Pentachlorophenol removal from aqueous matrices by sorption with almond shell residues

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Abstract

Sorption with activated carbon has been the technique preferred for pentachlorophenol (PCP) removal from contaminated waters, but regeneration needs and high operation costs are supporting a renewed interest in the search for alternative sorbents. Among them, almond shell, an agricultural by-product, provides interesting economical advantages, once shells account for 50% (in mass) of the whole almond.

In this work, the capacity of almond shells to remove PCP from waters without previous activation was studied in batch conditions. While PCP analysis was performed solid-phase microextraction (SPME) followed by gas chromatography with electron capture detection (GC-ECD), mercury porosimetry and Fourier transform infrared spectroscopy (FTIR) provided a preliminary physical and chemical characterization of the sorbent.

Almond shells were essentially a macroporous material, with an average surface area of $12.9 \pm 2.8 \, \text{m}^2/\text{g}$. The efficiency of PCP removal was $93 \pm 14\%$, in 24 h, with an initial concentration of $100 \, \mu\text{g/l}$ PCP and $5 \, \mu\text{g}$ PCP/g shell. Isotherm data adjusted better to Freundlich equation, where K_F and $1/n$ were $0.075 \pm 0.081 \, \text{mg}^{1-1/n} \, \text{l}^{1/n}$ and 1.882 ± 0.289, respectively. Average desorption efficiency was 7%, indicating strong adsorption capacity. Results proved that almond shells may be an excellent low-cost alternative for PCP removal from contaminated waters.

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1. Introduction

Trace organic pollutants, which include organochlorine compounds (OCs), represent a major environmental concern, due to their toxicity, poor biodegradability and carcinogenic and recalcitrant properties [1]. Chlorophenols (CP) are a group of 19 OCs with substituted chlorines in the phenolic ring, formed by chlorination and hydrolysis of chlorobenzenes [1]. CPs have been used since 1920 in different applications, such as wood preservatives, pesticides, flame retardants, solvents and in the paper industry. The worldwide annual production of CPs has been estimated to be 200,000 t [2].

Pentachlorophenol (PCP) is one of the seven CPs (mono-CP; 2,4-DCP; 2,4,6-TCP; 2,4,5-TCP; 2,3,4,5-TetraCP; 2,3,4,6-TetraCP; PCP) with industrial production. PCP has a tendency to accumulate in sediments and in aquatic systems, and further-

more, has a slow biodegradation rate [3,4]. Consequently, it is prone to enter the food chain, inducing reproductive and dysfunctional troubles [1].

Maximum legal limits were established worldwide, aiming both the reduction of the utilization and the environmental contamination. United States Environmental Protection Agency (US-EPA) fixed 1 μg/l as the maximum limit for drinking water, whilst the European Union limited to 1–2 mg/l PCP the maximum discharge concentration in industrial effluents (PCP-Na producer plants).

Complex and expensive treatment systems are used to eliminate these contaminants from water systems, adsorption with activated carbon being one of the most efficient processes [5–9]. Although being the most used adsorbent, granular activated carbon (GAC) is expensive, not only for its market price, but also due to the cost the regeneration process [10].

Therefore, the search for alternative sorbents has increased in the last few years, with the purpose of finding cheaper and functionally acceptable materials for the removal of organic compounds and heavy metals from wastewaters [11,12]. Among

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several agricultural by-products, such as almond, hazelnut, coconut and nutshells [13], pinewood, bamboo [14], pine bark [15] and sugarcane bagasse [16] can be referred. Some of these materials were used to prepare activated carbons, once they produce high-purity chars of appropriate hardness and bulk density [17]. The hardness, the low ash and heteroatom content of materials as almond husk [18], apricot [6], rice husk [19], olive cake [13], grape seeds and peach stones, cherry stones and wood from fast growing trees [14], makes them good candidates as precursors for activated carbons. However, many need physical and/or chemical activation in order to produce granular activated carbons with appropriate surface areas [17]. For example, almond shells can develop carbons with surface areas over $1200 \, m^2/g$ [20].

