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## HYDROCARBON REMOVAL FROM DIESEL-CONTAMINATED SOIL THROUGH REUSED ACTIVATED CARBON ADSORPTION

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### Abstract

Hydrocarbon spillages are an increasing problem in Mexico, which has left large areas of contaminated land that entail negative effects on environmental, economical and social aspects. Such soil contamination demands fast, efficient and cost-competitive remediation technologies. This work explores activated carbon (AC) adsorption as a fast soil treatment to lower hydrocarbon concentrations in a contaminated soil from Puebla, Mexico, reusing an AC residue for such purpose. Both, semi-wasted AC and soil were characterized, and treatment tests were performed by mechanically mixing both materials during different periods of time. The semi-wasted AC still presented an acceptable adsorption capacity, which successfully adsorbed 58% of the initial total petroleum hydrocarbons (TPH) concentration (55,141.4 mg/kg) in 60 minutes. It is possible to exploit the residual adsorption capacity of semi-wasted AC for remediation purposes, which could also reduce the environmental costs of AC production, regeneration or reactivation.

*Key words:* activated carbon, adsorption, contaminated soil, hydrocarbon, soil treatment

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### 1. Introduction

The use of petroleum has been present in humanity for a long time and today it is so important that in 2016, it remained as the number one energy source, globally (BP, 2017). Petroleum products can be released into the environment by superficial spillages or leaks, resulting in soil and water contamination (Iturbe et al., 2007a; Preda et al., 2017; Yang et al., 2017). Since total petroleum hydrocarbons (TPH) are often defined as a complex mixture of organic compounds derived from crude oil, some of its constituents are harmful to health and the environment (Speight and Arjoon, 2012). Hydrocarbon spillages frequently occur in soils and negatively alter their chemical, biological and physical properties, destroying terrestrial biota, producing fertility loss,

and inherently polluting air and water (Abbasian et al., 2016; Bello and Inobeme, 2015; Oyem and Oyem, 2013). The effects of soil contamination are not entirely environmental; there are also serious repercussions in economy and society, like the abandonment of degraded agricultural land, health problems, and economic losses (Abbasian et al., 2016; Bello and Inobeme, 2015; Semple, 2017).

There are several remediation technologies available that modify, extract or immobilize hydrocarbons. Adsorption, the adhesion of the molecules of gases, liquids or dissolved substances (adsorbate) to the surface of a solid or liquid particle (adsorbent) (Knödel et al., 2007), is often used to remove organic contaminants from fluids, but its use for soil treatment has been investigated in recent years (Hilber and Bucheli, 2010; Meynet et al., 2012;

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Vasilyeva et al., 2010). Activated carbon (AC) is one of the best adsorbents for organic compounds due to its hydrophobicity, high specific surface area, and porous structure (Gong et al., 2007; Itodo et al., 2010; Nunes and Guerreiro, 2011; Secula et al., 2018) that presents macropores (>50 nm), mesopores (2-50 nm) and micropores (<2 nm) (Roussak and Gesser, 2013). AC has been tested in soils and sediments, to remove a broad range of contaminants (Brändli et al., 2008; Gong et al., 2007; Hilber et al., 2009; Rahimnejad et al., 2018; Zimmerman et al., 2004), with removal efficiencies of up to 100% in laboratory studies (Hilber and Bucheli, 2010).

The AC used for environmental purposes is required to have certain characteristics and to be available in sufficient quantities, but the adsorptive capacity of carbons gradually deteriorates upon usage. When the carbon is exhausted, it has to be regenerated, reactivated, or disposed of. AC regeneration means reduced solid waste handling, but there are some disadvantages of this process associated with air pollution, energy requirements and process costs (An et al., 2015; Hutson et al., 2012; Ledesma et al., 2015). For these reasons, the use of 'spent' or 'semi-wasted' carbon has been investigated to remove organic matter from soils and leachate (Martínez-Gallegos et al., 2017), this means reusing previously used AC to exploit its residual adsorption capacity if its previous use did not involve any hazardous contaminants that could potentially desorb.

