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A preliminary feasibility study for pentachlorophenol column sorption by almond shell residues

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Abstract

Almond shells, by-products from the northern region of Portugal, were used for the adsorption of pentachlorophenol (PCP) from aqueous solutions. The use of almond shells, as agricultural waste products, may present several economical advantages, considering that 50% (in mass) of almonds are constituted by shells. No research has been conducted concerning their use as sorbent without previous activation treatment.

Besides performing column adsorption experiments, this study also focus on the structural and chemical characterization of the almond shells, as a way to understand the nature of sorption. Scanning electron microscopy (SEM), mercury porosimetry and Fourier transform infrared spectroscopy (FTIR) were techniques used, in addition to chemical analysis. PCP determinations in aqueous media were performed by gas chromatography with electron capture detector (GC/ECD) after sample extraction and clean-up using solid-phase microextraction (SPME).

Results proved that almond shells have a high affinity for PCP sorption, with removal efficiencies higher than 99.98%, where column experiments made PCP concentration decrease from 10 mg/L to values lower than the legal limit (1 μg/L). Column experiments with 5 and 10 g of sorbent (respectively 2.9 and 5.8 cm bed height), were passed with acidified PCP solutions (pH 2) at a flow rate of 4 mL/min, until saturation was achieved after 28 and 41 h. An adsorption capacity of 6322 mg/L was estimated using BDST model, which proved that the almond shells confirm to be an encouraging sorbent for cheap water remediation solutions.

Keywords: Almond shell; Adsorption; Pentachlorophenol (PCP); Column; Water treatment

1. Introduction

Trace organic pollutants, as pentachlorophenol (PCP), represent a major concern in water treatment systems. Chlorophenols are synthetic organic compounds, highly toxic, poorly biodegradable with carcinogenic and recalcitrant properties, obtained on large scales by phenol chlorination or chlorobenzenes hydrolysis. US-EPA established 1 μg/L as the maximum limit for drinking water, whilst the minimum objective of environmental quality for various types of water is 2 μg/L, accordingly to EU legislation.

Complex and expensive treatment systems have been developed to solve this type of pollution. Adsorption is one of the most efficient process of pollutants separation and water purification. It has been useful for treatments of industrial effluents and water treatment plants, like for example, the removal of organic compounds and heavy metals [1]. The most used adsorbent is the granulated activated carbon (GAC). Mollah and Robison [2] studied the PCP adsorption in granular activated carbon and made batch experiments at 30 °C with several PCP concentrations. Maximum adsorbed ratio of 157 mg of PCP per gram of GAC was achieved, when the initial PCP concentration was 1 mg/L. GAC has the disadvantage of becoming an expensive process, not only by its price, but also by the cost of the adsorbent regeneration process.

In the last years, the investigation towards new materials increased, with the purpose of finding new economically and functionally acceptable sorbents for organic compounds and heavy metals removal from waters. Low-cost and abundant materials are being tested as sorbents, with or without previous physical or chemical activation.

Several agricultural by-products, such as almond shells [3], hazelnut, coconut and nutshells [4], pine bark [5,6] and sugarcane bagasse [7] have been used for this purpose. Some of these

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materials were used directly as sorbents [3,8], but others were used to prepare activated carbons, as they produce high-purity chars of appropriate hardness and bulk density.

Some studies (batch) were made for the PCP sorption by other natural adsorbents, without previous activation treatment (physical and/or chemical). Brás et al. [6,9] evaluated the capacity of the pine bark to remove PCP from aqueous solutions, achieving an average removal efficiency of 92%, with 0.1 mg of PCP adsorbed per gram of pine bark. This ratio increases with the decrease of the PCP/bark mass ratio, and therefore if 10 mg PCP/g of bark was used, the efficiency was 66%. It was also found, as expected, that the PCP sorption in the pine bark increases with the decrease of the particles diameter and with the pH decrease.

