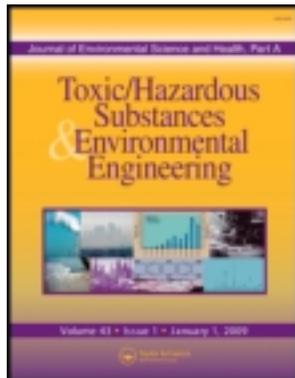


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Maria À. Olivella ^a, Patrícia Jové ^b & Anna Oliveras ^b

^a University of Girona, Department of Chemistry, Girona, Spain

^b Catalan Cork Institute, Girona, Spain

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The use of cork waste as a biosorbent for persistent organic pollutants—Study of adsorption/desorption of polycyclic aromatic hydrocarbons

MARIA À. OLIVELLA¹, PATRÍCIA JOVÉ² and ANNA OLIVERAS²

¹University of Girona, Department of Chemistry, Girona, Spain

²Catalan Cork Institute, Girona, Spain

The aim of this study is to determine the sorption-desorption behavior of a mixture of thirteen aqueous PAHs on cork waste at a particle of size 0.25–0.42 mm obtained from the remains of cork strips. The final purpose is to use this natural adsorbent as an alternative to activated carbon in an innovative approach for the removal of this class of toxic compounds, and significantly reduce the regeneration costs of the process. The chemical composition of the selected cork revealed that suberin (38.5 %) and lignin (31.6 %) were the main structural components of the cell wall. The high efficiency of cork as a biosorbent of PAHs is shown by the fact that just over 80 % of adsorption occurred during the first two minutes of contact time. Both Freundlich's and Langmuir's isotherms gave good fits to the sorption process. The highest adsorption affinities were exhibited for pyrene, anthracene, and phenanthrene. Desorption studies indicate a high degree of irreversibility for all PAHs, and especially so in the case of high molecular PAHs. The correlation with K_F and low molecular weight PAHs was the most significant. The quantity of cork required to reduce water pollution was estimated to be between 3 and 15 times less than the quantities required in the case of other materials (i.e. aspen wood and leonardite). This study demonstrates for the first time that cork is a potential biosorbent for PAHs and may have relevance in the future treatment of PAH-contaminated waters.

Keywords: Cork waste, biosorbent, sorption-desorption, organic pollutants, PAHs, water treatment.

Introduction

The widespread occurrence of many persistent toxic organic pollutants has become a serious environmental concern. The release of PAHs has been reported during the production and processing of plasticizers, dyes, and pigments; however, they mostly occur as a result of fossil fuel combustion, or as byproducts of an industrial or other production process, for instance coke manufacturing, or methods of cooking food such as grilling and smoking. The hazardous nature of PAHs is a result of their toxicity, in combination with their high chemical and biological stability, and a high degree of lipophilicity. For these reasons, the European Union has established very restrictive limits for these compounds in Directive 2006/0129 EC,^[1] which was approved by E.U. Notice No. 2007/C97/02.^[2] The limits of benzo[a]pyrene, anthracene, and fluoranthene

for surface waters were set at 0.1 $\mu\text{g/L}$, 0.4 $\mu\text{g/L}$, and 1 $\mu\text{g/L}$, respectively. These limits must be achieved by 2015.

Although the use of activated carbon is one of the best available environmental control technologies for the removal of PAHs from water,^[3,4] its high operational cost prohibits the treatment of large amounts of wastewater. Other adsorbents (e.g., alumina, zeolite, fly ash, soils, and clays) have also been used successfully to remove PAHs.^[5–8] The use of waste materials is very attractive because using them decreases the costs of waste disposal, thereby contributing to environmental protection.

Cork is the bark of the cork oak tree (*Quercus suber* L.), a natural, renewable and biodegradable raw material. It is a heterogeneous material mainly composed of suberin and lignin (hydrophobic biopolymers), and polysaccharides (cellulose and hemicellulose), which have a hydrophilic character that represent around 40 %, 24 %, and 20 % of its hardwood dry mass, respectively. The heterogeneous chemical composition of cork provides numerous bonding possibilities for a wide range of pollutants. For instance, the lignin phenylpropane units may provide for relatively hydrophobic regions, thereby attracting hydrophobic compounds such as PAHs. As a whole, there is wide interest

Address correspondence to Maria Àngels Olivella, Department of Chemistry, University of Girona, Campus Montilivi s/n, 17071 Girona, Spain; E-mail: angels.olivella@udg.edu
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in cork's unique characteristics and these factors make it a very interesting natural material to investigate further. Cork oak forests extend over an area of almost 2.2 million hectares, concentrated mainly in the Mediterranean region, in the South of Europe and in North Africa (Portugal, Spain, Italy, France, Algeria, Morocco, and Tunisia). Annual production is about 340,000 tons; 52 % from Portugal, 32 % from Spain and 6 % from Italy. Europe has about 60 % of the total production area (cork forests) and produces more than 80 % of the world's cork. In addition, the production of cork stoppers, the annual production of cork waste is around 50,000 tons, which corresponds to an average of 25–30 % of the quantity used in cork stopper manufacturing. The subject of this research study is the cork remaining as a by-product after the stoppers have been punched out of the cork strips. Cork by-products are mainly used as an energy source due to their low economic value and high capacity to burn. So far, few studies have focused on research into the use of raw cork by-products as a biosorbent.^[9,10]

In the search for high value-added applications of cork by-products, this paper is the first to show the sorbent qualities of raw cork on the sorption-desorption of PAHs.

