



Removal of polycyclic aromatic hydrocarbons from organic solvents by ashes wastes

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) can be formed during the refinery processes of crude petroleum. Their removal is of great importance. The same happens with other organic solvents used for the extraction of PAHs (hexane, acetonitrile...), which can be polluted with PAHs. Kinetic and equilibrium batch sorption tests were used to investigate the effect of wood ashes wastes as compared to activated carbon on the sorption of three representative PAHs from *n*-hexane and acetonitrile. Mussel shell ashes were discarded for batch sorption experiments because they were the only ashes containing PAHs. The equilibrium time was reached at 16 h. Physical sorption caused by the aromatic nature of the compounds was the main mechanism that governed the PAHs removal process. Our investigation revealed that wood ashes obtained at lower temperature (300 °C) did not show any PAHs sorption, while ashes obtained at higher temperature (>500 °C) have adsorbent sites readily available for the PAH molecules. An increase in the molecular weight of PAHs has a strong effect on sorption wood ashes wastes. As low the wood ashes particle size as high the sorption of PAHs, as a result of differences in adsorbent sites. The performance of wood ash wastes vs. activated carbon to remove 10 PAHs from organic solvents is competitive in price, and a good way for waste disposal.

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1. Introduction

PAHs are found naturally in crude oil, creosote, coal tar, and coal. The release of PAHs has been reported during production and processing of plasticizers, dyes, and pigments. However, most PAHs enter the environment via the atmosphere from incomplete combustion processes, such as the processing of coal and crude oil during refining, coal gasification, and coking. Crude petroleum oil is also distinguished by the relatively high ratio of compounds with saturated five-membered rings and the presence of highly strained molecules, such as 4,5-methylene phenanthrene [1–2]. PAHs are considered persistent environmental contaminants and many of them are suspected of being carcinogenic [3–5]. Hence, they are included in the US-EPA lists of priority pollutants. Taking into account that hexane and acetonitrile are usual organic solvents for extracting PAHs from different matrices, it would be very convenient to find a method for recovering these two organic solvents free of PAHs [6–8].

Many techniques (e.g., bioremediation [9–12], ozonation [13–16], photo-degradation, and adsorption [17]) have been applied successfully for the minimization of PAHs in wastewa-

ter of domestic and/or industrial plants and soils. The adsorption techniques are more frequently used in batch mode for the minimization of such complex species in liquid or gas phases due to its high efficiency and applicability to be used at high temperatures. Activated carbon was considered the most frequent and effective solid adsorbent in this field [2,18–20]. Other adsorbents (e.g., alumina, zeolite, fly ash, soils, aspen wood fibers, leonardite, wood ash and clays [21–25]) have also been employed successfully to remove pollutants. All these materials studied have specific advantages and limitations. Therefore, the need to develop low-cost adsorbents still exists. This paper examines the applicability of wood ash wastes as a low-cost material for adsorbing PAHs from organic solvents. However, the studies on the adsorption of PAHs from non-aqueous media are scarce [2,19].

Wood ash wastes are accumulated in the surroundings of timber industries, and there is a need for their waste disposal. Some of the disposal procedures used is enamel fabrication, production of construction materials for rural ways, or its use as a concrete additive. In the last years, there is an increased use of ash wastes for the remediation of polluted soils, or the fertilization of forestry and agricultural soils. For the latter aim, their advantages are due to their high contents in plant nutrients (Ca, P, Mg...) and their good liming properties, especially interesting for acid soils. Anyway, taking into account that wood ashes have very high carbon percentages, another application is its use as sorbent of pollutants

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such as pesticides, dyes or heavy metals [25–28], which could be found in water.

PAHs were selected because of their planar configuration as opposed to other bulky three-dimensional molecules (for instance, different pesticides). PAHs are expected to be less sterically hindered in its partition interaction with sorbing materials. Therefore, the objective of this work is to investigate the possibility of the minimization of representative PAH-compounds (Table 1) from organic media using activated carbon and alternative ash wastes. Furthermore, different factors affecting the adsorption process of PAHs (contact time, particle size, solvent polarity and, PAH concentration and type) from non-aqueous media will be investigated. This is important to know how to remove PAHs from polluted hexane or acetonitrile (non-polar; aliphatic; dielectric constant 1.90; acetonitrile: 37.5) by wood ash wastes, which would be an interesting utility for waste disposal. The impact of higher-molecular-weight PAHs on adsorption has not yet been researched extensively.

2. Materials and methods

2.1. PAHs

For Freundlich sorption isotherms, three PAHs with different molecular weight were selected: fluoranthene (F, 98%), benzo[b]fluoranthene (B[b]F, 98%), and benzo[g,h,i]perylene (B[ghi]P, 98%) with respectively, 202, 252 and 278 g mol⁻¹ (Table 1). For removal simulation of polycyclic aromatic hydrocarbons from polluted hexane, 10 selected PAHs were studied (Table 1): F (98%), pyrene (P, 98%), benzo[a]-anthracene (B[a]A, 98%), chrysene (Chr, 99%), B[b]F (98%), benzo[k]fluoranthene (B[k]F, 98%), benzo[a]-pyrene (B[a]P, 97%), dibenzo[a,h]anthracene (DB[ah]A, 97%), B[ghi]P (98%) and indeno[1,2,3-cd]pyrene (I[1,2,3-cd]P, 98%) were purchased from Sigma Aldrich (Madrid, Spain), and they were used as markers for the 15 PAHs of toxicological significance. F was selected as representative of three benzenic ring-PAHs. P, Chr, B[a]A, B[b]F and B[k]F were selected as markers of four benzenic ring-PAHs. B[a]P, DB[ah]A and I[1,2,3-cd]P were selected as being representative of the five benzenic ring group of PAHs. B[ghi]P was selected as marker of other six benzenic ring-PAHs.

2.2. Adsorbents

PAHs-polluted hexane was placed in contact with different adsorbent materials (see total C % in Table 2). Adsorption of some of these materials were also assay with PAHs-polluted acetonitrile. The description of the different selected adsorbents is as follows.