The study of the PCP sorption in almond shells, without previous activation treatment has other special feature, because of the economical importance provided by the use of agricultural by-products. In 2002, United States produced 386 million kg of almonds (Agricultural Statistics, 2002) and the processing of this product generated 193 million kg of almond shells [10].

The data found in literature about the utilization of almond shells without activation treatment to remove organic compounds from contaminated waters is scarce, and none of which applied almond shells in column flow processes. Although the continuous process has special importance at industrial scale, many investigators used batch experiments to determine kinetic and adsorption isotherm parameters, in order to try modelling the process, for future scale-up application to the treatment of residual water. Brás et al. [6] 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 [9], which are also part of the constitution of the almond shells. Estevinho et al. [3] performed batch experiments with almond shells, and with a PCP aqueous solution of 1 mg/L and pH of 2, obtained removal efficiencies over 96% for a ratio of 0.1 mg PCP per gram of shell. However, only the column experiences give a real vision about the practice of this technology, as isotherms cannot predict chemical and biological changes occurring in the adsorbent. Furthermore, results obtained by column experiences can explain the dynamics capacities, allowing extrapolating data for the projection of processes at industrial scale [11,12].

The main objective of this work is to study, by means of columns experiments, the capability of PCP removal from aqueous solutions, using almond shells, without any kind of activation treatment.

2. Experimental

2.1. Chemicals and materials

Pentachlorophenol, 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 obtained as a by-product from agricultural production, 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 the same solvent was obtained. Calibration standards with concentrations of 1, 2, 5, 10, 15, 20, and 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).

The feed solution used in column experiments was prepared daily from the PCP stock solution of 500 mg/L, by dilution with deionised water until 10 mg/L.

2.3. Sorbent preparation

The almond shells were grounded 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 average diameters of 82 μm were used in the experiments. The almond shells were dried for 72 h at 50 °C and kept dried until the column experiments.

2.4. Almond shell characterization

Preliminary physical and chemical characterization of the almond shells was performed. The distribution of the particle diameter was assessed by granulometry with a Coulter Counter, LS 230 Particle Size Analyzer (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^{TM} (Quebec, Canada).

The surface structure of the almond shells was observed by scanning electron microscopy (SEM) using a JEOL, JSM-6301 F Scanning Microscope, after sample preparation by pulverization of gold in a Jeol JFC 100 apparatus at Centro de Materiais da Universidade do Porto (CEMUP).

2.5. PCP analysis by SPME/GC-ECD

Samples were extracted and 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 (USA) hot plate/stirrer, with a thermometer and a water-bath, to control the stirring rate (750 rpm) and the temperature (40 °C).

Optimal conditions for SPME were adapted from Ribeiro et al. [13] and included: fiber immersion at 40 °C for 15 min, sample volume of 4 mL and 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 clean-up. Before sample extraction, blank runs (4 min in the GC injector) were performed to assess possible fibre 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.

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

2.6. *Continuous flow experiments*

These experiments were performed with a fixed bed, using glass columns (2 cm diameter and 28 cm height) filled with 10 and 5 g of almond shells. The columns were previously washed with 250 mL of deionised water. For the continuous flow experiments the operation conditions were: temperature of 20 °C, pH of 2 and initial concentration of the PCP solution of 10 mg/L. The solutions of PCP were passed through the column at fixed flow rates (3.1, 4.2 and 6.6 mL/min), in order to determine the optimal flow rate, which was fixed at 4 mL/min. The initial PCP solution was held in a 4 L flask and introduced in the column in an upflow configuration, via compressed air (Fig. 1). In these experiments the total volumes of PCP solution passing through the column with 10 and 5 g of sorbent were 11520 and 6720 mL, respectively. After sorption, a desorption assay was included, using 1 g of shells in contact with deionised water during 24 h and at 20 °C and 120 rpm.