Regarding the effective cost of production of these carbons, some research has been currently conducted aiming the direct utilization of these low-cost natural by-products. For instance, cork residues were used to adsorb pyrethroids from aqueous matrices [21] and pine bark was studied for its capacity to remove pentachlorophenol and other organochlorines from contaminated waters [22]. Brás et al. [15] showed that the PCP was strongly bonded to pine bark, achieving an average removal efficiency of 92%, with 0.1 mg PCP/g pine bark. The efficiency increased with the decreasing of PCP mass/sorbent mass ratio as well as with the diameter of the particles and the pH of the aqueous media [15].

In this work almond shell was tested for its capacity to remove pentachlorophenol from aqueous matrices. In 2000, Portugal had a national almond production of 27,000 t, of which about 90% was obtained in the northern region. Each almond has, on average, 50% of shell (in mass), which originates an extremely valuable by-product. In 2001, a production of 385,000 t of almonds in the United States generated 192,500 t of shells [23].

Few data are found in literature about the use of almond shells to remove organic compounds from contaminated waters. Ahmedna et al. [24] studied the application of carbons made from almond shells in drinking water treatments. This adsorbent was applied in "Envirofilters" (nutshell-based carbon system), which showed equal removal efficiency compared with conventional filters.

Considering that, to our knowledge, no research has yet been conducted on the direct employment of almond shells as sorbent for PCP removal, this work was intended as a feasibility study to evaluate the ability of this material to remove PCP from aqueous systems, without any kind of activation treatment.

2. Experimental

2.1. Chemicals and materials

Pentachlorophenol (PCP), 98% purity, was obtained from Supelco (Bellefonte, USA), isopropanol (99.8%) from Riedel-de Haën (Seelze, Germany) and sulphuric acid (95–97%) from Fluka (Buchs, Switzerland).

Almond shells were a by-product from agricultural production, obtained in the northern region of Portugal.

2.2. Standards preparation

A stock solution of 500 mg/l of PCP was prepared with isopropanol and from this a diluted stock solution of 5 mg/l of PCP in isopropanol was obtained. Calibration standards with concentrations of 1, 2, 5, 10, 15, 20, 25 μg/l of PCP were prepared from the latter solution in deionised water, where pH was adjusted to 2, with H_2SO_4 (1 ml of H_2SO_4 0.1 M in 25 ml of standards). The pH of the samples was adjusted in the same manner, prior to solid-phase microextraction (SPME).

2.3. Sorbent preparation

The almond shells were ground in a Retsch ZM 100 mill and sieved in Endecotts Test Sieves (London, England), Mesh No. 50 (297 μm) and Mesh No. 70 (210 μm). Shells with two different average diameters (81 and 275 μm) were used in the experiments. Each of the two granulometric portions were dried for 72 h at 50 °C and kept in dry conditions until the experiences.

2.4. Almond shell characterization

Under the preliminary physical and chemical characterizations, the distribution of the particle diameter was assessed by granulometry with a Coulter Counter-LS 230 Particle Size Analyser (Miami, USA). Other physical properties such as real density, pore volume, surface area and average pore diameter were obtained by mercury porosimetry, with a QuantaChrome-Pore Master (Boynton Beach, USA).

The surface chemical characterization was performed by Fourier transform infrared spectroscopy (FTIR) in a Bomem–MB Series, Arid-Zone™ (Qué., Canada).

2.5. PCP analysis by SPME/GC-ECD

Samples were pre-concentrated by solid-phase microextraction, prior to gas chromatography with electron capture detection (GC-ECD).

An 85 μm polyacrylate fiber Cat. No. PN 57304 and an SPME fiber holder Cat. No. PN 57330-U from Supelco (Bellefonte, USA) were used, as well as a PC-240 Corning hot plate/stirrer (Corning, USA), with a thermometer and a water bath to control the stirring (750 rpm) and the temperature (40 °C).