In this study, batch experiments were carried out and the data were based on the Freundlich and Langmuir adsorption models. The use of these models was necessary to obtain: (1) the sorption-desorption capacities of cork for a mixture of PAHs; and (2) an estimate of the quantity of cork required to remove PAHs from the contaminated effluents. The results are discussed in detail and are compared with those obtained by other authors using other sorbent materials. This comparison is essential to understand the high efficiency of raw cork as a new biosorbent. Results from this investigation will contribute to improve the knowledge of the sorption capacity of PAHs by cork to advance in the use of this material in the development of new technologies at preventing the water pollution.

Materials and methods

Sorbent and reagents

The remains of cork strips after stoppers had been punched out of them, were obtained from the southwest of Spain (Cáceres, Extremadura). They had initially been sampled in June 2008 and were subsequently supplied by a cork factory. The cork strips were cut into three sections with a hand saw: the back (the outermost bark), 6–10 mm thick; the cork itself (the central section used to make cork stoppers), 26–32 mm thick; and the belly, 3–5 mm thick. Each section was cut into small pieces (< 10 mm) and was milled in a ZM-200 (Retsch) ultracentrifugal mill, and a granulometric fraction of 40–60 mesh (0.25–0.42 mm grain size) was used for analysis. The back and the central section

were discarded, and only the belly was selected for this study, since it has a higher lignin content (32 %) than either the back (25 %) or the central section (24 %).^[11]

Deionized water was used for standard solutions and batch experiments. The methanol used was super purity grade from Romil (Cambridge). SPME fibers of 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) were supplied by Supelco (Bellefonte, PA, USA). Aqueous samples of 18 mL were collected using a 20 mL glass Luer tip syringe with a 6-inch, 22-gauge stainless steel needle, both supplied by Sigma Aldrich (St. Louis, MO, USA).

A mixture of PAHs (500 $\mu\text{g}/\text{mL}$ in methylene chloride), containing acenaphthylene, anthracene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, fluorene, indeno[1,2,3-cd]pyrene, phenanthrene, and pyrene. EPA 525 Fortification Solution (acenaphthene-d₁₀), [²H₁₂] chrysene (chrysene-d₁₂) and [²H₁₀] phenanthrene (phenanthrene-d₁₀) at 2000 $\mu\text{g}/\text{mL}$ were all purchased from Supelco (Bellefonte, PA, USA).

Thirteen EPA-PAHs were analyzed in this research study. The low molecular weight (LMW) compounds were: acenaphthene [Ace], fluorene [Flu], phenanthrene [Phe], anthracene [Ant], pyrene [Pyr]; and the high molecular weight compounds (HMW): benz(a)anthracene [BaA], chrysene [Chr], benzo(b)fluoranthene [BbF], benzo(k)fluoranthene [BkF], benzo(a)pyrene [BaP], indeno(1,2,3-cd)pyrene [Ind], dibenz(a,h)anthracene [DbA], and benzo(ghi)perylene [BgP].

Characterization of cork

The C, H, N, and S contents of cork were determined using a Perkin Elmer EA2400 Series II Elemental Analyzer, and the ash content was obtained by incinerating 2 g at 525 + 25°C in an oven during 1 h and weighing the residue. The oxygen content was calculated by measuring the difference. Extractives were determined by successive Soxhlet extractions with dichloromethane (6 h), ethanol (8 h), and water (20 h). The cork residue after extraction was air-dried and kept for subsequent analysis. Suberin was determined using methanolysis for depolymerization in extractive-free material.^[12] The suberin value included in this determination refers only to the long-chain fatty components, excluding glycerol, meaning that the total suberin content should be higher. Insoluble (Klason) lignin was determined gravimetrically after acid hydrolysis.^[13]

The point of zero charge (pHpzc) was determined by mass titration following the procedure described by Fiol and Villaescusa.^[14] Different masses of sorbent materials with particle sizes 0.5–0.75 mm and within the concentration range 20–90 g/L were put in contact with a 0.03 M KNO₃ solution. The aqueous suspensions were shaken for 24 h in a shaker at 200 rpm until equilibrium pH was

reached. The pH_{pzc} is the pH at which a plateau is arrived at when plotting equilibrium pH versus sorbent mass.

Solid Phase Microextraction (SPME) Procedure and gas chromatography-mass spectrometry (GC-MS) analysis

