110%.⁵⁰ Consequently, the percentages obtained in this study fulfill this parameter.

The detection and quantification limits were determined following the definition of the International Union of Pure and Applied Chemistry (IUPAC) adopted in 1975, which states that the limit of detection expressed as a concentration, or quantity, is derived from the smallest measure that can be detected with reasonable certainty for a given analytical procedure.⁵¹ The detection limit was calculated: DL=3.3S_b/m, where S_b is the standard deviation and m is the slope of the calibration curve of the system. The limit of quantification was

Table 3. Comparison of treatments of samples contaminated with BPA and removal efficiencies

Sample	Treatment	Removal %	Reference
Water	Heterogeneous photodegradation (titanium dioxide) of BPA	83	42
	Ion Fe(VI)	100	43
River water	Degradation by bacteria	99	44
	<i>C. mexicana</i>	24	13
	Membrane reactor	94	12
Domestic wastewater	Degradation and decantation	>90	45
	Activated sludge reactor	90	46
	Ozonation	70	
Landfill leachate	Single-walled carbon nanotubes	33	47
	Adsorption with zeolite	82	48
	Fenton process	88	49
	Two-stage MBR system	65	32
	Fenton-adsorption	>99	This work

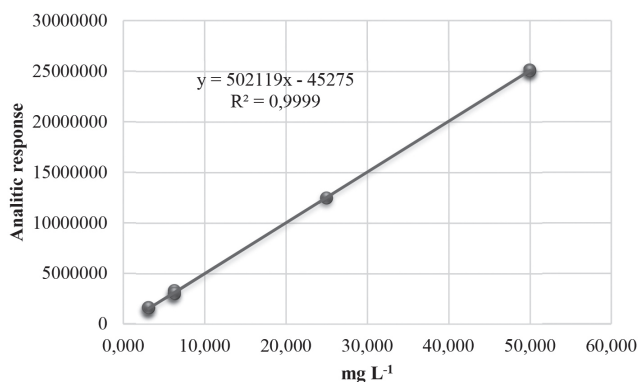


Figure 7. Calibration curve for the quantification of BPA

Table 4. Results of the recovery percentage study

Sample	% of recovery
Pure water	97.93
Matrix	76.02
Fenton sludge	75.63
Saturated carbon	78.83

determined with the equation $QL=10S_B/m$. Table 5 shows the limits established for liquid ($mg L^{-1}$) and solid ($mg g^{-1}$) samples.

Table 5. Detection and quantification limits

Detection limit (DL)	Quantification limit (QL)
0.0058 $mg L^{-1}$	0.0174 $mg L^{-1}$
0.0012 $mg g^{-1}$	0.0035 $mg g^{-1}$

CONCLUSIONS

The concentration of BPA in the raw leachate was $>12 mg L^{-1}$, which indicates that it is a potential source of contamination in water receiving bodies. The Fenton-adsorption treatment is efficient to remove the organic matter measured as COD and BPA, in both cases efficiencies $>99\%$ are obtained. The final concentration of BPA in the treated leachate is $<0.0174 mg L^{-1}$. The results indicate that most of the BPA is degraded in the Fenton oxidation; therefore, it is suggested to analyze in detail the BPA degradation route with this treatment to establish which compounds are being formed in each stage and to potentiate the degradation.

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