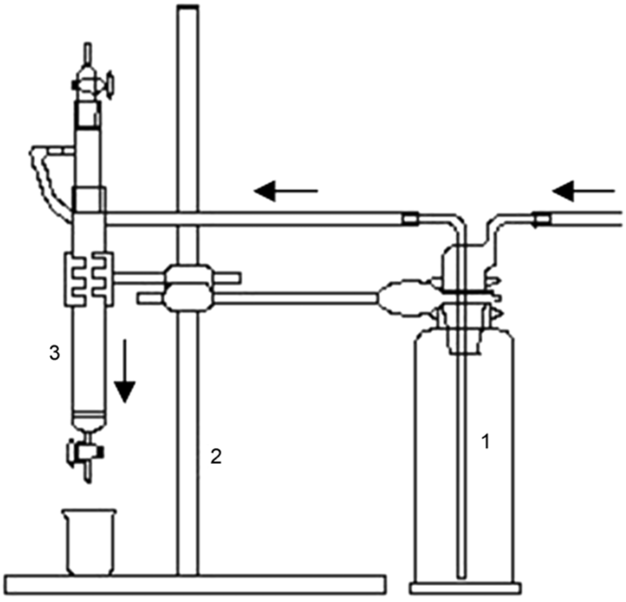

Fig. 1. Schematic diagram of almond shells adsorption column (1 – flask containing PCP solution; 2 – universal support; 3 – column for adsorption studies).

2.7. *Safety procedures and hazardous waste disposal*

Attending to pentachlorophenol risk and safety information *R 24-25-26-36/38-40-50/53 and S 22-36/37-45-60/61*, they must be handled with precaution, assuring the necessary ventilation and wearing gloves. All the material in contact with PCP was washed with acetone and the residues placed in a container labelled as ‘Danger Organic Compounds—Chlorophenols’. The isopropanol alcohol solutions could be purified by fractional distillation and reused on certain accurateness applications. The residues that remain from the distillation (pentachlorophenol) are placed in a container for chlorophenols as mentioned above.

3. Results and discussion

A preliminary physical and chemical characterization of the sorbent was performed, to help understand results obtained from sorption assays and to allow the comparison of performances with other sorbents, such as activated carbon. In order to provide a better comprehension of the significant differences that can be endorsed to sorption mechanisms rather than to the uncertainty of the analytical result, the analytical method was submitted to a validation process, whose main parameters are provided. Finally, column sorption studies are presented and discussed.

3.1. *Physical and chemical characterization of almond shells*

The characterization of the sorbent – almond shell – included the evaluation of textural characteristics, as granulometric analysis. Shells had particle diameters between 2 and 400 μm, with an average diameter of 82 μm. Comparing the size of the sorbent particles with those of activated carbon [14], it is estimated that particles from shells are between the average diameter of powdered activated carbon (PAC, <0.074 mm) and that of GAC (>0.1 mm).

Other physical properties of the sorbent are expressed in Table 1 where it can be seen that the surface area is extremely lower than that exhibited by GAC (700–1300 m^2/g) or PAC (800–1800 m^2/g), as it is common in this kind of natural sor-

Table 1
Almond shells properties

Properties	Values
Real density (g/cm^3)	1.42
Apparent density (g/cm^3)	1.07
Total surface area (m^2/g)	10.95
Total intruded volume (cm^3/g)	0.21
Total interparticle porosity (%)	9.56
Total intraparticle porosity (%)	12.56
Total porosity (%)	22.11
Pore diameter range (μm)	10.631–0.004
Pore diameter (mean) (μm)	0.075