The extraction of PAHs and the GC-MS analysis were performed following the procedure described by Fernández et al.^[15] For the SPME extraction, 18 mL of deionized water in 20 mL vials, capped with polytetrafluoroethylene (PTFE) coated septa. Aqueous samples of 18 mL were collected using a 20 mL glass Luer tip syringe with a 6-inch, 22-gauge stainless steel needle, both supplied by Sigma Aldrich Inc. (St Louis, MO, USA). The fibers were immersed in the aqueous phase with agitation at 60°C for 60 min. After extraction, the fiber was thermally desorbed for 10 min into the liner of the gas chromatograph injector port at 300°C. The splitless time was set at 4 min and the desorption time at 10 min. GC analysis was performed with an Agilent 6890 N chromatograph equipped with a Gerstel MPS2 autosampler and coupled to an Agilent 5973N mass spectrometer. The separation was achieved using an HP-5MS column (30 m, 0.25 mm, 0.25 μm film thickness) (J&W Scientific, Folsom, CA, USA) and a GC oven program starting at 50°C (3 min), increased by 6°C/min to 325°C (held for 20 min). The carrier gas was helium (99.999 %) from Abello Linde (Barcelona, Spain) with a constant flow rate of 1 mL/min. The transfer line temperature was set at 300°C and the ion source temperature at 250°C. The mass spectrometer was operated in selected ion monitoring mode (SIM), detecting the following ion masses: 152, 166, 178, 202, 228, 252, 278, 276. PAHs were quantified by comparing the areas for the monitored molecular ions to that of the internal standard, with calibration response curves generated from five different concentrations (0.05, 0.1, 0.5, 1, and 5 μg/L) of each target PAH. The calibration curves for the compounds were linear ($r > 0.99$) over the established range. Recoveries of PAHs were > 90 %. In addition, for each sequence (i.e. five points of the calibration curve plus 3 blanks and 5 samples) 2 controls—at concentrations of 1 μg/L and 5 μg/L—were analyzed. All the experiments were performed in triplicate.

Sorption experiments: Effect of contact time

Batch experiments were conducted to assess the time needed to reach equilibrium. A series of 250 mL capacity Pyrex glass bottles containing 100 mL of a 1 μg/L PAH mix were prepared. Then 0.3 g of cork was added to each bottle, which was then closed and wrapped with aluminum foil to prevent photodegradation. The solutions were mixed with a Vibromatic oscillating shaker at 700 oscillations/min. After shaking, 18 mL aqueous samples were collected at various contact times: 2, 30, 60, and 120 min and 24 h. (The first time, the sample was shaken by hand for 2 min). Three blanks were performed following

the same procedure as the samples (1) 100 mL of deionized water plus 1 μg/L PAHs (2) 0.3 g of cork plus 100 mL of deionized water; and (3) 100 mL of deionized water. A maximum loss of 10 % was observed for benz[a]anthracene at an initial concentration of 1 μg/L. However, one must be take into account that these data on the adsorption on the surface of the glass walls cannot be directly extrapolated to a cork/solution experiment due to the presence of cork. In order to control the losses of PAHs onto the glass walls in the presence of cork, after the equilibrium time the cork/solution in the bottle was emptied and refilled with 100 mL of deionized water which was vigorously shaken to rinse the glass walls of the flask. An 18 mL portion of water was collected and analyzed. The results indicate that, at an initial concentration of 1 μg/L, the PAH concentrations in solution were less than 1 %. The PAHs remaining in the solution (equilibrium concentrations) were analysed using the procedure described above. The pH at equilibrium time was measured using a pHmeter (Crison Instruments, Barcelona).

Models of sorption isotherms

Sorption experiments were conducted by the batch equilibrium technique. A small amount (0.3 g) of cork was weighted into each Pyrex glass bottle and placed with 100 mL of aqueous solution of a PAH mixture of varied concentration (1, 5, 10, 20, and 50 μg/L) for a contact time of 1 h. The bottles were closed and wrapped with aluminum foil, and the solutions were mixed with a Vibromatic oscillating shaker at 700 oscillations/min. After shaking, aqueous samples of 18 mL were collected and analyzed as described above. The amount of PAHs sorbed was considered to be the difference between the initial PAH concentrations and the equilibrium concentrations. To facilitate the estimation of the adsorption capacity, two commonly used empirical adsorption isotherm models, Freundlich and Langmuir, both of which correspond to heterogeneous and homogeneous adsorbent surfaces, respectively, were used in this study.

The Freundlich isotherm is described as:

$$q = K_F C_{eq}^{1/n} \quad (1)$$

where q is the adsorbed amount (μg/g); C_{eq} is the equilibrium concentration of adsorbate in solution after adsorption (μg/L); K_F is an indication of the adsorbent capacity ($[(\mu\text{g/g})/(\mu\text{g/L})]^{1/n}$); and $1/n$ is a measure of the nature and strength of the adsorption process or of the surface heterogeneity. To determine the constants n and K_F the linear form of Equation 1 was used. The plot of $\log q$ vs. $\log C_{eq}$ gives us the values of n and K_F from the slope and intercept, respectively.

The Langmuir isotherm can be written as:

$$q = \frac{K_L q_m C_{eq}}{1 + K_L C_{eq}} \quad (2)$$

where K_L is the Langmuir constant ($L/\mu\text{g}$) and q_m is the monolayer capacity ($\mu\text{g}/\text{g}$). The parameters K_L and q_m were obtained by plotting C_{eq}/q vs. C_{eq} .

To compare the validity of the isotherms, a normalized deviation (Δq) was calculated,

$$\Delta q = \sqrt{\frac{\sum_{i=1}^N (q - q_{\text{calc}})^2}{N - 1}} \quad (3)$$

where the subscript "calc" shows the calculated values and N the number of measurements.

The Langmuir isotherm assumes that maximum adsorption occurs when the surface is covered by the adsorbate, because the number of identical sites on the surface is finite. The Freundlich model is a generalization of the Langmuir model for heterogeneous surfaces. Its main limitation is that it does not take into account the saturation effect; the q value increases without limitation.