In Mexico, hydrocarbon spillages are common along the pipelines that run throughout the country. Studies by Iturbe et al. (2007a; 2007b), reported TPH concentrations as high as 101,759 mg/kg in the soil along pipelines in southern and northern Mexico. Current Mexican legislation (Official Mexican Standard NOM-138-SEMARNAT/SSA1-2012) establishes a maximum limit of 1,200 mg/kg for diesel range organics (DRO) in agricultural soils, and a limit of 5,000 mg/kg in industrial soils (SEMARNAT, 2013). By the end of 2016, Pemex, the state-owned energy company, reported 1,283.8 hectares of contaminated land by 213 hydrocarbon leaks and spillages, mainly caused by duct damage and criminal activity (Iturbe et al., 2007a; Pemex, 2016; Semple, 2017). In 2017, farmers from the state of Puebla reported 120,000 hectares of damaged land and 450 water wells, that affect 15,000 agricultural producers (Cravioto, 2017).

Given the increasing problematic of hydrocarbon-contaminated soils in agricultural areas of Mexico, this work aims to test AC adsorption as a feasible and fast treatment to reduce TPH concentrations in agricultural soils. This adsorption treatment was tested in a contaminated soil sample from the state of Puebla, Mexico, by exploiting the residual adsorption capacity of an AC cartridge originally designed for tap water treatment. The AC cartridge had been previously used for natural organic matter removal, whose desorption would not represent important soil contamination.

## 2. Material and methods

### 2.1. Soil sampling

A sample of contaminated soil (CSs) was extracted from a diesel-contaminated site in the municipality of San Martín Texmelucan, Puebla, Mexico. The spilled product was diesel and the spillage had been weathered for a month before the sampling was carried out. An additional sample of uncontaminated soil (USs) was taken from an adjacent spot where no contamination was evident, as a reference of the original soil quality.

Given the agricultural approach of this research, all samples were taken at a depth of 30 cm. After being pulverized with a hammer and sieved (2 mm mesh-size), each sample was separately stored in sacks inside hermetic and opaque plastic containers, at room temperature and in a well-ventilated spot. Both soil samples were characterized.

### 2.2. Soil characterization

Soil texture was determined in the soil textural triangle. The percentages of sand, silt and clay were obtained through the hydrometer method. Since USs was taken only 1.5 m away from the contaminated area, soil texture was determined in one sample.

pH was measured (Fernández-Linares et al., 2006) in a 1:10 soil-water solution, using a Thermo Scientific Orion 5-Star pH/ISE/Cond/DO Portable Meter (9107BNMD electrode). Same meter, equipped with a conductivity cell (Thermo Scientific Orion 013010MD) was used to measure electrical conductivity (EC) in a 1:5 soil-water solution (DSN, 2013).

Moisture content was determined gravimetrically through the methods described in the Official Mexican Standard NOM-021-RECNAT-2000 (SEMARNAT, 2002). Organic matter (OM) and organic carbon (OC) content determination followed the Walkley-Black method specified in the same Standard.

Cation exchange capacity (CEC) was determined through the ammonium acetate ( $\text{NH}_4\text{CH}_3\text{CO}_2$ ) method by titration (McKean, 1993). The collected ammonium acetate filtrate was analysed by Atomic Emission Spectroscopy to determine potassium ( $\text{K}^+$ ), using a PerkinElmer AAnalyst 200 Atomic Absorption Spectrophotometer. Available phosphorus (P) was measured colourimetrically in a VELAB UV/Vis Spectrophotometer (model VE-5100UV) after the Bray-Kurtz extraction method (SEMARNAT, 2002). Total nitrogen (N), was determined through the Kjeldahl method (Fernández-Linares et al., 2006) scaled with 1 g of soil to fit a macro-Kjeldahl equipment.

Surface area ( $S_a$ ), total pore volume ( $V_p$ ) and average pore diameter ( $D_p$ ) of the CSs were determined using the BET method.

Nitrogen adsorption tests were carried out at 77 K, using a BELSORP-max equipment. The soil sample ( $3.2 \times 10^{-1}$  g) was pre-treated (80°C; 21 h) in a BELPREP-vacIII equipment before the adsorption test.