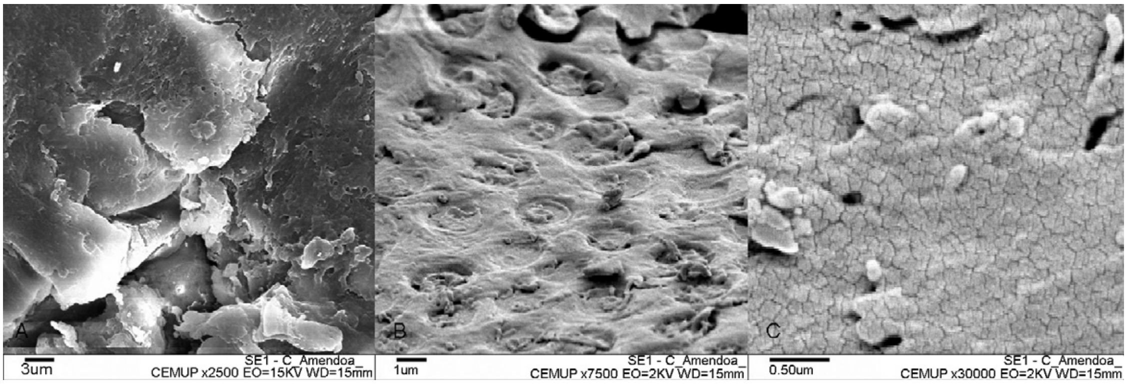

Fig. 2. SEM images of almond shells: (A) amplified 2500 times, beam intensity (E0) = 15 kV, distance between the sample and the lens (WD) = 15 mm; (B) amplified 7500 times, E0 = 2 kV, WD = 15 mm; (C) amplified 30,000 times, E0 = 2 kV, WD = 15 mm.

bents. The range of pore diameter allows the ranking of the surface pores as macropores (>25 nm) and mesopores (>1 and <25 nm).

The scanning electron microscope images from the shells are shown in Fig. 2. It was possible to identify pores, mainly macropores, in the surface of the shells. The shells exhibit rounded surfaces and with the beam of electrons the surface is easily destroyed, which could be associated to the presence of oil in the shells. Probably these oils come from the almonds to the shells by transport phenomena.

Chemical characterization of the sorbent surface was performed by FTIR analysis. The spectrum (Fig. 3) was obtained with KBr at 98%, at 21 scans/min, with a resolution of 4 $\mathrm{cm^{-1}}$ and expressed in transmittance in the 4000–450 $\mathrm{cm^{-1}}$ range. The more important absorption bands at frequency values that justify the existence of the corresponding functional groups were: O–H (3440 $\mathrm{cm^{-1}}$; stretch vibration), C–H aromatic and aliphatic (2904 $\mathrm{cm^{-1}}$; stretch vibration), C=O (1740 and 1650 $\mathrm{cm^{-1}}$; stretch vibration), C=C aromatic (1600 and 1507 $\mathrm{cm^{-1}}$; stretch vibration), C–H (1466 and 1377 $\mathrm{cm^{-1}}$; deformation vibration) and C–O (1161 $\mathrm{cm^{-1}}$; stretch vibration). The presence of hemicelluloses and cellulose is probably responsible for the appearance of these bonds. In fact, data from literature refers those compounds and lignin as the main constituents of almond shells [15]. Data from literature refers that composition (m/m%) of almond shells is on average: hemicelluloses 28.9%, cellulose 50.7%, and lignin 20.4% [15]. 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%.

Although assessing the nature of sorption exclusively by the presence of specific functional groups is rather complex, it may be supposed that the O–H and C=C aromatic bonds may induce hydrogen bonds and hydrophobic interactions between PCP molecules and the sorbent surface.

In this study, pH lower than 2 has been set for all solutions to assure the presence of the protonated form of PCP and therefore increases 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 in Refs. [16,17]. At pH of 2, where PCP deprotonation is avoided, log K_{ow} is between 5.04 [18] and 5.24 [19]. 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

