Activated carbon adsorption of PAHs from vegetable oil used in soil remediation

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Abstract

Vegetable oil has been proven to be advantageous as a non-toxic, cost-effective and biodegradable solvent to extract polycyclic aromatic hydrocarbons (PAHs) from contaminated soils for remediation purposes. The resulting vegetable oil contained PAHs and therefore required a method for subsequent removal of extracted PAHs and reuse of the oil in remediation processes. In this paper, activated carbon adsorption of PAHs from vegetable oil used in soil remediation was assessed to ascertain PAH contaminated oil regeneration. Vegetable oils, originating from lab scale remediation, with different PAH concentrations were examined to study the adsorption of PAHs on activated carbon. Batch adsorption tests were performed by shaking oil-activated carbon mixtures in flasks. Equilibrium data were fitted with the Langmuir and Freundlich isothermal models. Studies were also carried out using columns packed with activated carbon. In addition, the effects of initial PAH concentration and activated carbon dosage on sorption capacities were investigated. Results clearly revealed the effectiveness of using activated carbon as an adsorbent to remove PAHs from the vegetable oil. Adsorption equilibrium of PAHs on activated carbon from the vegetable oil was successfully evaluated by the Langmuir and Freundlich isotherms. The initial PAH concentrations and carbon dosage affected adsorption significantly. The results indicate that the reuse of vegetable oil was feasible.
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Keywords: Activated carbon; Adsorption; PAH; Vegetable oil; Recycle

1. Introduction

Remediation of soils contaminated with hydrophobic contaminants is always a challenge for soil and environmental scientists, because hydrophobic molecules often bind tightly to soil particles making them inaccessible to low cost remediation solutions and necessitating the use of costly capital energy and/or chemical treatment [1]. Polycyclic aromatic hydrocarbons (PAHs), which are made up of only carbon and hydrogen, are ubiquitous contaminants in soils and are well known for their toxic, carcinogenic, and mutagenic effects [2–4]. Most PAHs are hydrophobic with high boiling and melting points and possess low water solubility and electrochemical stability. Therefore, they can exist and be accumulated in soils for a long time [5]. Manufactured gas plant (MGP) sites, commonly found in many countries, are always contaminated with process residues that

include tars, sludges, lampblack, and other hydrocarbons. The primary components of concern in these process residues are PAHs [6,7].

Solvent extraction is an effective method for removal of PAHs from contaminated soils at a number of superfund sites. Vegetable oil, a natural non-toxic, cost-effective, and biodegradable extractant, was considered as a less hazardous solvent for use in the extraction of hydrophobic contaminants from soils by some scientists [8–10]. In a previous study, we found that sunflower oil can be used as a promising agent to remove more than 90% total PAH from MGP soils with total PAH concentrations between 1000 and 5000 mg kg^{-1} [11–13]. Regeneration and reuse of the oil in the process are quite essential for effective application of vegetable oil to extract PAH contaminants from soils. Thus, a method for subsequent removal of the extracted PAHs from the oil is necessary.

Methods for treating PAHs include biodegradation, scrubber absorption, high-energy electron beam irradiation, ozonation, and catalytic combustion [14–16]. However, these methods are always conducted in aqueous solutions, or are applied in the

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Nomenclature

A	Langmuir constant refers to concentration of PAH in oil at which half of G_0 has been achieved ($mg\,L^{-1}$)
C_e	equilibrium concentration of PAH in the oil ($mg\,L^{-1}$)
C_L	PAH concentration in the oil leachate ($mg\,L^{-1}$)
C_0	initial concentration of PAH in the oil ($mg\,L^{-1}$)
G_0	Langmuir constant refers to maximum adsorption amount per unit mass of adsorbent at equilibrium ($mg\,g^{-1}$)
k_f	Freundlich constant related to adsorption capacity $((mg\,g^{-1})/(g\,L^{-1})^{1/n})$
MGP	manufactured gas plant
n	Freundlich constant related to adsorption intensity
p	p-value of analysis of variance in the regression
PAHs	polycyclic aromatic hydrocarbons
q	PAH concentration in the activated carbon ($mg\,g^{-1}$)
q_e	PAH concentration in the activated carbon at equilibrium ($mg\,g^{-1}$)
R	multiple correlation coefficient of regression
V	volume of the oil (mL)
W	mass of activated carbon (g)