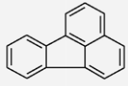
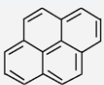
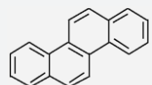
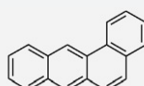
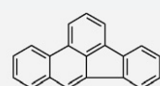
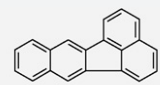
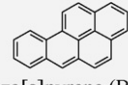
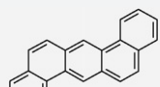
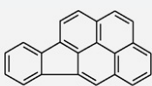
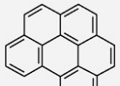
2.2.1. Powder of activated carbon (Panreac, Barcelona, Spain)

This material activated at temperatures of 1000 °C has a particle size range between 0.005 and 0.05 mm. Due to this material is usually used to sorbe multiple contaminants in water, organic solvents it was used for reference purposes to compare the performance on PAH sorption of the alternative waste materials. This material was separately placed in contact with two polluted organic solvents: hexane and acetonitrile.

2.2.2. Sawdust ashes obtained in the laboratory

These ashes were obtained from the 1:1:1:1 mixture of sawdust from different tree species (*Pinus pinaster*, *Eucalyptus globulus*, *Prunus avium* and *Castanea sativa*) and submitted to incineration in the oven without flame at temperatures of 300, 500 and 800 °C. Incineration time was for 10 min. The ashes obtained at 800 °C were separately placed in contact with two polluted organic solvents:

Table 1
Molecular weight, water solubility and log *K*_{ow} for studied PAHs.

PAH	pm (g mol ⁻¹)	S (mol L ⁻¹)	Log <i>K</i> _{ow}
 Fluoranthene (F)	202	6.3 × 10 ⁻⁷	5.2 ± 0.2
 Pyrene (P)	202	2.2 × 10 ⁻⁷	5.18 ± 0.2
 Chrysene (Chr)	228	4.2 × 10 ⁻⁸	5.61 ± 0.2
 benzo[a]anthracene (B[a]A)	228	6.4 × 10 ⁻⁸	5.9 ± 0.2
 benzo[b]fluoranthene (B[b]F)	252	2.0 × 10 ⁻⁸	6.4 ± 0.2
 benzo[k]fluoranthene (B[k]F)	252	1.3 × 10 ⁻⁸	6.4 ± 0.2
 benzo[a]pyrene (B[a]P)	252	7.4 × 10 ⁻⁹	6.4 ± 0.2
 dibenzo[ah]anthracene (DB[ah]A)	278	2.5 × 10 ⁻⁹	7.1 ± 0.2
 Indeno[1,2,3-cd]pyrene (I[1,2,3-cd]P)	278	6.8 × 10 ⁻⁹	6.9 ± 0.2
 benzo[ghi]perylene	278	5.9 × 10 ⁻⁹	6.9 ± 0.2

hexane and acetonitrile. The ashes obtained at 500 °C were sieved through 0.50 and also through 0.177 mm mesh.

2.2.3. Wood ashes from a timber industry

Timber industries include, within the productive process, the burning of trimming wastes in boilers reaching temperatures of 500 °C. As a result of this incineration, the wood ashes from a tim-

Table 2

Total carbon percentage in adsorbents, plus initial concentrations for PAHs in the batch sorption experiments at equilibrium.

Adsorbent	Total C (%)	Initial concentration (mg L ⁻¹)					
		Fluoranthene		B(b)FA		B(ghi)P	
		<i>n</i> -hex	AcN	<i>n</i> -hex	AcN	<i>n</i> -hex	AcN
Activated carbon at 1000 °C	93	20–100	–	50–400	–	60–350	–
Ash at 800 °C	89	2–20	–	3–20	–	5–40	5–20
Ash at 500 °C Particle size of 0.5 mm	76	1–12	–	1–15	–	3–20	–
Ash at 500 °C Particle size of 0.177 mm	76	1–12	–	1–15	–	3–20	–
Ash at 300 °C	64	1	–	1	–	3	–
Ash from a timber industry at 500 °C	55	1–12	–	1–15	–	3–25	–
Mussel shell ashes	12	–	–	–	–	–	–

ber industry are obtained and they were sieved through 0.177 mm mesh.

2.2.4. Mussel shell ashes

These ashes were obtained from a company, which incinerates mussel shells. The process that follows can be divided in several steps: reception and storage (to receive and unload the raw material); washing and dripping (to clean the shell with freshwater); drying and calcining (to dry at 190 °C and to calcine at 500–600 °C the shells); cooling (to be cooled the bottom ash from temperatures of calcining to 60 °C); milling and sorting, used to give to calcined shells an appropriate granulometry to the product to satisfy market requirements; final product storage and, packing and shipment. Samples used have a particle size <2 mm.

2.3. Determination of PAHs

Two different methods were used depending on the nature of the sample and the analytical purpose.

2.3.1. Determination of PAHs in the solid wastes

It includes different steps: extraction, clean-up, concentration and analysis by HPLC-Fluorescence. The analytical treatment, which gave recovery-rates higher than 85% with relative standard deviations lower than 5%, was based on a procedure previously reported by the authors [8].

Before sorption experiments, the 10 PAHs were determined in all ash wastes by HPLC-Fluorescence as follows in short. *Extraction*: 0.5 g of ashes were extracted with 10 mL *n*-hexane for 20 min in an ultrasonic bath (P-Selecta, Barcelona, Spain), and the extraction process was repeated 3 times, with subsequent centrifugation for 5 min at 1000 U/min. *Clean-up*: the 30 mL of extract were passed through a Silica Plus cartridge followed by 10 more millilitre of *n*-hexane. *Concentration*: the eluate was concentrated to dryness by means of a Turbo Vap (Caliper Life Sciences, Barcelona, Spain), and the residue was re-dissolved in acetonitrile (1 mL). *Analysis*: by HPLC-Fluorescence (Thermo Separation Products P2000 binary pump equipped with an AS1000 autosampler, a SCM1000 vacuum membrane degasser and a Jasco FP-1520 fluorescence detector) as previously published [6,8,29–30]. The only ashes with PAHs were those from mussel shells, and therefore they were discarded for batch sorption experiments.