Desorption isotherms

After the experimentally predetermined desorption period (6 h), the aqueous phase was removed by vacuum filtration and a glass bottle was refilled with contaminated cork content and 100 mL of deionized water. It was then shaken and the solution was analyzed, following the same procedure used for the sorption isotherms. The volume of removed solution was replaced once. The desorption experiments were performed in triplicate. Desorption hysteresis was calculated as the ratio of Freundlich exponents for desorption ($1/n_{\text{des}}$) to sorption ($1/n_{\text{ad}}$) as:

$$H = \frac{1/n_{\text{des}}}{1/n_{\text{ad}}} \quad (4)$$

Lower hysteresis index values indicate that sorbate molecules experienced increased difficulty in desorbing from the sorbent matrix.^[16,17]

Results and discussion

Characterization of the cork

The elemental composition of the belly part of cork from Extremadura was: %C: 60.2; %H: 7.5; %N: 3.1; %O: 29.3, and % ash: 0.99. The sulfur was below the limit of detection (0.44 %).

The study of the chemical composition of the selected cork from Extremadura reveals that suberin is the main structural component of the cell wall (38.5 %), followed by lignin (31.6 %). The lignin biopolymer, mainly composed of phenylpropane units, exhibits a more aromatic nature than suberin, whose polyester structure is composed of long chain fatty acids, hydroxy fatty acids, and phenolic acids linked by ester groups.^[18]

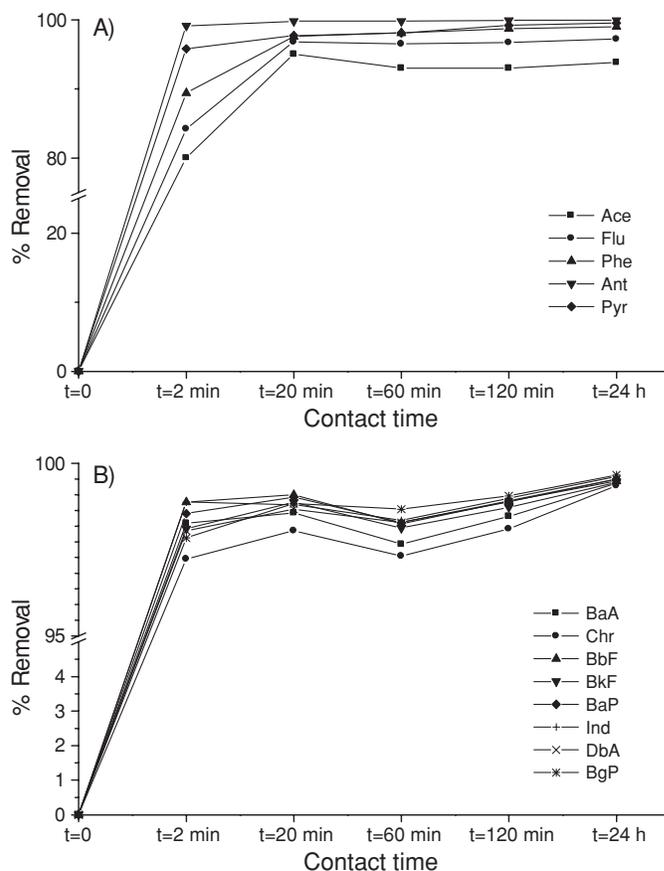


Fig. 1. Effect of contact time on adsorption of A) low molecular weight (LMW) PAHs: acenaphthene [Ace], fluorene [Flu], phenanthrene [Phe], anthracene [Ant], pyrene [Pyr]; and B) high molecular weight compounds (HMW) PAHs: benz(a)anthracene [BaA], chrysene [Chr], benzo(b)fluoranthene [BbF], benzo(k)fluoranthene [BkF], benzo(a)pyrene [BaP], indeno(1,2,3-cd)pyrene [Ind], dibenz(a,h)anthracene [DbA], benzo(ghi)perylene [BgP] on cork.

Polarity coefficient $(O+N)/C$, an important parameter to predict sorption and calculated from elemental analysis, has a value of 0.54, which is in range of some commercial lignins (0.33–0.94) reported in the literature^[19] and lower than untreated aspen wood (0.754).^[20]

The pH at point zero charge (pH_{pzc}) was found to be 3.5. This means that at solution pHs higher than pH_{pzc} , the cork surface is negatively charged, yet at pHs lower than pH_{pzc} , the solid surface is positively charged and could interact with negative species.

Effect of contact time

Figure 1 shows the adsorption data for the uptake of PAHs versus contact time. The results show that the sorption of the PAHs onto cork is very fast (just over 80 % of the adsorption occurred during the first two minutes of contact). At a contact time 20 min, the percentages of removal

exceeded 96 %. A contact time of 1 h was chosen to evaluate the subsequent adsorption isotherms of cork.