gaseous or solid phases. There is very little information in literature on the treatment of PAHs in vegetable oil phase from contaminated soils. Isosaari et al. [8] demonstrated the effective photodegradation of highly chlorinated tetra- to octachlorinated dibenzo-*p*-dioxins and dibenzofuran (PCDD/F) congeners at wavelength of 300–400 nm in the presence of olive oil, which was used as an extractant for removal of PCDD/Fs from soil. Our main aims were the regeneration and reuse of PAH-containing sunflower oil, hence we tested biodegradation, ozonation, and catalytic oxidation for the purpose of environmental PAH destruction. Some of these methods were effective when applied to sunflower oil spiked with <10 mg/L of phenanthrene and anthracene. However, when these methods were applied to real contaminated oil containing 700–3000 mg PAH L^{-1} oil, destruction efficiency became less acceptable.

It is reported that cleaning of contaminated oil can be achieved by activated carbon adsorption or biodegradation of the contaminated oil in an aqueous solution. If activated carbon is used, contaminated carbon can be recycled by conventional thermal treatment or by bioregeneration [10,17]. Adsorbents are extensively used to remove contaminants, including PAHs, from exhaust gases and wastewater [5,18,19]. Adsorption of PAH on activated carbon mainly depends on their porous texture [20,21]. Up till now, quantitative studies on adsorption of PAH from vegetable oil on activated carbons are rather limited. The study of PAH adsorption kinetics and equilibrium parameters is an important step forward for the regeneration and reuse of the vegetable oil in field remediation of PAH-contaminated soil.

The objectives of our study were to determine: (a) possibility of the vegetable oil regeneration after extraction of PAHs from the weathered MGP soil; (b) efficiency of adsorption of PAH from vegetable oil on activated carbon; (c) effect of PAH concentrations on adsorption efficiency; (d) PAH adsorption and adsorbent capacity.

2. Materials and methods

2.1. PAH-containing vegetable oil

Vegetable oil, which was sunflower oil used for family cooking, was purchased from a supermarket in Berlin, Germany. Two liters of sunflower oil were added stepwise to a column packed with 1 kg of MGP soil in order to remove the PAHs in the MGP soil. After two percolations, more than 80% of PAHs were removed, resulting in PAH-containing oil. As different MGP soils were used, four PAH-containing oils were eventually obtained. Total PAH concentrations of the oils ranged from 731.5 to 2970.7 mg L^{-1}. The concentrations of the various PAHs in the four oils are summarized in Table 1.

2.2. Activated carbon

Activated carbon (Carbontech, Germany) with a particle size rang between 0.5 and 2.0 mm was used as adsorbent. Physical characteristics of the activated carbon are shown in Table 2.

2.3. Batch adsorption experiments

Different amounts of activated carbons (0.7, 1.3, 2.0, 2.7, and 4.0 g for oil A and for oil B; 0.8, 1.2, 2.0, 2.8 and 3.2 g for oil C; 0.6, 0.9, 2.2, 4.5 and 9 g for oil D) were added to 40 mL of the oils, respectively, to obtain different values of final equilibrium concentrations of PAHs in oils A–D. Activated carbon and oil were mixed in sealed bottles, and all the bottles were shaken on a shaker at 160 rounds per minute for 1 day. The oil

Table 1
Original concentrations of PAHs in vegetable oils

PAHs	Oil A ($mg\,L^{-1}$)	Oil B ($mg\,L^{-1}$)	Oil C ($mg\,L^{-1}$)	Oil D ($mg\,L^{-1}$)
ACY	0	4.7	126.4	169.9
ACN	39.2	43.2	247.7	437.7
FLU	37.5	36.9	152.0	303.7
PHE	201.0	177.4	256.6	531
ANT	27.0	23.2	73.4	154.4
FLA	47.9	65.5	196.1	499.1
PYR	186.4	244.1	98.8	257.4
BaA	39.0	54.6	59.3	158
CHR	32.4	46.3	40.5	112.8
BbF	15.6	23.2	21.6	41.1
BkF	10.7	15.9	17.9	49
BaP	45.2	71.9	37.3	128.3
DahA	9.9	13.9	6.73	21.6
BghiP	31.3	51.6	15.7	38.5
IP	8.4	12.5	13.5	68.2
Total	731.5	884.7	1363.5	2970.7