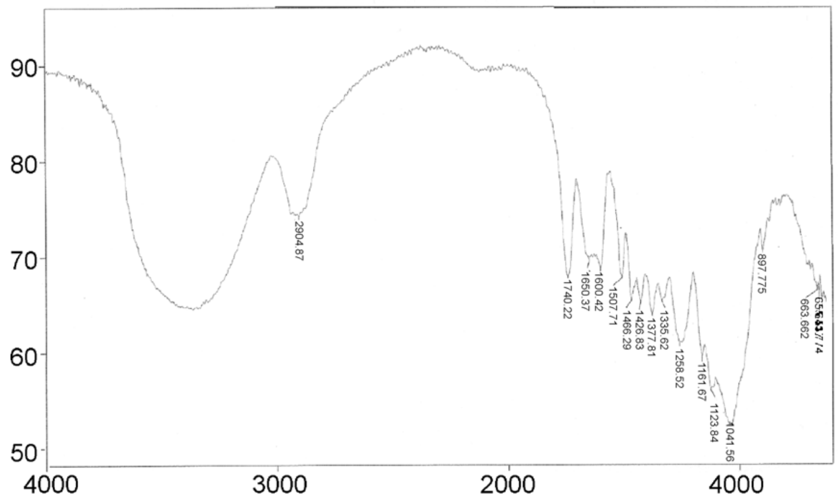

Fig. 3. Spectrum of FTIR analysis from almond shells (with KBr at 98%, at 21 scans/min, with a resolution of 4 $\mathrm{cm^{-1}}$).

aqueous phase, which makes the distribution ratio pH-dependent [16,20]. When the pH value is higher than pK_a, dissociation of chlorophenols to anions does increase. Therefore, in a real situation of water treatment plant, pH of the feed solution should be about 2, to assure a maximum efficiency for PCP removal.

3.2. Validation parameters of the analytical methodology

The analytical methodology employed provides simple and rapid analysis, once the extraction step and the chromatographic determination are completed in 15 min. Linearity was obtained in the range from 1 to 25 μg/L. The calibration curve was obtained with seven PCP standards extracted by SPME in the same conditions as samples, and the correlation was good (0.9985 for correlation coefficient). Experiments were performed in triplicate. Quality control was made daily, with a standard of PCP 15 μg/L.

The detection limit obtained by the calibration curve according to Miller and Miller [21] was 0.96 μg/L, which is lower than the minimum objective of environmental quality to various types of water (2 μg/L (EU)).

Precision was evaluated either by repeatability or intermediate precision assays for 14 determinations of 15 μg/L standards. The relative standard deviations (R.S.D.) were 9.2 and 17.3%, respectively. Repeatability of standards at lower concentration was worse, as expected, although never exceeding 20%.

3.3. Sorption studies

Previous work by adsorption batch experiments showed that PCP solutions (1 mg/L) in almond shells were at equilibrium after 4 h [3]. 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. In previous work, for the assays with 0.1 mg PCP/g shell, an average removal efficiency of 96% was obtained after 24 h. When a more concentrated PCP/sorbent ratio was used (equivalent to 1 mg PCP/g shell), the removal achieved values of approximately 65% [3]. The several adsorption batch experiments allowed 93% (on average) of PCP efficiency removal at a 0.1 mg/L level and a ratio of 0.005 mg PCP/g shell, when equilibrium was considered to be achieved. The desorption results revealed that PCP desorption is about 7%, thus indicating a strong adsorption to the shells [3].

In this study, higher concentrations of PCP were used in order to test the system in extreme conditions. The concentration of 10 mg PCP/L was thought to approach a real situation of a contaminated effluent discharge. Other authors, as Kao et al. [22] used higher levels of PCP and 2,4-DCP e PCP (about 100 mg/L) in sorption studies with fly-ashes. Nevertheless, the feed concentrations used in these experiments, as well as those reported in the studies of other authors [22,23] are not expected to happen in naturally contaminated environmental samples, where monitoring results show concentrations up to 100 μg/L [1,17,24].

In Figs. 4 and 5 results of the continuous experiences are represented. The outer concentration of PCP, after percolating the column in counter-current (with two different sorbent masses) is represented in function of the time in Fig. 4. The correspondent removal efficiency is shown in Fig. 5.