TPH concentration analysis was carried out gravimetrically, after the agitation-centrifugation extraction method (Fernández-Linares et al., 2006) with acetone as solvent ( $(\text{CH}_3)_2\text{CO}$ , 99.5%, RBM); suitable for high hydrocarbon concentrations and DRO. CSs was submitted to gas chromatography-flame ionization detection (GC-FID) analysis through the EPA 8015D/GC/FID method to determine both DRO and gasoline range organics (GRO).

### 2.3. AC characterization

The AC used was from a single source: a 10-inch impregnated AC cartridge (JMXKITR02, Merck) which had been previously used for tap water pre-treatment for a Millipore RiOs-DI 3 UV Water Purification System. The equipment protocol requires the replacement of this filter every 6 months, thus, this AC filter had been in use for 6 months before it was reused for this research. This AC was characterized to determine its residual adsorption capacity. The AC cylinder was taken out of its plastic cover, coarsely pulverized using a hammer, and air-dried for 24 hours.

pH was measured in a water-AC suspension (ASTM D3838-05, 2017). Moisture content in the AC was determined gravimetrically after drying (150°C; 3h). Methylene blue value (MBV) determination was performed in 0.1 g and 0.5 g AC samples, adding 50  $\mu\text{L}$  and 250  $\mu\text{L}$  of methylene blue test solution (1.2g/L) respectively, until discoloration of the solution occurred within 5 minutes (CEFIC, 1986). Iodine number (IN) was also determined with an AC sample (3 g) (CEFIC, 1986).

$S_a$  and  $V_p$  of the AC were determined using the BET method. The AC sample ( $6.4 \times 10^{-2}$  g) was outgassed (150 °C; 19 h) in a BELPREP-vacIII equipment before adsorption measurements. Nitrogen adsorption tests were carried out at 77 K, using a BELSORP-max equipment.

### 2.4. Adsorption tests

Dry semi-wasted AC was pulverized inside a plastic bag using a hammer. The powdered AC (PAC) was sieved through a standard sieve No. 200 (74  $\mu\text{m}$  mesh-size), to obtain a fine powder. All adsorption tests were performed in triplicates by mechanically mixing CSs with PAC. In order to simplify the analysis of remaining TPH in the soil fraction, the soil had to be separated from the PAC after mixing. To ease this separation, all CSs used for adsorption tests was also sieved through the 74  $\mu\text{m}$  mesh before the experiments. The coarse fraction was recovered and used to run the experiments while the fine fraction was discarded.

First batch of adsorption tests were carried out by mixing CSs with varying amounts of PAC: 0%,

5%, and 15% (w/w). These mixtures were placed in 30 mL glass vials, mixed with a vortex mixer, sealed with wax paper, and left undisturbed in the dark, at room temperature for 15 and 30 days. After the designated time points, samples were taken out of each flask and sieved to recover the soil fraction, which was quantified gravimetrically for TPH. After finding no significant difference between 5% and 15% PAC treatments, the 5% concentration was selected to carry out the rest of the adsorption tests. This statistical analysis was carried out through a one-way ANOVA, and comparing the means of the TPH adsorption, through Fisher and Tukey methods, using *Minitab 18 statistical software*.

With a PAC concentration set at 5% (w/w), the second batch of adsorption tests were carried out during 5 days, analysing TPH every 24 hours. The third batch of tests were performed during 150 minutes, analysing TPH at given time points. For both, second and third batches, 1 g of PAC and 19 g of CSs were accurately weighed in Erlenmeyer flasks; the flasks were sealed with wax paper and placed in a shaking incubator (Benchmark Incu-Shaker 10L) (30°C  $\pm$  0.1 °C; 250 rpm). At designated time points, 2 g of the mixture were extracted from the flasks. The soil from these aliquots was separated from the PAC by sieving them with the 74  $\mu\text{m}$  sieve. The PAC fraction was discarded and TPH in the soil were extracted and quantified. The remaining TPH concentration in the soil was plotted to find the time point where the maximum TPH adsorption by the AC was reached. The behaviour of the adsorption process was adjusted to a logarithmic model.