Table 2
Physical characteristics of activated carbon[a]

Property	Value
Chemical composition	Bituminous carbon
Size (mm)	0.5–2.0
Average particle diameter (mm)	1.25
Water content (%)	2
Actual particle density (kg L^{-1})	0.81
Specific surface area (m^2 kg^{-1})	1.2
Pore volume (mL g^{-1})	0.73
Pore diameter (nm)	2

[a] Data source: from manufacturer.

samples were then separated from the mixtures by membrane filtration, and analyzed to determine PAH concentrations. Since it is preferable to use weight concentration units for investigation of adsorption, the units of mg L^{-1} and mg g^{-1} for the PAH concentrations in the oil and activated carbon were used for data presentation. Amounts of individual PAHs adsorbed at equilibrium were calculated using the equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

where q_e is the adsorbate (PAHs) concentration in the activated carbon at equilibrium; C_0 and C_e are the initial concentration and the equilibrium concentration of PAH in oil, respectively. V is the volume of the oil and W is the mass of activated carbon loading. Each point was measured twice.

2.4. Column adsorption experiments

A glass column of 40.0 cm length and 2.5 cm internal diameter was used in the column studies. The column was packed with activated carbon uniformly with care to avoid air entrapment. PAH contaminated oil was poured on top of the activated carbon layer, percolating through the column under the force of gravity. Oil retention time in the column was up to 1 day. Experiments were carried out with varying activated carbon masses (W: 8 and 16 g for oils A and B; 5 g for oil C; 10 and 20 g for oil D), oil volumes (V: 50 mL for oils A and B; 20 and 40 mL for oil C; 90 mL for oil D), and oil concentrations (oils A–D). Amounts of individual PAHs adsorbed were calculated using the equation:

$$q = \frac{(C_0 - C_L)V}{W} \qquad (2)$$

where q is the adsorbate (PAHs) concentration in the activated carbon; C_0 and C_L are the PAH concentrations in original oil and in oil column leachate. V is the volume of the oil; W is the mass of activated carbon loading. Each treatment was performed in two replicates.

2.5. Analytical measurements

The oil sample was dissolved in petroleum ether and transferred to a silica gel column, made by filling a glass column with 10 g of activated silica gel (70–230 mesh, activated by oven-heating at 130 °C for 16 h and cooled in a desiccator at least for 10 min before use) and 10 g of anhydrous sodium sulphate. The silica column was eluted with 100 mL 2:1 toluene:petroleum ether (v:v). An aliquot of eluate was taken, dried by nitrogen gas, and finally dissolved in acetonitrile for HPLC analysis. Quantitative analyses of the soil and oil extracts were performed by an HPLC equipped with a gradient pump (KNAUER K1001), an autosampler (TSP AS100) and a reverse-phase C-18 column. Acenaphthylene (ACY) and indenopyrene (IP) were measured by a UV detector, while the other PAHs (acenaphthene (ACN), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(ah)anthracene (DahA) and benzo(ghi)perylene (BghiP)) were quantified by a fluorescence detector (TSP FL2000) at specific excitation/emission wavelengths. Elution conditions were as follows: water–acetonitrile mixture (1:1, v:v) was used as the solvent at a flow rate of 0.4 mL min^{-1} for the initial 5 min. During the following 15 min, acetonitrile in the mixture was increased linearly to 100% and maintained at that composition for 15 min. Thereafter, the solvent composition was returned to the initial conditions within the next 3 min. In all cases, 8 μL of sample was injected into the HPLC by the autosampler. An external standard 1647d SRM NBS mixture was used for the quantification of PAHs.