Optimal conditions for SPME were adapted from Ribeiro et al. [25] and included: fiber immersion sampling at 40 °C for 15 min, sample volume of 4 ml and sample pH adjusted to 2.

Chromatographic analyses were performed using a Finnigan 9001 GC gas chromatograph (Austin, USA) with split-splitless injection port and ^{63}Ni Ion Trap Detector. The column was a DB-5MS (30 m × 0.32 mm × 0.25 μm) from J&W Scientific (Folsom, USA).

The detector temperature was set to 350 °C. Carrier and make-up gas was nitrogen 5.0 (99.999%) from Air Liquide (Maia, Portugal) at a flow rate of 3 and 15 ml/min, respectively.

The fiber was previously conditioned in the GC injector for 2 h at 300 °C. Whenever needed, this procedure was repeated for fiber cleanup. Before sample extraction, blank runs (4 min

in the GC injector) were performed to assess possible fiber contamination or carryover.

The initial oven temperature was 130 °C, held for 1 min, and then increased to 280 °C, at 15 °C/min and kept for 1 min. After the extraction, the fiber was introduced in the injector at 280 °C for 4 min (desorption time) with the split valve closed. The total run time was 12 min.

CPs were quantified by peak area using the external standard method. Calibration curves were obtained with standards extracted in the same conditions as samples.

2.6. Batch sorption studies

2.6.1. Determination of equilibrium time

The determination of the equilibrium time was reached through batch experiments, with a PCP concentration of 1 mg/l and variable sorbent mass (from 1 g to 100 mg). Almond shell with two particle sizes (Shell 1 and Shell 2, with averages diameters of 81 and 275 μm, respectively) were studied. Assays were conducted in duplicate, in 250 ml Erlenmeyer beakers with 100 ml of PCP solutions which were placed in a Gallenkamp orbital incubator (Leicester, UK) at constant temperature (30 °C) and rotation (120 rpm). Samples were taken after 15, 30, 60 min, 4, 8, 24, 48 and 72 h, filtered with Whatman 40 ashless filter paper and kept at 4 °C until quantification.

2.6.2. Determination of adsorption isotherms

Adsorption isotherms were determined after equilibrium time was reached (24 h). The assays were conducted in duplicate, for Shell 1, with 100 ml of PCP solutions. The PCP concentration used in these experiments was 100 μg/l, with variable sorbent mass (from 10 mg to 10 g), therefore allowing PCP/sorbent mass ratios from 0.001 to 1.

2.6.3. Desorption studies

Following the adsorption assays (in duplicate) the shells were removed and immersed in 100 ml of deionised water and desorption evaluated after 24 h of contact time at 30 °C.

2.7. Safety procedures and hazardous waste disposal

PCP is dangerous chemical (risk phrases 24-25-26-36/38-40-50/53) and must be handled with precaution, assuring the necessary ventilation and body protection (safety phrases 22-36/37-45-60/61). All material in contact with PCP was washed with acetone and the residues placed in a container labelled as 'danger-organic compounds—chlorophenols' to be further sent to external treatment. The isopropanolic solutions were purified by fractionated distillation and reused on certain less accurate applications. The residue from the distillation (containing PCP) was placed in a proper container, as mentioned above.

3. Results and discussion

All results were based on the analysis of PCP by SPME/GC-ECD. In order to provide a better comprehension of the significant differences that can be endorsed to sorption mecha-

nisms rather than to the uncertainty of the analytical result, the method was submitted to a validation process, from which main parameters are presented. A preliminary physical and chemical characterization of the sorbent was performed afterwards, to help understanding results obtained from sorption assays and to allow the comparison of performances with other sorbents, such as activated carbon. Finally, sorption studies are presented and discussed.

3.1. Parameters of validation of the analytical methodology

The analytical methodology employed provides a simple and rapid analysis, once the extraction step and the chromatographic determination are completed in 15 min. The detection limit obtained by the calibration curve according to Miller and Miller [26] was 0.96 μg/l. Precision was evaluated either by repeatability or intermediate precision assays and their average coefficients of variation (CV%) for 11 determinations of 15 μg/l standards were 10 and 19%, respectively. Repeatability of standards of lower concentration was worse, as expected, although never exceeding 20%.