2.3.2. Determination of PAHs in the organic solution at the end of the kinetic or equilibrium experiments

It is based on a direct analysis by spectrofluorimetry. Since samples were analysed directly without any pre-analytical step, such as extraction, clean-up or concentration, recoveries were kept at about 100%.

Single PAH concentrations in solution after the batch sorption experiments were measured by spectrofluorimetry. Bandwidth was set at 5 nm. Sensitivity was established as high, medium or

low depending on the expected concentration in solution: <20, 20–90, and >100 mg L⁻¹. Second derivative excitation was used for quantification after measuring the peak-valley distance in the range 286–297 for F ($\lambda_{em} = 464$), and 300–310 for B(b)F ($\lambda_{em} = 446$) and B(ghi)P ($\lambda_{em} = 406$). For the quantification of a mixture of the 10 PAHs, the selected peak-valley distances were selected in the following wavelengths ranges: 273–282 ($\lambda_{em} = 387$) for P, Chr and B(a)A, and 288–297 ($\lambda_{em} = 422$ or 500-only for I[1,2,3-cd]P) for the rest.

2.4. Batch sorption experiments

For these assays, three PAHs were selected as representative of increasing molecular weight (202, 252 and 278 g mol⁻¹) and aromaticity (3, 4 and 6 benzenic rings): F, B(b)F and B(ghi)P, respectively (Table 1).

2.4.1. Sorption kinetics of selected PAHs to wood ashes obtained at 500 °C

Sorption kinetics of PAHs to ash were monitored to know whether the time necessary for equilibrium or constant sorption can be lower than 24 h. Kinetics were measured by triplicate in *n*-hexane at a ratio of 0.1 g sorbing material/10 mL of solvent separately spiked at 3 mg L⁻¹ for F, and 5 mg L⁻¹ for B[b]F and B[ghi]P. Samples were then stirred at 25 °C and PAHs remaining in solution were determined after 15 min, 1, 2, 3, 6, 9, 16 and 24 h following the direct determination by spectrofluorimetry. The quantity of PAHs adsorbed was determined by difference between the initial concentration added to the sorbate-solvent mix and the final concentration in the solvent. A control containing only hexane and PAHs was maintained until the kinetic study was completed to check for degradation. The PAHs remaining in the solution were determined using the procedure described above under Section 2.3.2.

To interpret experimental data on PAH kinetics in the batch experiments, three consecutive steps were considered. The first is related to PAH transport across the boundary layer to the exterior of active adsorbent surfaces (*i.e.*, where adsorption or degradation occurs). Then, the PAH is transported within the pores to the inner active surfaces. Finally, chemical or physical binding, or degradation on surface occurs.

In most of the cases, the dynamic processes in adsorbents are limited by diffusion. Several models were used in order to identify the mechanism controlling adsorption. Therefore, first order, second order, simplified Elovich, parabolic diffusion and power-function models were tested. Model equations [taken from Ref. [31]] are as follows:

First order: $\ln X^* = \ln X - k_1 t$

Second order: $1/X^* = 1/X + k_2 t$

Simplified Elovich: $X^* = a + b \ln t$

Parabolic diffusion: $X^* = X + Dt^{1/2}$

Power law: $X^* = kt^b$

Table 3
Fitting results of simplified Elovich kinetic model.

PAH	<i>b</i>	<i>a</i>	<i>r</i> ²
F	1.368	0.036	0.901
B[b]F	1.741	0.020	0.912
B[ghi]P	1.943	0.014	0.926

Simplified Elovich: $X^* = a + b \ln t$; *a* (mmol kg⁻¹), *b* (mmol kg⁻¹).

X is the equilibrium adsorbed concentration (mmol kg⁻¹) in adsorbent, and *X*^{*} at non-equilibrium.

X is the equilibrium adsorbed concentration (mmol kg⁻¹) in ash, and *X*^{*} at non-equilibrium. The best results were obtained for Elovich model (Table 3).

2.4.2. Experiments at equilibrium for selected PAHs into adsorbents

The three PAH adsorption was determined by using a batch equilibrium technique in independent experiments. To check for the efficacy in sorbing PAHs from two different organic solvents, such as hexane and acetonitrile, the ashes obtained at 800 °C and activated carbon were separately placed in contact with both solvents.

Different quantities of PAHs (shown in Table 2) were added to 10 mL of organic solvent containing 0.1 g of sorbing material. The mixture was shaken at 25 °C throughout the 16 h-equilibration period, afterwards the solvent was used to directly measure the free PAHs as described above. Ashes obtained at 300 °C were discarded because they show very poor sorption after a batch experiment run in triplicate: B[b]FA remained in solution at 97.3% after 16 h-equilibration period.

To facilitate estimation of adsorption capacity, a commonly used empirical adsorption model, Freundlich, which corresponds to heterogeneous adsorbent surfaces was employed in this study. The empiric Freundlich equation establishes that the sorption strength exponentially decrease with the increment in saturation of the sorption surface: $X = K C^n$ where *X* is the quantity of sorbed PAH by mass unit of sorbate (mmol kg⁻¹). *K* is a constant parameter measuring sorption affinity and is related with the sorption capacity of the sorbates at sorbing PAHs. The constant *n* is an exponential coefficient related with the intensity of sorption and the distribution of active sites in the sorbate [32–33]. Fitting was done by the Levenberg-Marquardt least-squares algorithm [34].