2.6. Curve fitting

Fitting of the experimental data with the isothermal models was achieved by the use of software, Sigma Plot 9.0 (Systat Software, Inc.) with C_e and q_e being designated as independent and dependent variables, respectively. A non-linear least-square method was used to estimate parameters of the isothermal models in the curve fitting. Analysis of variance (ANOVA) was also performed on the curve fitting to determine correlations and coefficients.

3. Results

3.1. Batch adsorption

Fig. 1 shows the effect of activated carbon dosage on PAH removals from the four oils. It can be observed that with an increase in the activated carbon dosage, percentage of PAHs adsorbed on activated carbon also increased. More than 90% of PAHs in 40 mL of oils were removed when the activated carbon dosage was >3 g for oils A–C. However, the activated carbon dosage should be at least 9 g to remove 90% of PAHs in 40 mL of oil D, which contained 2970.7 mg PAH L^{-1} oil. The adsorption capacities were 6.9–24.5, 8.5–16.4, 16.1–41.7, and 12.3–47.8 mg PAH g^{-1} activated carbon for oils A–D, respectively, in the experiments.

To facilitate estimation of adsorption capacity, two commonly used empirical adsorption models, Freundlich and Langmuir, which correspond to heterogeneous and homogeneous adsorbent surfaces, respectively, were employed in this study.
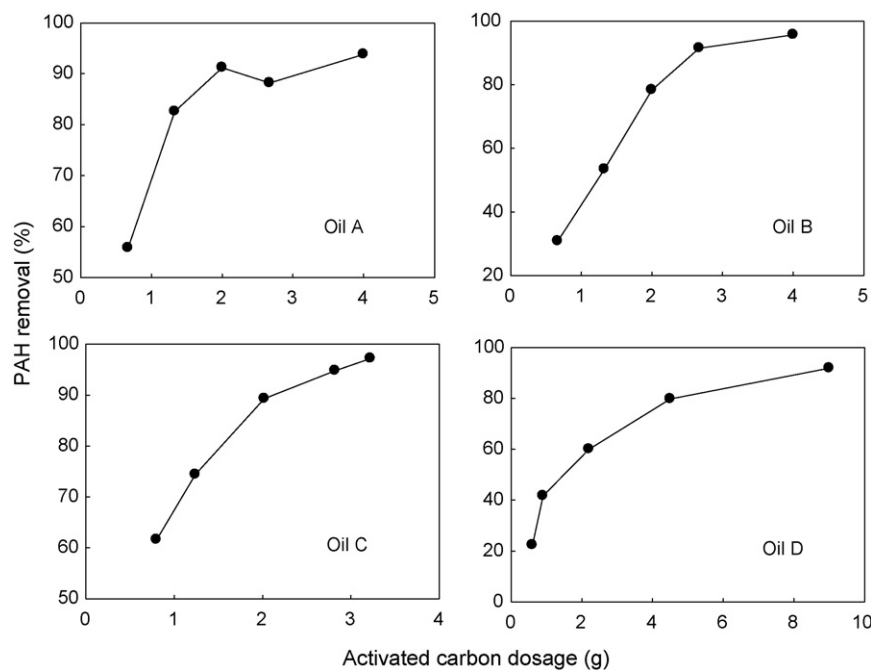
Fig. 1. Effect of carbon dosage on amount of PAH adsorbed in the batch adsorption experiments.

The Freundlich model is given by the following equation:

$$q_e = k_f C_e^{1/n} \quad (3)$$

where k_f and n are the Freundlich constants related to adsorption capacity and intensity, respectively [22,23].

In the second model, the Langmuir equation assumes maximum adsorption occurs when the surface is covered by the adsorbate, because the number of identical sites on the surface is finite. The Langmuir equation is given as follow:

$$q_e = \frac{G_0 C_e}{A + C_e} \quad (4)$$

where G_0 is the amount adsorbed per unit mass of adsorbent corresponding to complete coverage on the surface by adsorbate at C_e, i.e. maximum adsorption capacity. A is the constant related to the affinity of binding sites, it can be explained as the concentration at which half of G_0 has been achieved.