## 3. Results and discussion

### 3.1. Soil characterization results

The characteristics of both soil samples are shown in Table 1. The particle-size distribution of the soil (Fig. 1) showed a high percentage of sand (particle sizes between 0.05 - 2 mm), and low silt and clay contents (0.002 - 0.05 mm, and <0.002 mm, respectively), obtaining a loamy sand textural class. The area has deposits of sand and gravel, and young soils with presence of rocks, calcium carbonate, iron and magnesium (INAFED, 2010). The permeability of a soil increases with increasing particle size; therefore, it is likely that vertical migration of the contaminant occurred. Soils with high percentages of sand present high porosity, little resistance to root growth, low water and nutrient-holding capacity, leaching of nutrients, and low OM content (Stirling et al., 2016).

The  $S_a$ ,  $V_p$ , and  $D_p$  indicate that the migration of the contaminant to other environmental compartments through leaching or volatilization may be favoured. Being a non-aqueous phase liquid (NAPL), the contaminant migrates downward through the soil pores, and a fraction of it adsorbs to the soil particles and is retained. Sandy soils will not adsorb as much contaminant as clay soils, however OM boosts  $S_a$  (Knödel et al., 2007); with a medium content of

OM, the adsorption of hydrocarbons onto the studied soil particles is high, despite the loamy sand texture.

The  $V_p$  and  $D_p$ , indicate that the sand particles, allow air and other fluids to move easily through the soil (Stirling et al., 2016). Both pH values can be classified as neutral. EC values indicate low salinity and no important effects of it (SEMARNAT, 2002). Moisture content of both samples shows a low water retention in the soil. The USs had a medium OM content, whereas the hydrocarbon contamination elevated the OM content from medium to high (SEMARNAT, 2002), this difference is related to the presence of TPH. Hydrophobic molecules, like TPH, are sorbed into the soil particles and bind tightly to them, associating with soil natural OM (Gong et al., 2007; Saddler and Connell, 2003).

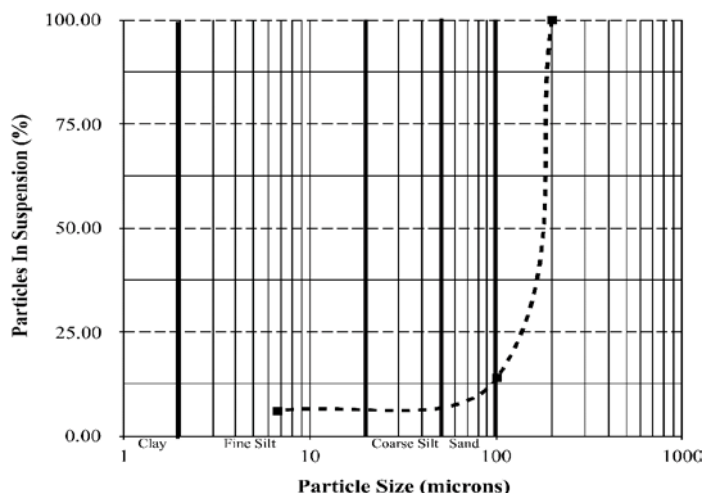
Phosphorus (P), nitrogen (N) and potassium (K), macronutrients for plants and soil microorganisms (Fernández-Linares et al., 2006; Stirling et al., 2016), are present in high levels in the USs (SEMARNAT, 2002). In CSs the concentration of P is still high but it was clearly diminished by the hydrocarbon spillage by over 50% (Bello and Inobeme, 2015). Total N content before the hydrocarbon spill was medium and dropped to low

after the spillage (SEMARNAT, 2002). Finally, the amount of  $K^+$  was high in both samples, still the hydrocarbon contamination diminished the amount of  $K^+$  in the soil (Bello and Inobeme, 2015). These effects on soil nutrients have been widely observed in previous studies regarding hydrocarbon contamination (Bello and Inobeme, 2015; Marinescu et al., 2011; Obire and Nwaubeta, 2002; Shukry et al., 2013). Since USs and CSs were taken only 1.5 m apart, these changes cannot be attributed to variability between both samples.