2.5. Thermal desorption experiments

These experiments were performed to recover the adsorbates applied to the ashes wastes by a thermal regeneration process. The goal of this experiment is to check for the relative efficiency in PAHs adsorption of two materials:

- The original wood ashes obtained at 800 °C for 10 min (0.1 g) were placed in contact with an hexane solution of 10 PAHs at a total concentration of 5 mg L⁻¹ (10 mL) and their efficiency in PAHs adsorption was monitored.
- Then, the above sample after adsorption of 10 PAHs was thermally regenerated with a new treatment of 800 °C for 10 min. This regenerated material was again placed in contact with an hexane solution of 10 PAHs at a total concentration of 5 mg L⁻¹ (10 mL) and their efficiency in PAHs adsorption was monitored.

2.6. Removal simulation of polycyclic aromatic hydrocarbons from polluted hexane

A 0.1 g of sorbent material was exposed to 10 mL of a solution of *n*-hexane containing 10 PAHs (Table 1) at levels ranging 2.5 (B[k]F)–100 (P) mg L⁻¹. The suspension was shaken for 16 h to

reach equilibrium and the solution was used to monitor the remaining PAHs in solution. A second cycle was necessary by repeating the experiment with the remaining solution plus a new 0.1 g of sorbing material.

3. Results and discussion

3.1. Detected PAHs levels in the ashes

Depending on the incineration process, ashes could contain PAHs [7]. For this reason, it is necessary to check in advance for their native levels. The only ashes with PAHs were those from mussel shells with the following results: 14.3 (F), 8.1 (P), 7.1 (B[a]A), 7.6 (B[b]F), 2.4 (B[k]F) and 2.3 (B[a]P) μg kg⁻¹. Therefore, they were discarded for batch sorption experiments.

3.2. Sorption kinetics for selected PAHs in wood ashes obtained at 500 °C

The adsorption phenomenon is a manifestation of complicated interactions among the adsorbent, the adsorbate, and the solvent involved. The affinity between the adsorbent and the adsorbate is the main factor controlling the adsorption process [35]. The analysis of PAHs in a control solution showed that there was no degradation of these compounds. This is due to the properties of these chemical compounds, because PAHs are very chemically inert. Their bond linkages give them chemical stability.

Fig. 1 shows the sorption kinetics for 3 PAHs with different molecular weights (F, B(b)FA and B(ghi)P) onto the ashes obtained at 500 °C (0.177 mm in size). The low molecular weight PAH, F, was sorbed more slowly than the other 2 (B[b]FA and B[ghi]P), which were adsorbed at 95% after 15 min-contact. After 2 h-contact, PAH sorption reached 96% for F and 98% for the others, mainly due to rapid hydrophobic interactions. After 2 h, sorption efficacy decreases and gradually approaches equilibrium with 97–99% sorption at 16 h (97% for F and 99% for the others), due to a much more slowly migration of PAHs to less accessible sites into the ashes [23–24]. Time for equilibrium was established in 16 h.

Several models were used in order to identify the mechanism controlling adsorption: first order, second order, simplified Elovich, parabolic diffusion and power-function. The best results were obtained for Elovich model (Table 3). This model describes a number of reaction mechanisms that include bulk and surface diffusion. A linear relationship between transient adsorbed concentration (*X*^{*}) and Ln(*t*) was obtained (*r*² > 0.901). The fitting of results for the three PAHs to simplified Elovich model shows that kinetic rates (*b*) are increasing with the molecular weight and aromaticity of the PAHs. Instead, at short contact times, the kinetic constant (*a*) for the lower molecular weight PAH was about 2.6 times that of the higher-molecular-weight PAH. Also, note that *X*^{*}

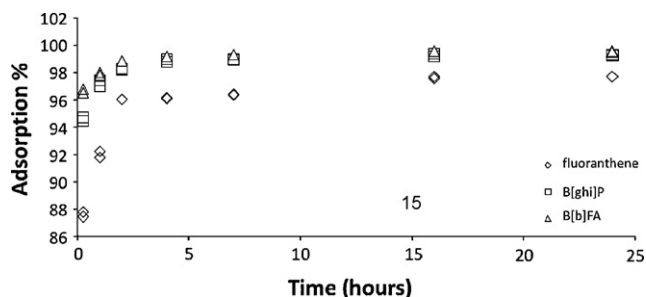


Fig. 1. Sorption kinetics for PAHs in wood ashes obtained at 500 °C and sieved at 0.177 mm.

increases at incubation times of 24 h, suggesting that diffusion is still the limiting step at late stages of the process.

The prevalent mechanism in the uptake of PAHs by these adsorbents is a physical adsorption caused by the aromatic nature of PAHs, probably combined with Van der Waals strength. Therefore, a large amount of PAHs is expected to be progressively adsorbed by the adsorbent matrices as contact time increases. Moreover, the hydrophobic sites available on the adsorbent matrices were used more rapidly by the most non-polar compounds.

3.3. Freundlich sorption isotherms for selected PAHs in the adsorbents

Percent total carbon, as measured by the CHN analyzer, in wood ash wastes and activated carbon was found to be a useful predictor variable for estimating surface area of wood ash wastes [25]. All the

ashes were incinerated between 300 and 800 °C. During pyrolysis (heat treatment to <700 °C), small molecules, such as water, carbon dioxide, carbon monoxide, alcohols, carbonyls, and aliphatic acids, are volatilized and lost from the cellulosic structure of wood. As small molecules are removed from the original macromolecular network, the resultant chemically reactive lattice immediately condenses around the vacancies created by the loss of volatiles. Consequently, a new lattice is continuously created with a composition of higher carbon-to-hydrogen ratios because of preferential loss of hydrogen and oxygen. The newly created lattice, richer in carbon than the original cellulosic lattice, possesses considerable strain energy and is not in thermodynamic equilibrium because the more stable state is the graphite-like planar aromatic structure. When the wood reaches temperatures in the carbonization range (>700 °C), the unstable network becomes more carbonaceous and more aromatic as carbon atoms readjust their positions to approxi-