This equilibration time is significantly shorter when compared to the approximately 24 h it took to reach equilibrium between monoaromatic hydrocarbons and Douglas fir and Ponderosa pine,^[21] or the 298 h needed between PAHs and aspen wood fibers.^[22] Ratola et al.^[23] found that during the first 2 h around 80 % of lindane and heptachlor were removed by pine bark sieved to a grain size of 125–300 μm of grain size and Zeledón-Toruño et al.^[24] found that 70 % removal was tested after 2 h of contact of PAHs with leonardite sieved to a grain size of 0.09–0.2 mm. According to Barton,^[25] the equilibration time can be estimated from the radius of the wood aggregate and the wood diffusion coefficient. Thus, differences in equilibration times could be attributed to the size of cork particle, which were much smaller than in Mackay and Gschwend^[21] and Boving and Zhang.^[22]

Adsorption isotherms

The adsorption isotherms of all PAHs for cork were obtained. According to the classification of Giles et al.,^[26] the equilibrium sorption curves for LMW PAHs follow an L-type profile, close to C and almost linear (Fig. 2A). Phe, Ant, and Pyr exhibited almost the same isotherm profile. The C-type is characterized by a constant partitioning of the adsorbate in the adsorbent and is obtained for solutes that penetrate into the solid more readily than the solvent. C-type isotherms have also been reported in different pesticides,^[27,28] phenols^[29] and chlorophenols.^[30]

The convex initial curve of the adsorption isotherms of HMW PAHs indicate an L-type profile according to the classification of Giles^[26] (Fig. 2B), which means that, as adsorption sites are occupied, it becomes increasingly difficult for adsorbate molecules to find vacant sites. L-type isotherms were also observed in bifenthrin and α -cypermethrin on cork.^[9,10] All isotherms are far from the saturation point in the ranges of studied concentrations (1–50 $\mu\text{g/L}$).

Adsorption isotherms fit well with the Freundlich and Langmuir models, which predicted the adsorption of PAHs onto cork with high correlation coefficients (Table 1). However, the Freundlich model was demonstrated to be better than the Langmuir model. The Freundlich model states that only physisorption takes place, while the Langmuir model takes into account chemical interactions that occur between sorbent and sorbate. The fact that both models are verified could indicate that the interactions that take place between sorbent and sorbate are weak interactions (e.g., π - π interactions). Analyzing the data with the Freundlich equation also reflects the heterogeneity of the cork surface. The coefficients obtained from the Freundlich and Langmuir models are shown in Table 1.

The efficiency of the adsorption process can be predicted by the dimensionless equilibrium parameter R_L , which is

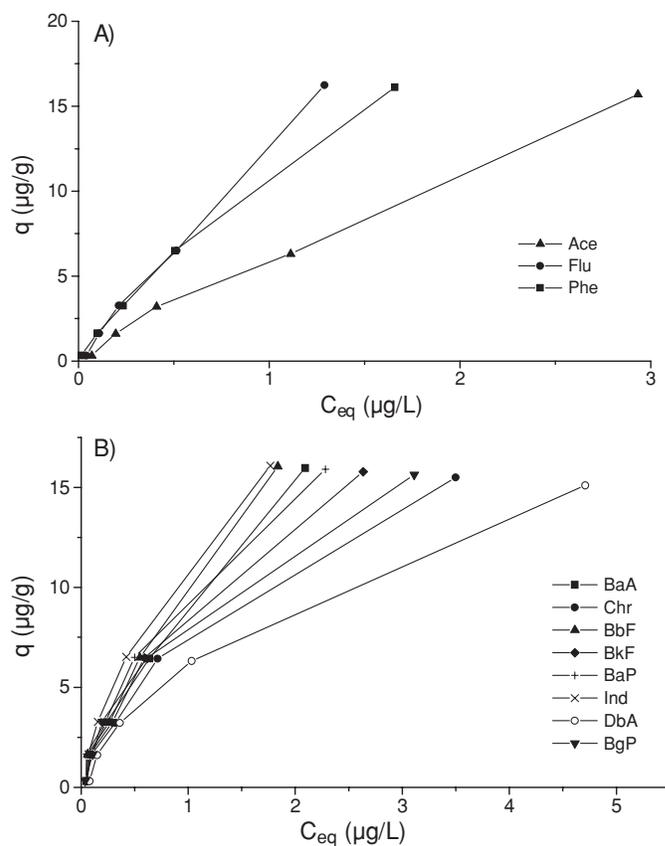


Fig. 2. Sorption isotherms of (A) low molecular weight (LMW) PAHs: acenaphthene [Ace], fluorene [Flu], phenanthrene [Phe], anthracene [Ant], pyrene [Pyr] and (B) high molecular weight (HMW) PAHs: benz(a)anthracene [BaA], chrysene [Chr], benzo(b)fluoranthene [BbF], benzo(k)fluoranthene [BkF], benzo(a)pyrene [BaP], indeno(1,2,3-cd)pyrene [Ind], dibenz(a,h)anthracene [DbA], benzo(ghi)perylene [BgP] on cork.

defined as $R_L = 1/(1 + K_L C_0)$ (where C_0 is the initial concentration of adsorbate, PAHs).^[31] An isotherm is considered to be unfavourable, linear, favourable or irreversible depending on the value of R_L . The condition for favourable adsorption is $0 < R_L < 1$; for unfavourable $R_L > 1$; irreversible $R_L = 0$; linear $R_L = 1$ (linear). As is shown in Table 1, R_L values have been found to be below 1, ranging from 0.2 to 0.6, and suggesting favorable adsorption of PAHs onto the investigated adsorbent. The Freundlich constants, K_F values, considered as a measure of the adsorption capacity, were higher for Pyr (18), Ant (13), and Phe (11), and the lowest value was for DbA (3). Pyr, Ant, and Phe are classified within the alternant aromatic compound category. The reason for the higher affinity with these compounds could be their aromaticity.