Both adsorption isotherms predicted well the adsorption of PAH on the activated carbon with high correlation coefficients (Table 3). Values of k_f and n were in the range of 1.2–5.0 $(mg\,g^{-1})/(g\,L^{-1})^{1/n}$ and 2.0–5.0, respectively. It indicated a favorable adsorption for all the oils

A–D. Values of Langmuir constants, G_0 and A were in the range of 16.3–86.3 mg PAH g^{-1} activated carbon and 31.7–1756.8 mg PAH L^{-1} oil, respectively. Isotherms of PAH adsorption are presented in Fig. 2.

3.2. Column adsorption

Column adsorption experiments were also performed to test adsorption capacities. Total PAH as well as individual PAHs are presented in Fig. 3 to show the adsorptions in detail. Effect of initial PAH concentration on the adsorptions was examined with different oils, which had total PAH concentrations ranging from 731.5 to 2970.7 mg L^{-1}. It was observed that the activated carbon was effective in the adsorption of PAH from all the oils. To test more adsorption conditions, activated carbon mass and oil volume were decreased for oil C, and were increased for oil D. The results showed that at all the conditions, activated carbon was effective in adsorption of PAHs. Activated carbon dosage in the column played an essential role in the adsorption. Like the batch adsorption, when activated carbon dosage was increased, additional adsorption was expected, oils B and C obviously showed this. However, this effect was not

Table 3
Isotherm parameters for adsorption of PAHs in vegetable oils onto activated carbon

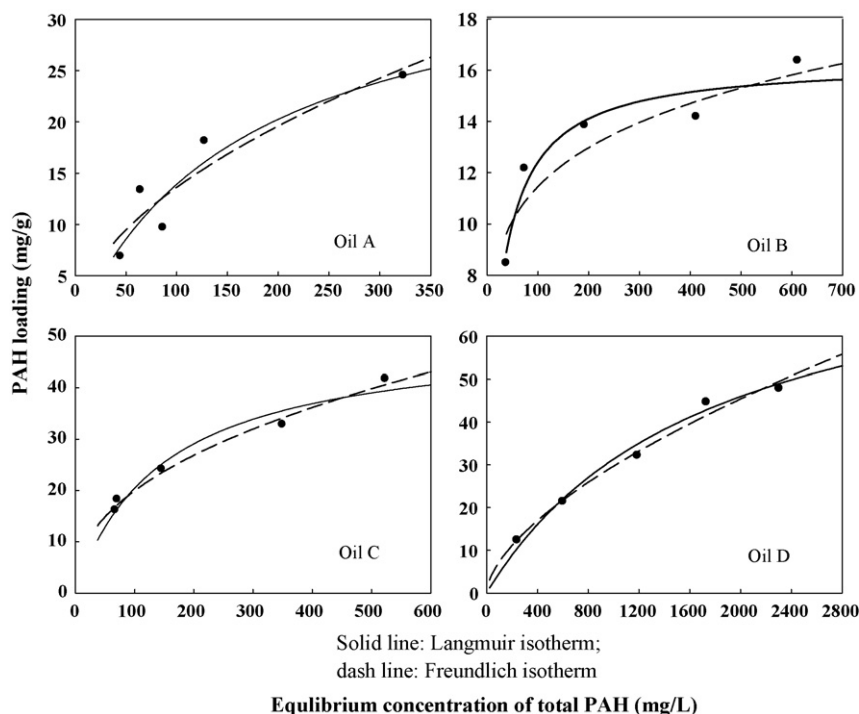| Oil name	Freundlich				Langmuir			
	k_f $((mg\,g^{-1})/(g\,L^{-1})^{1/n})$	n	R	p	G_0 $(mg\,g^{-1})$	A $(mg\,L^{-1})$	R	p
Oil A	1.2 ± 0.8	1.9 ± 0.5	0.93	0.0226	37.2 ± 9.3	162.7 ± 79.8	0.94	0.0176
Oil B	5.0 ± 1.2	5.4 ± 1.2	0.93	0.0193	16.3 ± 0.8	31.7 ± 7.5	0.96	0.0079
Oil C	2.8 ± 0.4	2.3 ± 0.2	0.99	0.0005	50.5 ± 4.6	147.4 ± 34.8	0.98	0.0031
Oil D	0.4 ± 0.2	1.6 ± 0.2	0.99	0.0007	86.3 ± 12.7	1756.8 ± 494.2	0.99	0.0009

Fig. 2. Isothermal adsorption of PAHs on activated carbon in the batch adsorption experiments. The four plots represent Oils A, B, C, and D, respectively.