3.2. Physical and chemical characterization of almond shells

The first step of this work was a preliminary characterization of the sorbent (almond shell) in order to understand the process of sorption and the way that they interact with the surrounding medium. Two samples of sorbent – Shell 1 and Shell 2 – were used in the experiments. Granulometric analysis showed that Shell 1 had particle diameters between 2 and 400 μm, with an average diameter of 81 μm, and those of Shell 2 were between 6 and 600 μm, with an average diameter 275 μm. Comparing the size of the sorbent particles with those of activated carbon [5], it is estimated that particles from Shell 1 are between the average diameter of PAC < 0.074 mm and that of GAC > 0.1 mm. Particles from Shell 2 are similar to GAC.

Other physical properties of the sorbent are expressed in Table 1, where it can be seen that the surface area is extremely lower than those exhibited by GAC (700–1300 m²/g) or PAC (800–1800 m²/g), as common in this kind of natural sorbents. The range of pore diameter allows the ranking of the surface pores as macropores (>25 nm) and mesopores (>1 nm and <25 nm).

Table 1
Some physical properties of the almond shell groups (1 and 2) used in this work

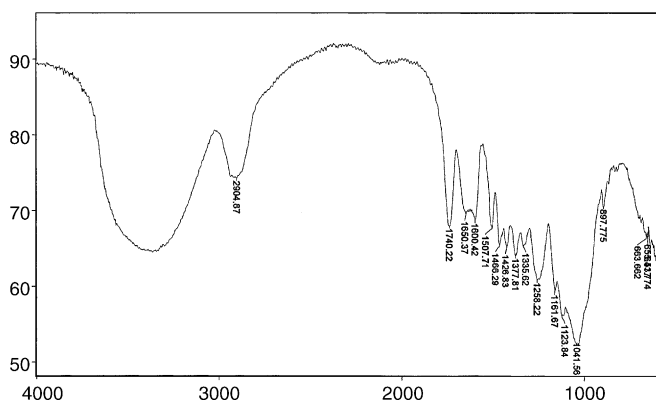| Properties	Shell 1	Shell 2
Real density (g/cm³)	1.42	1.42
Apparent density (g/cm³)	1.07	1.20
Total surface area (m²/g)	10.95	14.84
Total interparticle porosity (%)	9.56	3.26
Total intraparticle porosity (%)	12.56	13.16
Total porosity (%)	22.12	16.42
Pore diameter range (μm)	10.631–0.004	10.469–0.004
Pore diameter (mean) (μm)	7.5×10^{-2}	3.8×10^{-2}

Fig. 1. Spectrum of FTIR analysis from almond shells (with KBr at 98%, at 21 scans/min, with a resolution of 4 cm^{-1}).

Fig. 2. Influence of the PCP/shell mass ratio and of the particle diameter of almond shells in the PCP removal efficiency.

Chemical characterization of the sorbent surface was performed by FTIR analysis. The spectrum (Fig. 1) was obtained with KBr at 98%, at 21 scans/min, with a resolution of 4 cm^{-1} and expressed in transmittance in the 4000−450 cm^{-1} range. The more important absorption bands at frequency values that justify the existence of the corresponding functional groups (bonds) were: O−H (3440 cm^{-1}; stretch vibration), C−H aromatic and aliphatic (2904 cm^{-1}; stretch vibration), C=O (1740 and 1650 cm^{-1}; stretch vibration), C=C aromatic (1600 and 1507 cm^{-1}; stretch vibration), C−H (1466 and 1377 cm^{-1}; deformation vibration) and C−O (1161 cm^{-1}; stretch vibration). The presence of hemicelluloses and cellulose is probably responsible for the appearance of these bonds. In fact, data from literature refer to those compounds and lignin as the main constituents of almond shells [27]. The composition (% of mass weight) of almond shells was: hemicelluloses 28.9%, cellulose 50.7%, lignin 20.4% [27]. The percentage of mass weight for fixed carbon is on average 22.7%, for volatile matter is 7.4% and for extractive matter (alcohol/benzene (1/1, v/v) extractives) is 2.5%.