Given that aromaticity is the property that sustains induced ring electron current, this group composed of alternating bonding and non-bonding orbital, offers better conduction for electron movement, making the interactions between the aromatic rings stronger. In conjunction

Table 1. Sorption coefficients of PAHs on cork determined by the Freundlich and Langmuir equations.

PAHs ^a	Langmuir ^b					Freundlich ^c				
	$q_m \pm SD^d$ ($\mu\text{g g}^{-1}$)	$K_L \pm SD^d$ ($L \mu\text{g}^{-1}$)	r^e	Δq_L	R_{mL}	$K_F \pm SD^d$ ($[(\mu\text{g g}^{-1})/(\mu\text{g L}^{-1})]^{1/n}$)	$n \pm SD^d$	r^e	Δq_F	
Ace	46 ± 25	0.08 ± 0.1	0.85	6	0.6	4 ± 0.5	1.1 ± 0.05	1.00	2	
Flu	49 ± 26	2.08 ± 3	0.77	30	0.4	7 ± 2.3	1.1 ± 0.08	1.00	7	
Phe	32 ± 5	0.55 ± 0.1	0.85	10	0.4	11 ± 1.7	1.2 ± 0.030	1.00	6	
Ant	26 ± 18	0.93 ± 0.2	0.92	12	0.3	13 ± 2	1.3 ± 0.044	0.99	7	
Pyr	32 ± 4	0.96 ± 0.1	0.79	13	0.5	18 ± 3.4	1.2 ± 0.014	0.99	7	
BaA	26 ± 8	0.66 ± 0.4	0.91	9	0.3	8 ± 1, 4	1.4 ± 0.3	0.99	5	
Chr	23 ± 5	0.56 ± 0.3	0.96	8	0.4	6 ± 0.04	1.4 ± 0.2	0.99	4	
BbF	28 ± 12	0.79 ± 0.6	0.83	9	0.3	8 ± 0.05	1.6 ± 0.4	1.00	6	
BkF	21 ± 7	0.70 ± 0.3	0.96	9	0.3	6 ± 0.1	1.5 ± 0.14	0.99	4	
BaP	21 ± 5	1.03 ± 0.7	0.97	9	0.2	8 ± 0.2	1.5 ± 0.3	1.00	5	
Ind	20 ± 18	1.33 ± 0.2	0.94	11	0.2	9 ± 0.8	1.6 ± 0.13	1.00	6	
DbA	16 ± 3	0.49 ± 0.2	0.97	8	0.6	3 ± 1.2	1.6 ± 0.22	0.98	3	
BgP	23 ± 2	0.66 ± 0.2	0.93	10	0.6	7 ± 1.3	1.4 ± 0.13	0.99	5	

^aAbbreviations: acenaphthene [Ace], fluorene [Flu], phenanthrene [Phe], anthracene [Ant], pyrene [Pyr], benz(a)anthracene [BaA], chrysene [Chr], benzo(b)fluoranthene [BbF], benzo(k)fluoranthene [BkF], benzo(a)pyrene [BaP], indeno(1,2,3-cd)pyrene [Ind], dibenz(a,h)anthracene [DbA], benzo(ghi)perylene [BgP].

^bThe Langmuir parameters (q_m , K_L): K_L is the Langmuir constant; q_m is the monolayer capacity; Δq_L is the normalized deviation of the Langmuir equation; R_{mL} is the average of equilibrium parameters measured at the initial concentrations (C_0) of 1, 5, 10, 20, and 50 $\mu\text{g/L}$ where $R_L = 1/(1+K_L C_0)$.

^cThe Freundlich parameters (K_F , n): K_F is the Freundlich capacity coefficient; and n (dimensionless) describes the isotherm curvature; Δq_F is the normalized deviation of the Freundlich equation.

^dSD, standard deviations of triplicate experiments.

^er, correlation coefficients.

with their aromaticity, the smaller size of these molecules would facilitate their penetration into the binding sites and prevent the easy access of larger molecules (HMW PAHs), despite their higher hydrophobicity. This could also explain why DbA, an alternant PAH, has the lowest K_F . The isotherms obtained displayed n values from 1.1 to 1.6. These isotherms can be considered nonlinear because the n values were in general outside the $0.95 < n < 1.05$ range established by Pignatello et al.^[32] as suitable for an isotherm to be considered linear. Nonlinear isotherms have been also found for the sorption of several PAHs using aspen wood;^[22] using Spanish leonardite;^[24] using black, carbon-free biopolymers;^[19,32] using wooden chars of aspen wood;^[20] and using wood chars.^[33] Sorption spectroscopic studies show that the condensed (or glassy) domain is mainly attributed to aromatic moieties, which produce isotherm nonlinearity.^[34] Xing^[35] observed that there was a positive relationship between aromatic carbons and isotherm nonlinearity for several soil humic acids.