Table 4
Adsorption capacity in the column adsorption experiments

Oil A (mg g^{-1})		Oil B (mg g^{-1})		Oil C (mg g^{-1})		Oil D (mg g^{-1})	
8 g: 50 mL[a]	4.0	8 g: 50 mL	4.0	5 g: 40 mL	7.4	10 g: 90 mL	21.3
16 g: 50 mL	2.1	16 g: 50 mL	2.5	5 g: 20 mL	4.0	20 g: 90 mL	12.3

[a] Before the colon is the mass of activated carbon: after the colon is the volume of oil.

remarkable for oils A and D. As the smaller dosage had already removed almost all the PAHs, possibility of adsorption improvement became less (Fig. 3). Total PAH removals in the column adsorption experiments were in the range of 68.1–93.5%. The best adsorption capacity was obtained from oil D, which had the highest total PAH concentration, at 10 g of activated carbon with 90 mL of oil, with the total removal being 79.7%, and adsorption capacity being 21.3 mg PAH g^{-1} activated carbon (Table 4). Adsorption capacities in the column adsorption varied significantly. In particular, adsorption capacity for oil A (16 g of activated carbon:50 mL of oil) was only 2.1 mg PAH g^{-1} activated carbon, which was much lower than those obtained in the batch adsorption.

4. Discussion

It was interesting to observe that for oils A–C, adsorption behaviors of individual PAHs were analogous in the column adsorption, with nearly the same removals. However, for oil D, the PAH removals through adsorption on activated carbon increased with increasing molecular weight of individual PAHs. It is well known that high molecular weight PAHs, such as benzo(a)anthracene, chrysene, benzo(a)pyrene,

and benzo(ghi)perylene are recalcitrant organic compounds, and their environmental removal are quite difficult. Thus, both extraction of PAHs from MGP soils using vegetable oil and ultimate adsorption of these PAHs on activated carbon showed promising potentials with regards to the high molecular weight PAHs [13]. Generally, the batch adsorption showed better results than the column adsorption. This clearly showed that the contact between the oil and activated carbon was not sufficient in the column adsorption, while the batch system provided a better contact between the activated carbon and oil. Similar results and explanation were observed by Kumar et al. [24]. In this study, the four oils were originated from four different soils. As other soil-bound organic materials may be co-extracted into the oil, the four oils were different not only due to different PAH concentrations. The co-extracted organic materials may compete with PAHs for adsorption sites. This was also a reason for the difference among PAH adsorptions.

Pannu et al. [10] demonstrated the potential to use activated carbon to remove anthracene from contaminated vegetable oil, with 0.2 g of activated carbon adsorbing up to 4.2 mg kg^{-1} of anthracene from 2 g contaminated oil. This study scaled up the result, showing that activated carbon was a good adsorbent to remove all kinds of PAHs from contaminated oil. Adsorption capacity of the activated carbon was much higher than 4.2 mg kg^{-1}. An assumed adsorption capacity of 20 mg g^{-1} by Pannu et al. [10] was easily achieved in this study. We expect that the adsorption capacity can be further improved, and a potential capacity of 50 mg g^{-1} can be expected.