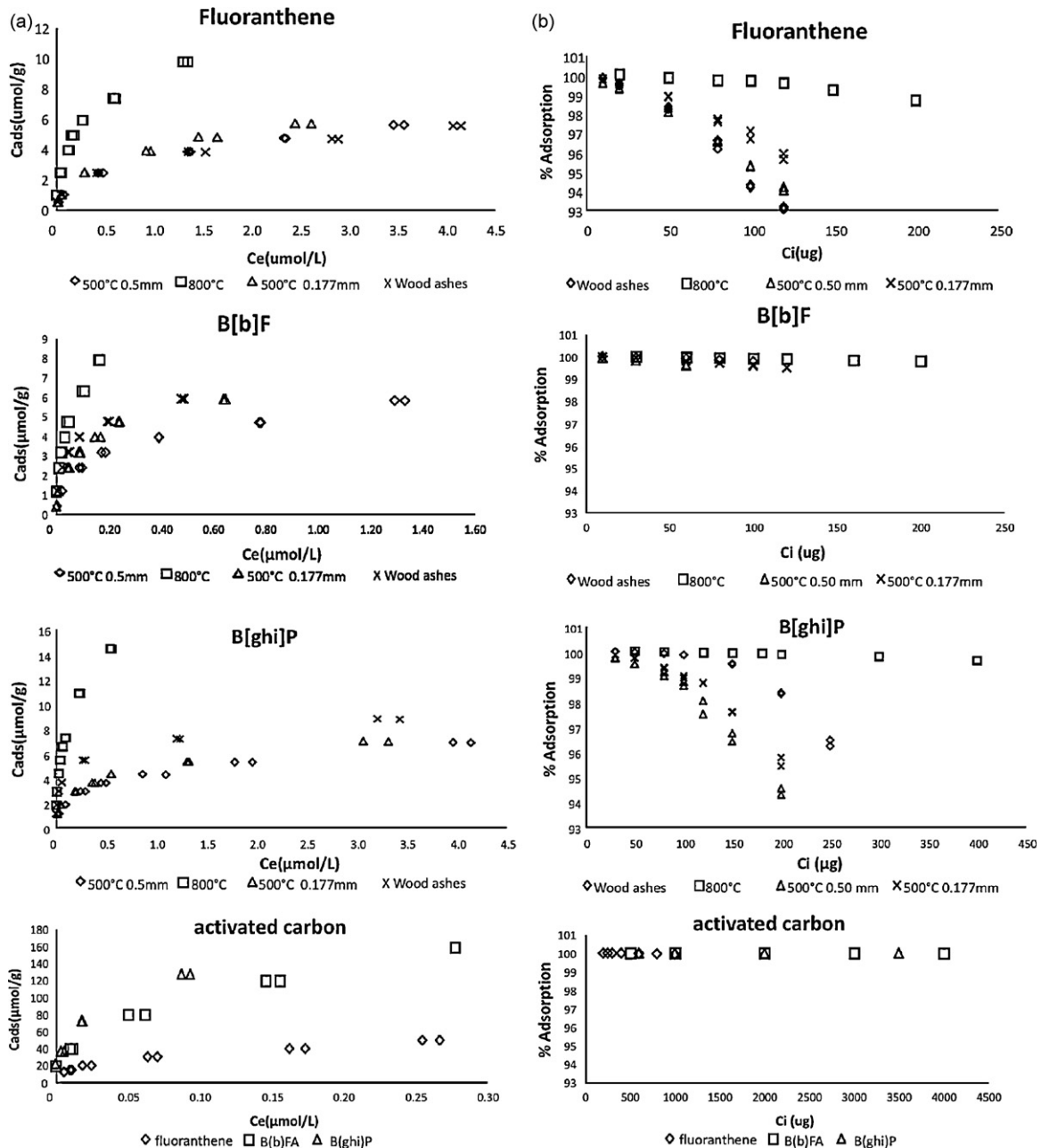


Fig. 2. Sorption isotherms (a) and sorption percentages (b) for PAHs in different wood ashes (obtained at 800 °C, 500 °C and those from a timber industry) and activated carbon.