As a glassy biopolymer, lignin is highly aromatic.^[19] In our study, the high presence of lignin in cork (32 %) could be responsible for the nonlinear isotherms. Understanding the role of biopolymers of cork on sorption of PAHs has been investigated elsewhere.^[36] In the mentioned study it is indicated that suberin more than lignin plays a significant role on sorption of these toxic pollutants.

Table 2. Desorption coefficients of PAHs on cork determined by the Freundlich equation.

PAHs ^a	$K_{FD}^b \pm SD^c$ ($[(\mu\text{g g}^{-1})/(\mu\text{g L}^{-1})]^{1/n}$)	$n_d^b \pm SD^c$	r^d	H^e
Ace	10 ± 5	0.90 ± 0.31	1.0	1.2
Flu	33 ± 20	0.96 ± 0.23	1.0	1.2
Phe	54 ± 5	0.96 ± 0.02	1.0	1.3
Ant	101 ± 18	0.88 ± 0.07	1.0	1.5
Pyr	255 ± 12	0.95 ± 0.02	1.0	1.3
BaA	137 ± 21	1.00 ± 0.04	0.7	1.4
Chr	150 ± 43	0.84 ± 0.09	1.0	1.6
BbF	375 ± 32	0.83 ± 0.01	1.0	1.9
BkF	232 ± 23	0.88 ± 0.01	1.0	1.7
BaP	378 ± 27	0.87 ± 0.00	1.0	1.7
Ind	352 ± 20	1.2 ± 0.12	1.0	1.3
DbA	395 ± 30	1.2 ± 0.12	1.0	1.3
BgP	177 ± 8	1.3 ± 0.02	1.0	1.1

^aAbbreviations: acenaphthene [Ace], fluorene [Flu], phenanthrene [Phe], anthracene [Ant], pyrene [Pyr], benz(a)anthracene [BaA], chrysene [Chr], benzo(b)fluoranthene [BbF], benzo(k)fluoranthene [BkF], benzo(a)pyrene [BaP], indeno(1,2,3-cd)pyrene [Ind], dibenz(a,h)anthracene [DbA], benzo(ghi)perylene [BgP].

^b K_{FD} , n : Freundlich coefficients: K_{FD} is the desorption capacity; n_d (dimensionless) describes the curvature of the desorption isotherm.

^cSD, standard deviations of triplicate experiments.

^dr, correlation coefficients.

^eH, Hysteresis coefficients calculated as n/n_d .

Table 3. Estimation of cork used to reduce pollution in 1 L of water from 50 $\mu\text{g/L}$ to 0.1 $\mu\text{g/L}$ and comparison with other materials reported in literature.

<i>PAHs^a</i>	<i>Freundlich</i>		<i>Langmuir</i>				
	<i>Isotherm</i>	<i>Cork usage</i> (g L^{-1})	<i>Isotherm</i>	<i>Cork usage</i> (g L^{-1})	<i>Dowaidar et al.^[37]</i> <i>Activated carbon usage</i> (g L^{-1})	<i>Huang et al.^[20]</i> <i>Aspen wood fibers</i> <i>usage</i> (g L^{-1})	<i>Zeledón et al.^[24]</i> <i>Leonardite usage</i> (g L^{-1})
Ace	$q = 4C_{\text{eq}}^{1/1.1}$	114	$q = 0.080*46*C_{\text{eq}}/(1+0.080*C_{\text{eq}})$	105			
Flu	$q = 7C_{\text{eq}}^{1/1.1}$	54	$q = 2.08*59*C_{\text{eq}}/(1+2.08*C_{\text{eq}})$	8			218
Phe	$q = 11C_{\text{eq}}^{1/1.2}$	30	$q = 0.55*32*C_{\text{eq}}/(1+0.55*C_{\text{eq}})$	36		166	
Ant	$q = 8C_{\text{eq}}^{1/1.4}$	33	$q = 0.66*26*C_{\text{eq}}/(1+0.66*C_{\text{eq}})$	39			
Pyr	$q = 13C_{\text{eq}}^{1/1.3}$	24	$q = 0.93*26*C_{\text{eq}}/(1+0.93*C_{\text{eq}})$	30	10		
BaA	$q = 18C_{\text{eq}}^{1/1.2}$	19	$q = 0.96*32*C_{\text{eq}}/(1+0.963*C_{\text{eq}})$	24	5	52	159
Chr	$q = 6C_{\text{eq}}^{1/1.4}$	45	$q = 0.56*23*C_{\text{eq}}/(1+0.56*C_{\text{eq}})$	50			
BbF	$q = 8C_{\text{eq}}^{1/1.6}$	27	$q = 0.79*28*C_{\text{eq}}/(1+0.79*C_{\text{eq}})$	31			
BkF	$q = 6C_{\text{eq}}^{1/1.5}$	37	$q = 0.70*21*C_{\text{eq}}/(1+0.70*C_{\text{eq}})$	46			345
BaP	$q = 8C_{\text{eq}}^{1/1.5}$	29	$q = 1.03*21*C_{\text{eq}}/(1+1.03*C_{\text{eq}})$	34			360
Ind	$q = 9C_{\text{eq}}^{1/1.6}$	23	$q = 1.33*20*C_{\text{eq}}/(1+1.33*C_{\text{eq}})$	31			
DbA	$q = 3C_{\text{eq}}^{1/1.6}$	68	$q = 0.49*16*C_{\text{eq}}/(1+0.49*C_{\text{eq}})$	78			
BgP	$q = 7C_{\text{eq}}^{1/1.4}$	40	$q = 0.66*23*C_{\text{eq}}/(1+0.66*C_{\text{eq}})$	44			198

^aAbbreviations: acenaphthene [Ace], fluorene [Flu], phenanthrene [Phe], anthracene [Ant], pyrene [Pyr], benz(a)anthracene [BaA], chrysene [Chr], benzo(b)fluoranthene [BbF], benzo(k)fluoranthene [BkF], benzo(a)pyrene [BaP], indeno(1,2,3-cd)pyrene [Ind], dibenz(a,h)anthracene [DbA], benzo(ghi)perylene [BgP].