The results obtained in the column filled with 10 g of almond shells showed that removal efficiencies higher than 99.99% and therefore PCP concentrations to values lower than the legal limit of 1 μg/L can be achieved. At the beginning of the experiments (until about 15 h), the outer concentration of PCP was lower than the detection limit of the analytical method used (0.96 μg/L). The column achieved the saturation after about 41 h and the breakthrough time was 37 h, considering that breakthrough occurs when the outer concentration achieves 5% of the initial concentration and that the saturation is assumed to have occurred when the effluent concentration is equal to 95% of the influent concentration [14].

The results obtained with the column filled with 5 g of almond shells showed removal efficiencies higher than 99.98%. In this case, reduction of PCP concentration until values lower than the legal limit of 1 μg/L, could not be obtained. The breakthrough time was 13 h and saturation was achieved after 30 h. It may be evidenced that the time until saturation is dependent on the sorbent amount, as expected. If the breakthrough time was expected to be obtained for a smaller time than that for the 10 g column, the shape of this curve is not so pronounced as expected, which may be due to the heterogeneity of the material.

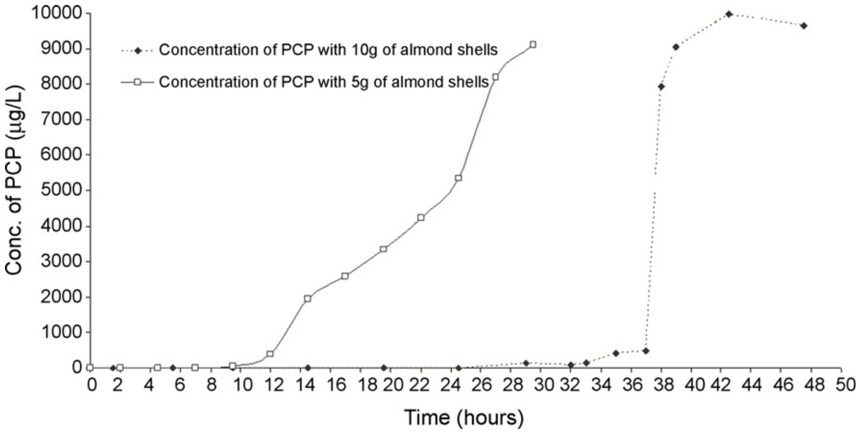

Fig. 4. Variation of outer PCP concentration with time (flow rate = 4 mL/min).

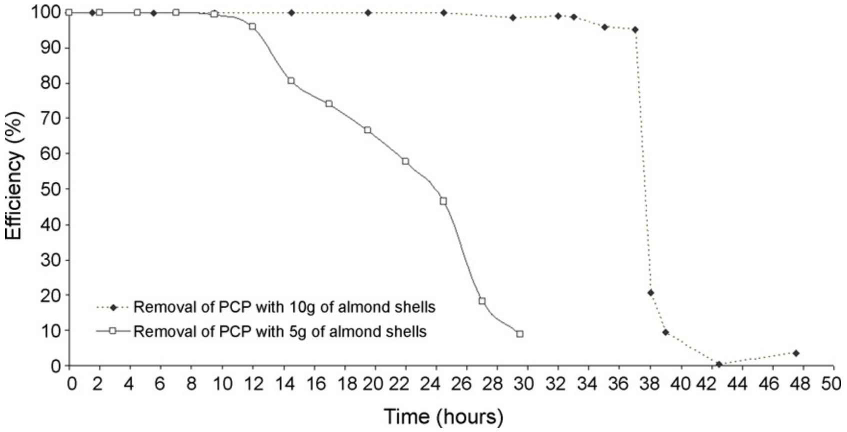

Fig. 5. PCP removal efficiency with time.