The presence of O−H and C=C aromatic bonds may induce that PCP molecules can establish, respectively, hydrogen bonds and hydrophobic interactions with the sorbent surface.

In this study, pH lower than 2 has been set for all solutions to insure the presence of the protonated form of PCP and therefore increase the interaction (possibly by hydrogen bonding) with the hydroxyl groups of the cellulose and hemicellulose of almond shells. The dependence of K_{ow} with pH is described in literature [28]. At pH of 2, where PCP deprotonation is avoided, log K_{ow} is between 5.04 [29] and 5.24 [30]. When pH is slightly above the pK_a, the neutral species are dominant in the octanol phase and the anionic species become dominant in the aqueous phase, which makes the distribution ratio pH-dependent [28,31]. Brás et al. [15] obtained better results for the adsorption of PCP in pine bark with low pH (pH 2). The pine bark consisted mainly on hemicelluloses, cellulose and lignin [15], which are also part of the constitution of the almond shells. Aksu and Yener [32] studied the adsorption of *o*-chlorophenol and *p*-chlorophenol at different values of pH in fly ash, in dried activated slurry and in activated carbon and concluded that the an increase to the initial pH of over 1.0 led to a reduction on the sorbent capacity of the
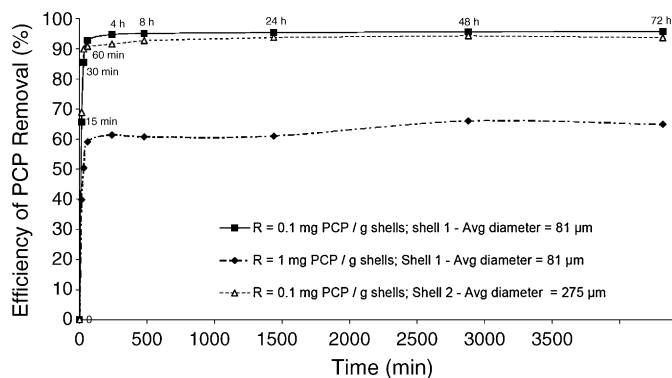
mono-chlorophenol for each sorbent. Mollah and Robinson [8] studied PCP adsorption in GAC, using batch assays at 30 °C and concluded that the amount of PCP adsorbed at equilibrium was a function of the pH of the solution, being the maximum amount of PCP adsorbed at pH 6 and the minimum at pH 11.

3.3. Sorption studies

In order to obtain the adsorption isotherms, batch assays were conducted previously, to evaluate the necessary contact time to achieve equilibrium. Figs. 2 and 3 present the results from those experiments, obtained for the two sizes of the sorbent tested in this work (Shell 1 and Shell 2). Fig. 2 expresses both the variation of efficiency of the sorption with the contact time for two of PCP/sorbent mass ratios and the influence of the particles diameter in the efficiency of PCP removal from aqueous solutions.

Although the variation of the PCP removal efficiency after 4 h of contact time can be considered negligible, an equilibrium time of 24 h was set for subsequent experiments. For the assays with 0.1 mg PCP/g shell, an average removal efficiency of 96% was obtained after 24 h, but 93% was already verified after 1 h. When a more concentrated PCP/sorbent ratio was used (equivalent to 1 mg PCP/g shell), the removal achieved values of approximately 65%. It can be noticed that the particles with higher diam-
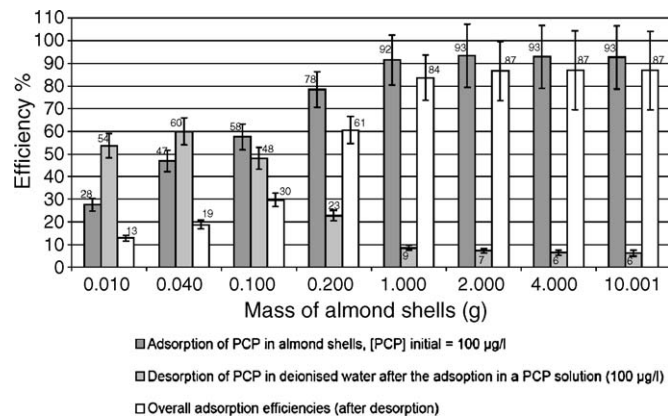