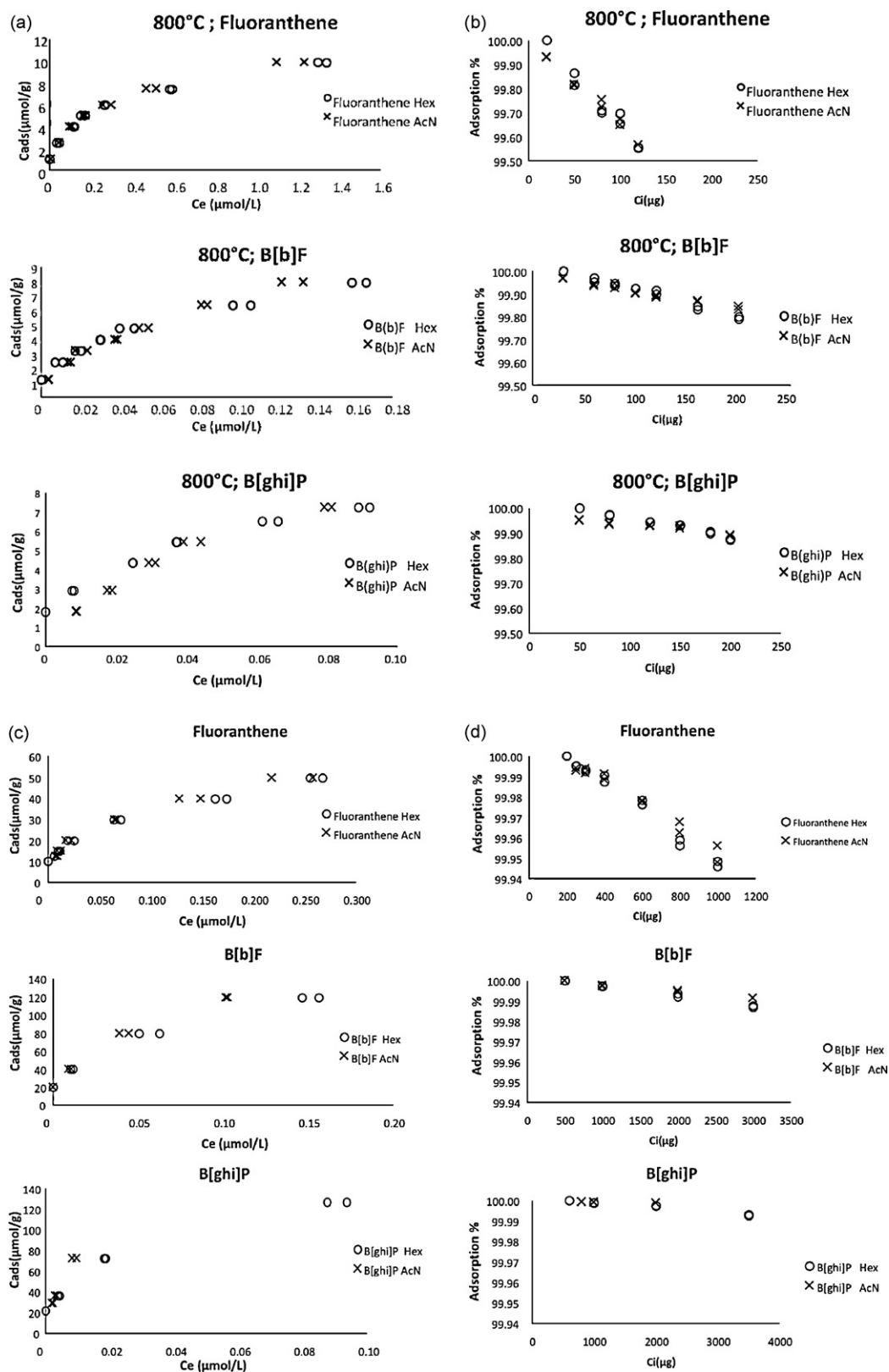


Fig. 3. PAHs sorption isotherms (a/c) and sorption percentages (b/d) in ashes obtained at 800 °C (a/b) and activated carbon (c/d) both with hexane and acetonitrile.

mate six-membered ring systems. Further increases in temperature cause further removal of oxygen, hydrogen, nitrogen, and sulphur [36]. The high surface area in ash results from random bonding of carbon during the carbonization process, and the defective nature of aromatic clusters results in microporosity, or voids, in the car-

bonaceous material. It is the microporosity of wood ash that is responsible for the sorption [37].

Ashes obtained at 300 °C were discarded because they show very poor sorption after a batch experiment run in triplicate: B(b)FA remained in solution at 97.3% after 16 h-contact. At 300 °C

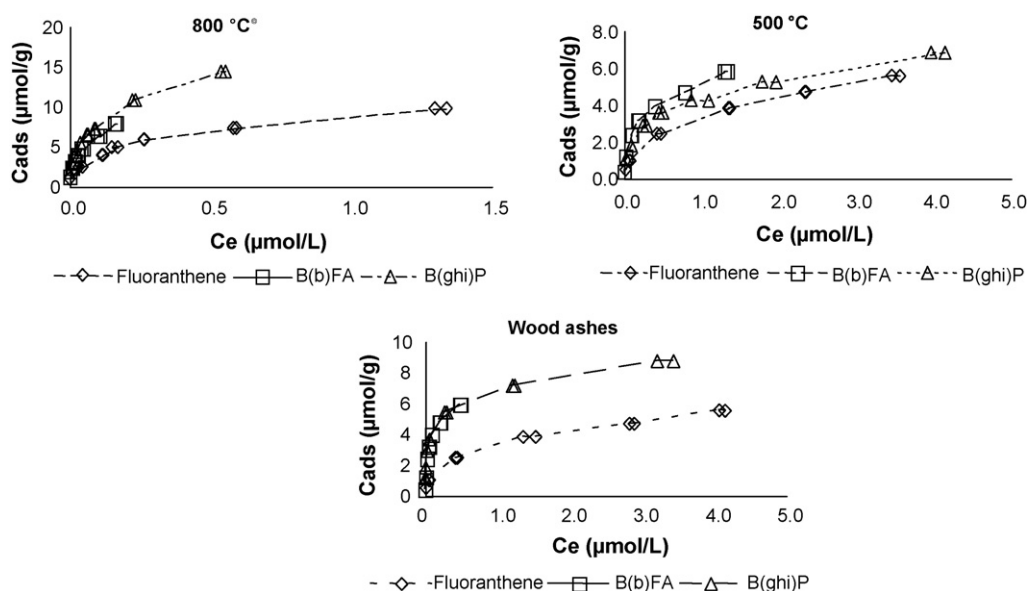


Fig. 4. Sorption isotherms for PAHs in wood ashes obtained at 800 °C, 500 °C and those from a timber industry.

some of the decomposition products, the small molecules, are volatilized, but others like tars (mainly hydrocarbons) remain sorbed into the pores of the amorphous carbonaceous material, explaining then why PAHs sorption is blocked. For the rest of wood ashes, together with activated carbon, the isotherms are drawn in Figs. 2–4. Due to the higher sorption strength of activated carbon, PAHs concentrations need to be higher (Table 2; Fig. 2). At the same time, sorption percentages at different initial concentrations are shown. We can see the effect of different factor such as:

- *Effect of the material to be charred and charring conditions (Fig. 2):* It was seen that charred mussel shells already contain themselves PAHs and were discarded as material for PAHs removal. The efficacy in sorbing PAHs was activated carbon >800 °C wood ashes >timber industry wood ashes >500 °C wood ashes (0.177 mm) >500 °C wood ashes (0.5 mm). The increase in temperature can elevate the number of micropores, contributing to an increase in surface activity and the sorbing properties of the material [25].
- *Effect of particle size (Fig. 2):* This was a very low effect, but in general ashes obtained at 500 °C and sieved by a 0.177 mm mesh showed a slightly higher sorption than those sieved by a 0.5 mm mesh. Mondal et al. [38] also established that particle size of activated carbon has shown negligible effect on the removal of arsenic and Fe species.
- *Effect of solvent polarity (Fig. 3):* This was a very low effect, especially for fluoranthene and wood ashes obtained at 800 °C, where the sorption from hexane is a bit higher at the lowest fluoranthene concentrations (Fig. 3). There was no effect for the higher-molecular-weight PAHs both in wood ashes at 800 °C and activated carbon.
- *Effect of molecular weight and aromaticity of PAHs (Fig. 4):* The increase in their molecular weight conditions their hydrophobicity and therefore their sorption strength. The effect is more clear for the PAH with the lowest molecular weight, fluoranthene (Fig. 4). Only in the most sorbing materials (activated carbon and wood ashes obtained at 800 °C), B[ghi]P had a slightly higher sorption than B[b]FA. This clearly shows how the adsorption capacity of the adsorbents towards PAHs in organic solvents is a function of the adsorbents molecular weight, which is in turn in connection with the number of their benzene rings. An increase in the number of aromatic rings in a PAH molecule

increases its adsorption ability to adsorbent [2,20,23–24, 39–42].

It is found that the isotherms (Table 4; Figs. 2–4) are not linear ($n \neq 1$). It is assumed that the heterogeneity of the sorbent materials can contribute to the non-linear sorption. A non-linear least-square method was used to estimate parameters of the isothermal models in the curve fitting. The Freundlich adsorption isotherm model has been useful because it shows that the lower the concentration of as substance, the greater fraction is sorbed to carbon. The physical and chemical properties of individual PAHs and carbon in ash contributed to the results in this study. The parameters K and n estimated using Freundlich equation are reported in Table 4. The n values for all studied systems range between 0.240

Table 4
Freundlich parameters for PAHs studied in the experiments at equilibrium.

	Freundlich equation: $X = KC^n$		
	K	n	r^2
Fluoranthene			
1000 °C Activated carbon Hex	79	0.370	0.952
1000 °C Activated carbon AcN	86	0.391	0.991
800 °C Hex	8.9	0.357	0.973
800 °C AcN	9.4	0.390	0.989
500 °C 0.5 mm Hex	3.3	0.430	0.998
500 °C 0.177 mm Hex	3.9	0.422	0.995
500 °C Timber industry Hex	3.2	0.376	0.997
B[b]FA			
1000 °C Activated carbon Hex	270	0.427	0.957
1000 °C Activated carbon AcN	344	0.470	0.932
800 °C Hex	16.4	0.408	0.951
800 °C AcN	23.8	0.540	0.993
500 °C 0.5 mm Hex	5.3	0.350	0.991
500 °C 0.177 mm Hex	7.2	0.350	0.984
500 °C Timber industry Hex	7.5	0.298	0.981
B[ghi]P			
1000 °C Activated carbon Hex	328	0.394	0.920
1000 °C Activated carbon AcN	1439	0.631	0.982
800 °C Hex	18.3	0.377	0.983
800 °C AcN	32.8	0.589	0.981
500 °C 0.5 mm Hex	4.3	0.337	0.991
500 °C 0.177 mm Hex	4.9	0.319	0.994
500 °C Timber industry Hex	6.7	0.240	0.985