The area on the breakthrough curve (Fig. 4) represents the adsorbed mass within the column [14]. Comparing the performance obtained with the columns with 10 and 5 g of sorbent, the adsorbed PCP was 94.0 and 49.0 mg at the saturation with an initial PCP concentration of 10 mg/L. The correspondent mass ratio at saturation was 9.6 mg PCP/g sorbent on average (9.40 and 9.80 mg PCP/g almond shells, respectively).

The breakthough curves (Fig. 4) could be used to calculate the volumes of solution (10 mg/L of PCP) treated in the columns. It was possible to process 3.1 and 8.9 L, respectively for the column with 5 and 10 g of almond shells, until breakthrough occurs. Therefore, about 1 kg of almond shells would be able to treat 620–890 L of a PCP solution with a concentration of 10 mg/L. Obviously if the concentration of PCP decreases, the volume of solution treated will increase.

From mini-columns sorption experiments it is usual to obtain the parameters for scale-up from models as Bed-Depht-Service-Time (BDST). The service time until t_b, may be obtained from Eq. (1), if the initial concentration of the solution fed to the column (C_0), the rupture concentration (C_b), the linear velocity of the solution (v), the bed height (H) and the sorption parameters (N_0—sorption capacity of the bed, k—kinetics constant) are known.

$$t_b = \frac{N_0}{C_0 v} H - \frac{1}{k C_0} \ln\left(\frac{C_0}{C_b} - 1\right) \quad (1)$$

In this study, the limited number of bed heights tested inhibits the adequate utilization of the BDST model, but if it could be applied, the sorption capacity was 6322 mg/L and the kinetics constant was 2.68 L/mg h.

The total surface area of the almond shells (10.95 m^2/g) is more than 70 times lower than those exhibited by GAC (700–1300 m^2/g) [14], but the removal capacity of PCP is only 15 times smaller than GAC, if an average value of 150 mg PCP/g GAC is taken from Ref. [25]. Similar results were obtained for PCP sorption in pine bark [11], but using much lower feed PCP concentrations (100 μg/L). The pine bark particles size ranged from 150 to 400 μm, the surface area was 0.74 m^2/g and the sorption capacity was 1.7 mg/g. On the other hand, Mollah and Robinson [2] studied PCP adsorption in GAC, performing batch assays at 30 °C, with variable PCP concentrations and a sorbent ratio of 1 g GAC per 0.2–1.5 L of solution. They observed a strong pH-dependent interaction of PCP with the sorbent surface, with an average sorption capacity of 157 mg PCP/g GAC, using an initial PCP concentration of 1 mg/L. This means that the almond shells exhibit an high potential for PCP adsorption, if other factors are not considered. Considering the PCP removal capacity of the GAC and of the shells and both price (around €2000 per ton of granular non-impregnated activated carbon by Natale et al. [26]), the almond shells may reveal an economical potential to the treatment of PCP wastewaters.

Regarding to the final destination of the PCP-contaminated sorbent, future work will be needed to study the possible alternatives of oxidation treatments, biodegradation processes or waste disposal at specific sites for toxic materials.

Also before trying to implement pilot experiments, two fundamental tasks should yet be performed. The first is the study of the leaching interferences from the sorbent, as coloured substances and non-toxic organics in general. The second is the study of some trace contaminants (as pesticides), incoming from the raw material treated in agricultural media, that could be released to waters during treatments.

4. Conclusions

The main conclusion of the present work is that almond shells may represent good natural sorbents for PCP, reaching average percentage removals (>99.98%), high enough to be considered an excellent alternative to activated carbon or others synthetic materials. The PCP concentration can decrease to values lower than the legal limits, at specified experimental conditions.

The saturation time of the almond shells columns was higher than 30 h. The values of the ratios of PCP/almond shells are very similar, so we can conclude that the ratio is approximately 10 mg PCP/g almond shell.

Continuous flow experiments using almond shells-packed columns should be considered as a necessary to simulate more closely real treatment environmental and to employ almond shells as an innovative and adsorbent material.

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