As the oil will be reused in the MGP soil remediation, quality of the regenerated oil should not be limited to completely clean. Compared with large amounts of PAHs in the MGP soils, PAH residuals in the vegetable oil after adsorption with activated
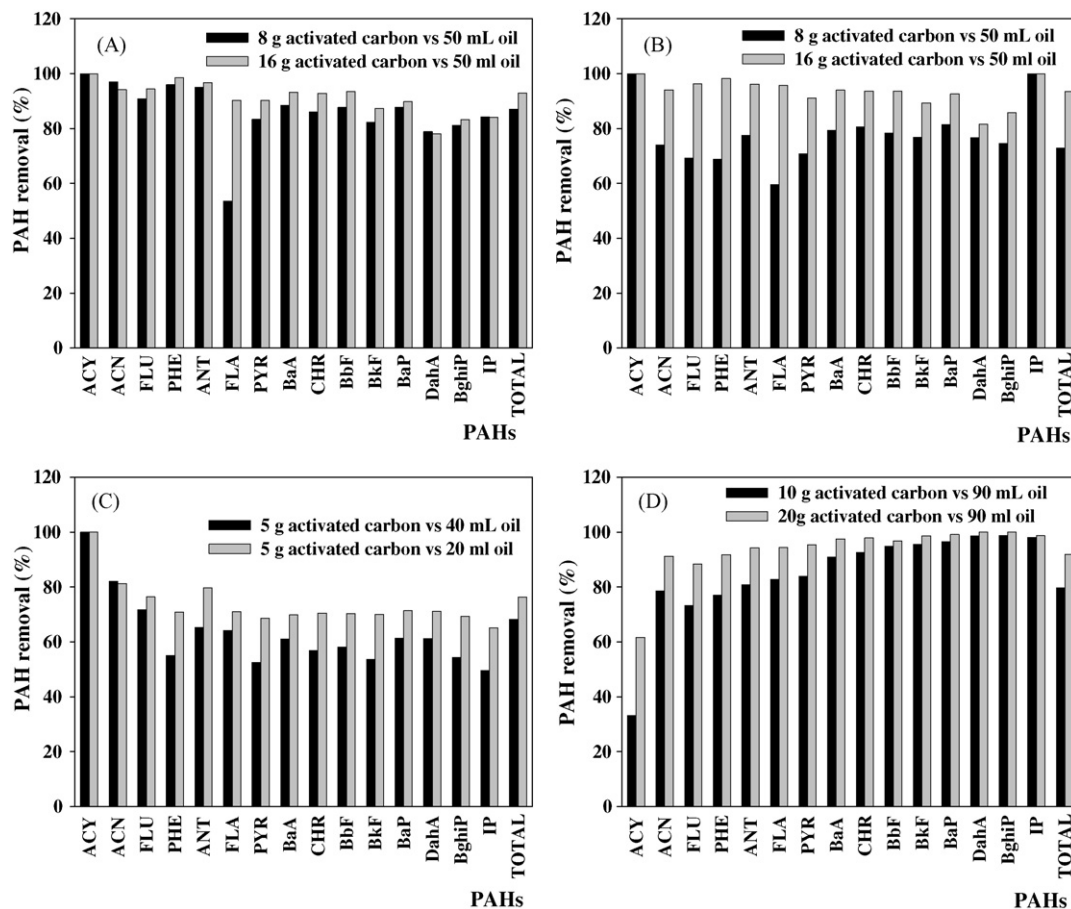
Fig. 3. Removals of individual and total PAHs in vegetable oils by activated carbon in the column adsorption experiments. The four plots represent oils A–D, respectively.

carbon should be negligible. It is certain that reemployment of the regenerated oil will remove more PAHs from the MGP soils rather than bring in more contaminants. Thus, an economical activated carbon dosage can be determined by considering the combination of satisfied adsorption efficiency and capacity.

5. Conclusions

The results presented in this study clearly revealed the effectiveness of using activated carbon as an adsorbent to remove PAHs from vegetable oils for reemployment of the oil in remediation. Adsorption capacity was dependent on the initial concentrations of the PAHs in the vegetable oil, the higher the concentrations, the more PAHs adsorbed. Batch adsorption exhibited a better performance as compared to column adsorption, as vigorous shaking provided more contact and more adsorption sites. More than 90% of PAHs in the vegetable oils were removed when suitable amount of activated carbon was used in the batch adsorption. Total PAH removals from oils in the column adsorption experiments were in the range of 68.1–93.5%. Activated carbon is a promising adsorbent because it can adsorb high molecular weight PAHs as effectively as, or sometimes more than, low molecular weight PAHs.

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