The GC-FID analysis results for DRO and GRO are shown in Table 2. GRO detected were significantly smaller than DRO signals, confirming that the contaminant present in the soil is diesel. Initial TPH concentration resulted in 55,141.4 mg of TPH per kg of dry soil ( $55,141.4 \text{ mg/kg} \pm 6,721.3$ ). The concentration of TPH in the CSs is quite high; for every kg of soil, there are over 55 g of diesel present, either adsorbed onto the soil particles or as a NAPL. Such value is nearly 46 times the maximum permissible limit for agricultural and residential soils (1,200 mg/kg) established in Official Mexican Standard NOM-138-SEMARNAT/SSA1-2012 (SEMARNAT, 2013).

**Table 1.** Results of soil characterization tests

Parameter (unit)	USs	CSs
Texture	Loamy sand	Loamy sand
Sand (%)	86.0	Not determined
Silt (%)	8.0	Not determined
Clay (%)	6.0	Not determined
pH	6.6	6.9
EC (dS/m) at 25 °C	$2.0 \times 10^{-1}$	$1.6 \times 10^{-1}$
Moisture content (%)	1.1	3.1
OM (%)	2.8	4.5
OC (%)	1.6	2.6
CEC (cmol(+)/kg)	14.2	15.7
Available P (mg/kg)	164.3	74.4
Total N (%)	$1.3 \times 10^{-1}$	$6.0 \times 10^{-2}$
$K^+$ (cmol(+)/kg)	2.0	1.6
$S_a$ ( $m^2/g$ )	Not determined	2.2
$V_p$ ( $cm^3/g$ )	Not determined	$5.2 \times 10^{-3}$
$D_p$ (nm)	Not determined	9.3
TPH (mg/kg)	Not detected	55141.4



**Fig. 1.** Particle-size distribution curve of the soil

**Table 2.** DRO and GRO found in CSs through GC-FID analysis

<i>GRO compound</i>	<i>Analytic result (mg/kg)</i>	<i>DRO compound</i>	<i>Analytic result (mg/kg)</i>
Benzene	$< 1.0 \times 10^{-2}$	Decane	110.0
Toluene	$2.6 \times 10^{-1}$	Dodecane	466.2
Ethylbenzene	$< 1.0 \times 10^{-2}$	Tetradecane	545.4
m-p-Xylene	2.9	Hexadecane	514.9
o-Xylene	3.5	Octadecane	432.0
1,3,5-Trimethylbenzene	19.4	Eicosane	350.7
1,2,4-Trimethylbenzene	71.9	Docosane	204.9
Naphthalene	$< 1.0 \times 10^{-2}$	Tetracosane	88.9
		Hexacosane	31.0
		Octacosane	$< 1.5$

**Table 3.** Results of AC characterization tests

<i>Parameter (unit)</i>	<i>Semi-wasted AC</i>
pH	7.1
Moisture content (%)	3.9
MBV (mg/g)	9.6
IN (mg/g)	244.2
$S_a$ ( $m^2/g$ )	387.3
$V_p$ ( $cm^3/g$ )	$2.5 \times 10^{-1}$
$D_p$ (nm)	2.6

### 3.2. AC characterization results

AC characterization results are summarized in Table 3. Regarding pH, when it is activated, AC should be washed until it reaches a pH value ranging from 6 to 8 (Ahmedna et al., 2000; Itodo et al., 2010; Ospina-Guarín et al., 2014); the pH of the semi-wasted AC is still within the neutral range. Moisture content for packed AC is usually less than 5%; the moisture content of the analysed semi-wasted AC was 3.9%.

Adsorption tests with methylene blue and iodine provide information on the structure of AC. Methylene blue is adsorbed in mesopores and iodine is adsorbed in micropores. MBV of the semi-wasted AC was 9.6 mg/g, meaning that the 0.1 g AC sample adsorbed 800  $\mu$ L of methylene blue solution, and the 0.5 g AC sample adsorbed 4.0 mL of such solution. The IN was 244.2 mg/g. MBV usually ranges from 11 to 28 mg/g, and IN goes from 500 to 1200 mg/g (Itodo et al., 2010). As expected, the MBV and IN of the semi-wasted AC, are outside of their usual range, since its adsorption capacity had diminished due to its previous use. Since the MBV is closer to the reference range than the IN, it can be inferred that the semi-wasted AC has a dominantly mesoporous structure. Since adsorbents with high IN perform better in the removal of small sized contaminants (Itodo et al., 2010), and high MBVs indicate better performance with big sized molecules, the studied AC has the capacity to remove contaminants with big molecular sizes, like hydrocarbons.