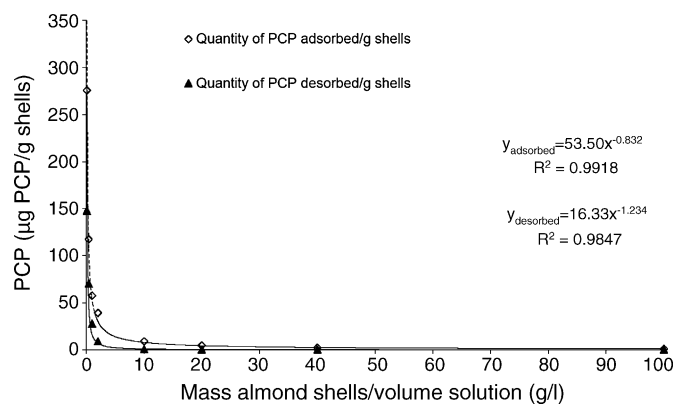Fig. 3. Efficiencies of PCP adsorption and desorption in almond shells.

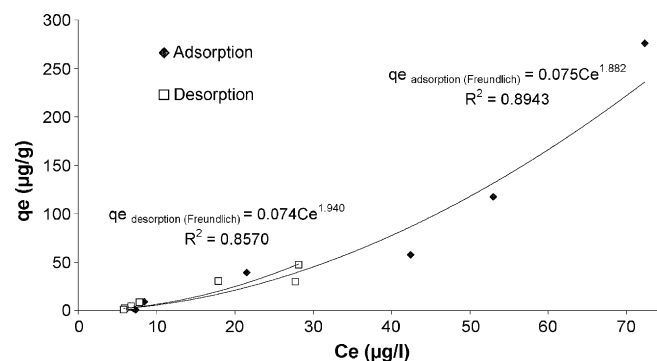Fig. 4. Adsorption and desorption of PCP as a function of the amount of almond shells in solution.

Fig. 5. PCP sorption and desorption data for almond shells (q_e and C_e are the solute concentration in shells and in solution, respectively).

eter have a poorer sorption capacity towards PCP, as expected if the available surface area for adsorption is a dominant factor of the sorption process. Being sorption a surface phenomenon and therefore the sorption capacity of materials limited by the surface area available, the variation of particle diameter has a strong impact for high pore size sorbents. In the case of almond shells (mainly macroporous), results obtained agree with that conclusion. If micropores existed (as in activated carbon) it would not be expected that the particle diameter influenced the sorption equilibrium.

Adsorption and desorption processes can be analysed from the results presented in Fig. 3. While adsorption efficiency increases with the increase of the mass of almond shells or with the decrease of the PCP/shell mass ratio, the inverse trend seems to occur for desorption, meaning probably that PCP is strongly adsorbed in the surface. When almond shells are saturated with PCP, it is desorbed in a higher extent than when it is less saturated. The adsorption and desorption behaviour, referred as the PCP concentration per mass of almond shell as a function of the quantity of almonds shells in the solution with PCP are depicted in Fig. 4. From these data, it was possible to establish a correlation between the quantity of shells in solution and the amount of PCP adsorbed, with good coefficients of correlation ($R^2 = 0.9918$ for adsorption and $R^2 = 0.9847$ for desorption).