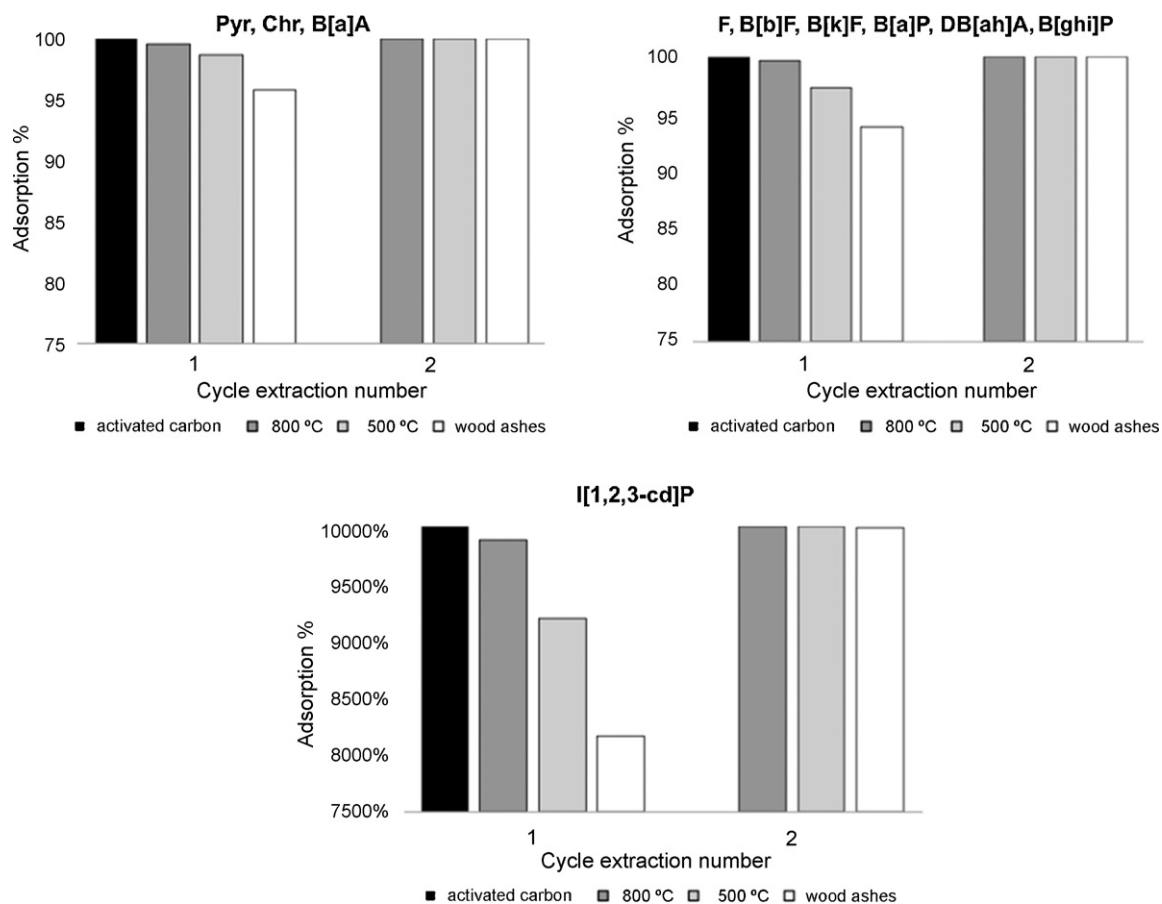


Fig. 5. Sorption for a mixture of 10 PAHs in wood ashes obtained at 800 °C, 500 °C and those from a timber industry, as compared to activated carbon, after 2 extraction cycles.

and 0.589. The minimum value being for adsorption of B[ghi]P to timber industry ash waste while the maximum value is for its adsorption to ashes at 800 °C. The highest K values obtained are for adsorption of B(ghi)P to the systems with the highest C contents while the lowest values are for the adsorption of fluoranthene to the systems with the lowest C contents. As aromaticity is the property or ability to sustain induced ring electron current, the B[ghi]P, composed of alternating bonding and non-bonding orbital, offer better conduction to electron movement, and can be considered as “true aromatic”. In fluoranthene and similar, less symmetric, the circulation is somewhat interrupted due to five-membered ring symmetry (Table 1), and can be seen as less aromatic.

Particle size demonstrates not to have a large influence on the sorption capacity of the ashes obtained at 500 °C: slightly higher K_s were obtained for that sieved at 0.177 mm vs. that at 0.5 mm. What is clear is that the results for sorption of PAHs on activated carbon are the best among those reported, due to its most homogeneous matrix with high aromaticity and its adsorptive properties.

3.4. Thermal desorption of PAHs from wood ashes obtained at 800 °C

Thermal regeneration, as usually applied to reactivate adsorbent carbon, can be thought as the process of choice by pyrolysis and burning off of adsorbed organic substances. In order to avoid igniting the ash carbon, it is heated to about 800 °C in a controlled atmosphere. This is the widely used method and regenerates the carbon very well, but it has two disadvantages: it requires considerable investment in either a multiple-hearth furnace and it causes partial carbon losses.

The relative efficiency in PAHs adsorption of the two materials assayed was as follows:

- The original wood ashes obtained at 800 °C for 10 min (0.1 g) in contact with a hexane solution of 10 PAHs at a total concentration of 5 mg L⁻¹ (10 mL) adsorbed 4893 ppb of the total PAHs (98% adsorption).
- Whereas the above sample after adsorption of 10 PAHs, which was thermally regenerated with a new treatment of 800 °C for 10 min, and again placed in contact with a hexane solution of 10 PAHs at a total concentration of 5 mg L⁻¹ (10 mL) resulted in a lower adsorption of 3005 ppb of the total PAHs (60% adsorption).

This thermal regeneration process (800 °C/10 min) reduces the efficiency in PAHs adsorption of the ashes at 800 °C for 10 min from 98% to 60%. The 800 °C during 10 min thermal treatment removes about a 60% of the total PAHs adsorbed.

3.5. Removal simulation of polycyclic aromatic hydrocarbons from polluted hexane

This experiment was performed to demonstrate that wood ashes can effectively be used to remove PAHs from organic solvents like *n*-hexane. All 10 PAHs were spectrofluorimetrically quantified.

In Fig. 5, it can be seen that activated carbon can sorbe 100% PAHs in the first cycle. Although wood ashes do not reach total sorption, after the first cycle, all of them can sorbe more than 80% PAHs. The ash obtained at 800 °C is the one with the largest sorption percentages (99.6 (for P, Chr and B[a]A), 98.6 (for B[b]F, B[k]F, B[a]P, Db[ah]A and B[ghi]P) and 98.8% (I[1,2,3-cd]P). The ash from a

timber industry has the lowest sorption percentage (81.7% for I[1,2,3-cd]P). After a 2nd sorption cycle with the ashes, the ash obtained at 800 °C reached 100% sorption for all PAHs, while the ashes at 500 °C and those from a timber industry gave sorption percentages higher than 99.9% for all PAHs. These materials can be used as a low-cost alternative to activated carbon for removing PAHs from organic solvents.

4. Conclusions

The contact time is an important factor in the adsorption of PAHs. The equilibrium time was reached at 16 h. The adsorption was controlled by two transport processes, one fast due to rapid hydrophobic interactions followed by one slow migration to less accessible sites. The parameters controlling sorption of polycyclic aromatic hydrocarbons (PAHs) to the selected sorbates in hexane were estimated based on the Freundlich equation. Both precursor material and charring temperature condition carbon percentage. Higher carbon content in adsorbents generally resulted in increased sorption of PAHs. Because carbon content and surface area are strongly related, it seems that the high surface area of carbon in combusted residuals is responsible for PAHs sorption. Both particle size of the adsorbents and organic solvent has shown negligible effect on the removal of PAHs. An increase in the number of aromatic rings in a PAH molecule increases its adsorption ability to adsorbent.

This study shows that activated carbon was a good adsorbent to remove all kinds of PAHs from hexane. The removal percentages at the concentrations evaluated and found in organic solvents, suggest that specially the ashes obtained at 800 °C can be useful for abating some complex and toxic PAHs. After a 2nd sorption cycle with the ashes, the ash obtained at 800 °C reached 100% sorption for all PAHs, while the ashes at 500 °C and those from a timber industry gave sorption percentages higher than 99.9% for all PAHs. These materials can be used as a low-cost alternative to activated carbon for removing PAHs from organic solvents.

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