Furthermore, the  $S_a$  of the analysed semi-wasted AC was 387.3  $m^2/g$ . The  $V_p$  was  $2.5 \times 10^{-1}$   $cm^3/g$ , with a  $D_p$  of 2.6 nm, which proves that AC is a highly porous media with high  $S_a$ . With a  $D_p$  of 2.6 nm, this AC can be considered a mainly mesoporous

media, confirming the results of the MBV and IN previously discussed. In a study carried out by Nunes and Guerreiro (2011), they analysed the  $S_a$  and  $V_p$  of several AC samples through the BET method. According to their findings, The  $S_a$  varied from 199 to 2,015  $m^2/g$ , and the  $V_p$  from 0.09 to 1.11  $cm^3/g$ ; the semi-wasted AC,  $S_a$  and  $V_p$  values still enter in those ranges, therefore, even though the AC had been previously used, it still has an acceptable adsorption capacity.

### 3.3. TPH adsorption tests

The results of the first batch of tests can be found in Table 4. The mixture of contaminated soil with 5% (w/w) PAC reduced significantly the TPH concentration in the soil. Since no liquids were added to the soil-AC mixture, it is likely that mass transfer of TPH from soil to AC took place by direct contact. After statistical analysis of this data, shown in Fig. 2, no significant difference was observed between 5% and 15% PAC treatments. The comparisons of the means confirmed that in fact, 5% and 15% PAC treatments were significantly different when compared to the control treatment with 0% PAC; but when compared to each other, 5% and 15% PAC treatment means were not significantly different. The colour of the soil after the PAC addition changed significantly, turning almost completely black with a 15% PAC concentration in the mixture. Another effect observed was the formation of lumps of soil particles with PAC. These effects were not as perceptible with 5% PAC. Given these results, 5% PAC concentration was selected to carry out the subsequent adsorption tests, in order to reduce the introduction of PAC in the soil and optimize the use of the material.

Following adsorption tests were carried out to optimize the amount of time needed for TPH removal. The results of the second batch of adsorption tests are shown in Fig. 3, where it is evident that the adsorption of TPH stabilized from day 1 to day 5, with an average TPH removal of 58% (23,130 mg/kg of TPH remaining in the soil), the same amount adsorbed in the 15-day treatment mentioned above. Although most soil treatment research with AC considers higher contact times (Hilber and Bucheli, 2010) that range from 35 days to over 1000 days (Vasilyeva et al., 2010), the obtained results led to the assumption that the adsorption process was quite rapid (less than 24 hours).

The results of the third batch of tests, shown in Fig. 4, confirmed that indeed stabilization at a removal of 58% was reached after 60 minutes. Thus, this reused semi-wasted PAC at a 5% concentration reaches a maximum TPH adsorption of 58% in a matter of minutes. Previous research results have shown reduction of low concentrations of PAH in soil/water suspensions by 99% (Brändli et al., 2008), meaning there is a high effectiveness of PAC in moderately contaminated media.