Although other isotherm models are mentioned in literature, the most commonly applied to describe sorption in wastewater systems are the linear equation (Eq. (1)), the Langmuir equation (Eq. (2)) and the Freundlich equation (Eq. (3)):

$$q_e = K_d C_e \tag{1}$$

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \tag{2}$$

$$q_e = K_F C_e^{\frac{1}{n}} \tag{3}$$

In these equations, q_e and C_e are the solute concentration in shells and in solution, respectively (Fig. 5). K_d is defined as the distribution coefficient in the linear isotherm. In the Langmuir equation, Q^0 is considered the maximum sorption capacity related to the total cover of the surface and b is associated to sorption energy. From the Freundlich model, K_F represents the sorption capacity and $1/n$ is related to the energy distribution of the sorption sites.

The Langmuir isotherm was not applicable. This may indicate that monolayer adsorption, assumed in this model, is not valid for these specific experiments. The results obtained for linear and Freundlich approaches are presented in Table 2. The best correlations were obtained for the Freundlich equation, with $R^2 = 0.8943$ for the adsorption and $R^2 = 0.8570$ for the desorption.

For the commonly used activated carbon, Mollah and Robinson [8] concluded that PCP adsorbed strongly to GAC (a PCP solution with the concentration of 1 mg/l attained an equilibrium load of 157 mg PCP/g GAC). Furthermore, Jung et al. [9] obtained adsorption isotherms with activated carbon for five chlorophenols (2-CP, 4-CP, 2,4-DCP, 2,4,6-TCP and PCP) and verified that Freundlich isotherm model was the best approach to correlate results.

Wu et al. [33] studied the adsorption of PCP in waste materials (such as sewage sludge, municipal wastes, brick and mortar debris, harbour sludge, sand fills, wastes from coking plants and coal mines) and achieved a good correlation for PCP with

Table 2
Parameters obtained for the linear and Freundlich model isotherms

	Linear		Freundlich		
	K_d (l/g)	R^2	K_F (mg$^{1-1/n}$ l$^{1/n}$)	$1/n$	R^2
Adsorption	2.811 ± 0.653	0.8144	0.075 ± 0.081	1.882 ± 0.289	0.8943
Desorption[a]	1.364 ± 0.264	0.8524	0.074 ± 0.076	1.940 ± 0.354	0.8570

[a] Values estimated considering the results of seven samples in duplicates.

the Freundlich isotherm. They also concluded that the method proposed for estimating the sorption of PCP in natural soils based on their organic carbon is equally valuable for this kind of wastes.

Previously published data on PCP sorption using different materials (such as pine bark, suspended biomass into soils and quitosan) state that the linear and the Freundlich isotherm models are those that seem to describe better the process. Jacobsen et al. [34] obtained a linear isotherm for PCP sorption in suspended microbial biomass, with K_d of 3.27 l/g. Jianlong et al. [35], describing the PCP sorption to activated sludge, obtained a K_F from the Freundlich approach close to 34.12. Published data report in general values of K_F from 0.048 to 34.12, and $1/n$ from 2.144 to 0.74 [35,36]. Results obtained in this work fall within the given range of results.

4. Conclusions

The main conclusion of the present work is that almond shells may be a good natural sorbent for PCP, reaching efficiencies of removal high enough to be considered an excellent alternative to activated carbon or other synthetic materials.

The particles of the almond shells were characterised and found to be mainly comprised by macropores and mesopores. The average surface area is lower than those commonly found in activated carbons but, on the other hand, the presence of several functional groups may confer to almond shells the chemical affinity to adsorb PCP strongly to their surface.

Equilibrium time was set in 24 h for batch assays and the adsorption of PCP was higher for particles with smaller diameter. The efficiency of PCP removal was $93 \pm 14\%$ (24 h), with an initial concentration of 100 µg/l PCP and 5 µg PCP/g shell. The desorption trend was opposite to that of the adsorption for the different PCP/shell mass ratios.

Freundlich isotherm was the best approach for sorption equilibrium data correlation.

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