The mean final pH at the equilibrium time of the solutions was measured to be 6.4 ± 0.35 . With a pH_{pzc} of 3.5, this means that the cork surface is negatively charged. Because PAHs are molecular, the high efficiency obtained indicates that a negative charge would not significantly interfere with the adsorption process.

The assumption of linear isotherms was considered justified for LMW PAHs because of $1/n$ is close to 1. Correlations between the K_{F} adsorption constants, the values of K_{ow} of the PAHs and solubility, S , molar weight, MW , and F number were determined. F number is used as a descriptor of the molecular size of PAHs. The log forms of K_{ow} and K_{F} was used to decrease the uncertainty of the results. Only considering LMW PAHs, highly significant correlation coefficients (r) were obtained (Equation 5).

$$\log K_{\text{F}} = -1.38(\pm 0.5) + 0.522(\pm 0.11)\log K_{\text{ow}} \quad (5)$$

$$(r = -0.94, p < 0.01)$$

K_{F} and S were inversely correlated according to the following equation:

$$K_{\text{F}} = -3.17S(\pm 0.8) + 14.83(\pm 1.56) \quad (6)$$

$$(r = -0.92, p < 0.02)$$

As indicated in Equation 7, K_{F} increases with increasing F :

$$K_{\text{F}} = 8.16F(\pm 1.78) + 46.77(\pm 12.5) \quad (7)$$

$$(r = 0.94, p < 0.01)$$

Also highly significant ($r = 0.99$, $p < 0.001$) was the linear regression between K_{F} and MW . The corresponding equation was:

$$K_{\text{F}} = 0.29MW(\pm 0.02) - 41.6(\pm 4.96) \quad (8)$$

$$(r = 0.99, p < 0.001)$$

The sorption of HMW PAHs could be strongly affected by the greater π - π interactions in conjunction with the small size of certain PAHs (e.g., Pyr, Ant, Phe). This competition could explain the low correlation coefficients (r) obtained by the HMW PAHs.

Desorption isotherms

After the predetermined equilibrium desorption time of 6 h, Pyr, Ant, Phe, and Ace were released into the solution at the low percentages of 0.2 %, 0.5 %, 1.1 %, and 4.6 %, respectively. For the HMW PAHs, the percentages released into the solution were more insignificant (< 0.044 %). The desorption isotherms of PAHs on cork fit the Freundlich equation (Table 2). The desorption coefficients (K_{FD}), which represent the amount that remains sorbed after desorption for an equilibrium concentration equal to unity, are shown in Table 2, together with the hysteresis coefficient H .

K_{FD} values of the desorption of all PAHs were higher than K_{F} values, which is in accordance with the hysteresis

coefficients > 1 obtained. The low values of desorption coefficients and hysteresis indexes (Table 2) reflect that PAH desorption from the cork matrix was relatively difficult, and indicate high sorption irreversibility. A higher irreversibility was observed for the HMW PAHs with K_{FD} values ranging from 137 to 395, which is consistent with their hydrophobicity. All desorption isotherms showed hysteresis.

Estimation of cork usage

Both the Freundlich and the Langmuir isotherms provide useful information to estimate the feasibility of using cork to effectively remove PAHs from contaminated effluents (e.g., wastewater and stormwater).

Table 3 shows the amount of cork required to reduce pollution in 1 L of water from $50 \mu\text{g/L}$ to $0.1 \mu\text{g/L}$. As can be seen, the lower the q_{max} and K_{F} , the greater the amount of cork that was calculated. In comparison with other materials, it is shown that the amount of cork needed is between 7 and 15 times less than the amount of leonardite,^[24] between 3 and 5 times less than the amount of aspen wood fibers^[20] and between 2 and 4 times higher than the amount of activated carbon.^[37] Thus, the results indicate that raw cork could be a potential for the removal of PAHs from wastewater. In comparison with activated carbons or resins, the main advantage of waste cork is its economic feasibility (0.35 €/Kg).

Conclusions

The remainders of cork strips, an excess by-product of the cork industry, left over after the punching out of cork stoppers, sieved at a grain size of 0.25–0.42 mm grain size, were found to be highly effective for the removal of PAHs from water. The batch experiments showed that the sorption was very fast. After 2 min, more than 80 % of all PAHs were removed and at contact time 20 min, the percentage of the removal of PAHs exceeded 96 %. The desorption experiments indicate a greater irreversibility for all PAHs, and especially so in the case of HMW PAHs. The results obtained in this research indicate that the by-products of cork stopper production could be used as effective and economical biosorbents for the removal of PAHs in PAH-contaminated waters.

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