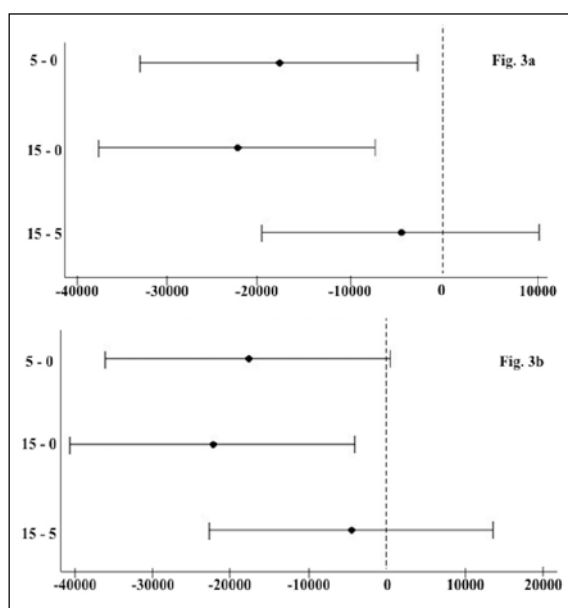
The results obtained in this work show that this semi-wasted PAC can be successfully reused to adsorb hydrocarbons from soil, up to a concentration of 32,011.0 mg/kg, in 60 minutes. TPH adsorbed could be removed from the contaminated soil through sieving if there is a significant difference between the soil and AC's particle-sizes.

If the separation of soil and spent AC is not feasible, further research is needed to explore the use of AC merely to prevent TPH leaching. Still, the possibility of reusing semi-wasted AC supposes a fast and highly efficient method for TPH adsorption, which could alleviate the demand for new AC production, as well as the environmental and economical costs of AC reactivation (An et al., 2015; Hutson et al., 2012; Ledesma et al., 2015). The goal of this work was met, since the initial concentration of TPH (55,141.4 mg/kg) was successfully reduced to 23,130.0 mg/kg through semi-wasted AC adsorption, which represents an adequate 58% adsorption in a heavily contaminated soil.

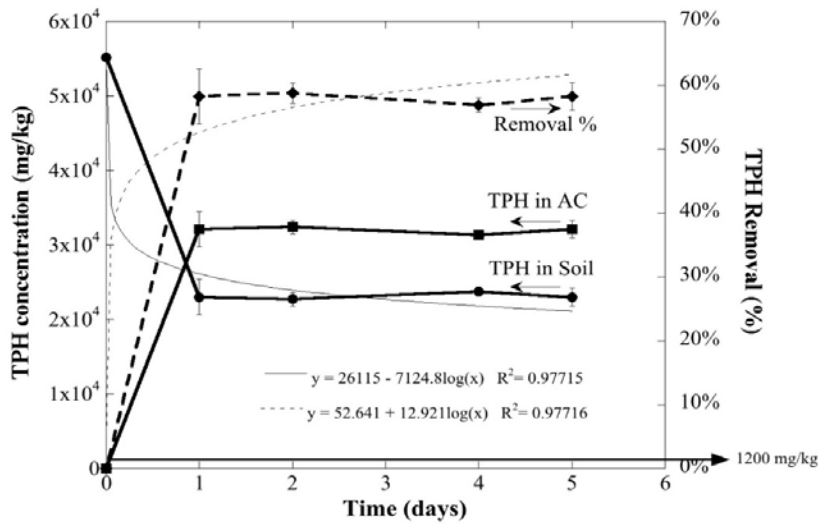
Since the initial TPH concentration of the soil sample was high, this adsorption treatment with reused PAC alone was not enough to reach the maximum permissible limit of 1,200 mg/kg (SEMARNAT, 2013), as seen in Figs. 3 and 4. Still, the treatment proved to be a feasible and fast treatment to reduce TPH concentrations in hydrocarbon-contaminated soils. After its use for TPH adsorption, PAC can be separated from sandy soils through sieving, in order to avoid desorption and migration of the adsorbed TPH. Alternatives for the disposal of this spent material require further research, as well as the use of this treatment in other types of soil. The environmental benefits of reusing AC and lowering the demand for new AC should not be overlooked (Thompson et al., 2016).

**Table 4.** Results of the first batch of adsorption tests with 5% and 15% (w/w) PAC concentration after 15 and 30 days contact time

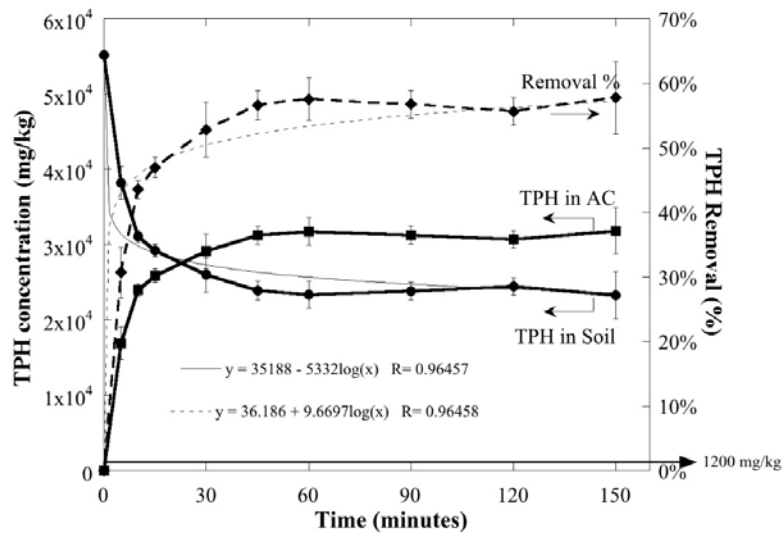
PAC concentration	Initial TPH (mg/kg)	TPH 15 days (mg/kg)	TPH removal	TPH 30 days (mg/kg)	TPH removal
0% (w/w)	55141.4	47815.5 ± 1599.5	13.3%	48499.6 ± 4349.9	12.1%
5% (w/w)	55141.4	23285.3 ± 2565.2	57.8%	21016.1 ± 365.2	61.9%
15% (w/w)	55141.4	13432.6 ± 4332.5	75.6%	15812.6 ± 1610.2	71.3%



**Fig. 2.** Mean comparison of adsorption treatments through Fisher (3a) and Tukey (3b) methods, individual confidence intervals of 95%. If an interval does not contain zero, corresponding means are significantly different



**Fig. 3.** TPH concentrations and removal over 5 days adsorption treatment. Continuous lines represent TPH concentrations in soil and reused PAC. Dotted line reads on secondary Y-axis and represents TPH removal (%). Stabilization occurs from day one



**Fig. 4.** TPH concentrations and removal over 150 minutes adsorption treatment. Continuous lines represent TPH concentrations in soil and reused PAC. Dotted line reads on secondary Y-axis and represents TPH removal (%). Stabilization occurs after 60 minutes

The availability of semi-wasted AC for soil remediation purposes depends on the generation of this material as waste. AC market is vast: up to 2014, there were 35 drinking water treatment plants operating with AC filters with a total outflow of 26 L/s in Mexico (CONAGUA, 2015). AC is commercially the most common adsorbent used for the removal of organic compounds from air and water streams (Ioannidou and Zabaniotou, 2007). Actually, the demand for AC is on the rise, due to its application on several processes, and the increase of environmental regulations.

The need for AC and raw materials for its production have led to a rise on AC prices, which has increased the demand for reactivated carbon. Global market for AC was estimated at \$2.7 billion USD in 2015, and expected to reach \$6.2 billion USD by 2022 (ReportBuyer, 2017). Given this promising future for AC production, the reuse of this material for soil

remediation is viable, making this treatment a feasible technology to lower TPH concentrations in soils.

#### 4. Conclusions

A heavily contaminated soil from Puebla, Mexico, presented an initial TPH concentration of 55,141.4 mg/kg, which was successfully lowered by 58% using the adsorption treatment tested in this research. This heavily impacted soil presented an important increase in its OM content.

This semi-wasted AC adsorption treatment method proved to be fast and efficient for hydrocarbon adsorption from soils. An important contribution of this research was the successful reuse of an AC residue as the adsorbent. Therefore, it is possible to exploit the residual adsorption capacity of semi-wasted AC, and reduce the environmental costs of AC production and regeneration. The adsorptive treatment demonstrated

in this study, effectively transferred TPH from soil to AC. The AC used for the treatment was to be discarded due to its previous use for tap water pre-treatment. The mass transfer of hydrocarbon initially found in the contaminated sandy soil to the AC, occurred in less than 90 minutes. Maximum permissible limits may be reached in contaminated soils with TPH concentrations below 30,000.0 mg/kg, otherwise further treatment may be required.

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