Sorption of pentachlorophenol on pine bark

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Abstract

The minimization of pentachlorophenol (PCP) transport in the environment driven by industrial wastewater discharges can be accomplished by sorption in natural, available and low cost by-products like pine bark. Taking into account that PCP is a chemical which behaviour is highly dominated by the surrounding features, this work intended to evaluate the sorption kinetics and equilibrium parameters according to the pH and temperature as well as the pine bark particle size. The PCP uptake by pine bark showed to be faster in the initial phase followed by a slower process, being 24 h the suitably time to reach the sorption equilibrium in the range of pH studied. The neutral PCP species showed to have higher binding capacity to pine bark than the anionic PCP, which was reflected in a decrease in the distribution coefficient ($K_d$) of the linear sorption isotherm with the increase of solution pH from 2 to 7. On the other hand, between 10°C and 35°C, the temperature does not seem to play a significant role in the PCP sorption by pine bark, while the sorbent size is a key parameter to enhance the overall process.

Keywords: Pentachlorophenol (PCP); Pine bark; Sorption equilibrium; Sorption kinetics; Hydrophobic ionizable organic compound (HIOC)

1. Introduction

Several substances like pesticides are introduced in the environment with a specific intention but usually have unwanted side effects related to the amounts applied and/or their properties. Some pesticides, classified as persistent organic pollutants (POPs) are typically hydrophobic and lipophilic, and therefore they accumulate in the fatty tissues of living animals (Jones and Voogt, 1999) and they have a long half-life in soils, sediments, air, or biota. Although Pentachlorophenol (PCP) does not belong to the primarily elaborated list of 12 POPs, it is considered a persistent compound in the environment. PCP is produced with the aim of preserve timber and lumber but also for a wide variety of agriculture and industrial application as fungicide, bactericide, herbicide, molluscicide, algicide and insecticide (Crosby, 1981). Although PCP utilization had declined, restricted discharges to the environment are still imposed by European and Portuguese legislation, which define the quality...
goal for inland surface, estuary, internal coastal and territorial waters, a PCP concentration of less than 2 \( \mu \text{g l}^{-1} \) (Council Directive 86/280/CEE, 1986).

Several authors studied the fate of pesticides in the environment and methodologies to reduce their negative impact in human and other animals life quality. Soils are often referred as an important medium to minimize the mobility of pesticides due to the affinity of pesticides for the organic matter coupled to the soils (Brownawell et al., 1990; Murphy and Zachara, 1995). In order to increase the prevention of the environment contamination, particularly driven by wastewater, some methods are referred in the literature like biodegradation (Kontchou and Gschwind, 1999), co-precipitation (Ying et al., 1988) and oxidation (Robert and Malato, 2002). Our interest encloses the application of sorption to reduce the PCP release into the environment. Some of the sorption studies that had been conducted to sorb PCP took place in materials like biomass (Bell and Tsezos, 1987; Wang et al., 2000), organoclays (Ake et al., 2003), activated carbon (Mollah and Robinson, 1996) or carbonized bark (Edgehill and Lu, 1998).

The application of lignocellulosic materials in the wastewater treatment was object of interest for several authors owing to their natural abundance in the environment or because they are wastes from industrial activities. Although pine bark fulfills these requests its potential has been underestimated. A few studies were published suggesting good efficiencies in heavy metals removal from wastewater by pine bark (Vazquez et al., 2002) owing to its exchangeable surface cations. Regarding to the sorption of organic pollutants by pine bark, Brás et al. (1999) and Ratola et al. (2003) reported interesting results for organochlorine pesticides, while Haussard et al. (2003) and Chiu et al. (2003) attained acceptable sorption for hydrocarbons. In integrated systems, Lens et al. (1994) used pine bark and other natural materials in percolating columns to reduce suspended solids, chemical oxygen demand, biological oxygen demand and nitrogen in a domestic wastewater, while Diaz et al. (2003) reported the utilization of pine bark as a source of organic carbon to denitrifying bacteria in open air batch reactors.

Keeping in mind that the kinetics and the extent of sorption in the equilibrium are dependent of the physical and chemical characteristics of the sorbate, the sorbent and the experimental system and that previous results pointed to the effectiveness of pine bark to retain hydrophobic compounds, the present study intends to evaluate the effectiveness of pine bark to sorb PCP from contaminated water as well as all the parameters that may improve this goal. In order to fulfil these intents the pine bark surface charge was evaluated along with its textural properties. Kinetic studies and equilibrium sorption isotherms were performed at different solution acidities and temperatures, and the particle size was also evaluated in the sorption extent.

2. Experimental

2.1. Pine bark preparation and characterization

The pine bark was collected in a sawmill in the north of Portugal. After grinding it in a Reischt mill and being sieved in Endecotts EFL 2000/1 siever the 0.15–0.45 mm and 0.60–1.18 mm fractions were separated and dried at 105 ⁰C ± 2 ⁰C for 48 h in the oven. The textural characterization was performed by mercury porosimetry with a Quantachrome Poremaster-60 and by helium picrometry. The chemical analysis of pine bark was performed by proximate analysis with a Mettler TA 4000 thermal analyzer, by elemental analysis with a Carlo Erba 1108 Elemental Analyser and the determination of surface charge was performed by pH drift tests described elsewhere (Faria et al., 2004). The pine bark surface has an acidic behaviour and acts as a buffer offering resistance to changes in pH from pH 4 to 10. The overall obtained properties of pine bark are shown in Table 1.

2.2. Reagents

PCP was obtained from Supelco (Cat N-4-8555). Sodium sulfate anhydrous p.a. and sulfuric acid 95–97% p.a. were purchased to Merck. The aqueous PCP solutions of various concentrations were prepared from an intermediate 5 mg l\(^{-1}\) PCP stock solution made from a 2440 mg l\(^{-1}\) stock solution in NaOH 0.1 N. The calibration standards were done by dilution of the intermediate stock solution with distilled and deionized water at pH 2 saturated with Na\(_2\)SO\(_4\). The pH adjustment was carried out with H\(_2\)SO\(_4\) 5 N or NaOH 1 N as needed. The buffer solutions were made with KH\(_2\)PO\(_4\)-K\(_2\)HPO\(_4\) (Merck) with a total phosphate concentration of 0.01 M.

2.3. Sorption studies

The equilibrium sorption experiments of PCP between the aqueous phase and the solid pine bark were performed in closed Erlenmeyer flasks inside a shaker with a water bath at fixed temperature. The required equilibrium time of 24 h was previously determined in

Table 1

<table>
<thead>
<tr>
<th>Properties of pine bark</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Real density (g cm(^{-3}))</td>
<td>1.34</td>
</tr>
<tr>
<td>Pore volume (cm(^3) g(^{-1}))</td>
<td>0.10</td>
</tr>
<tr>
<td>Surface area (m(^2) g(^{-1}))</td>
<td>0.74</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>2.990–0.101</td>
</tr>
<tr>
<td>Organic matter (wt%, dry basis)</td>
<td>99.63</td>
</tr>
<tr>
<td>Ashes (wt%, dry basis)</td>
<td>0.37</td>
</tr>
<tr>
<td>( f_{oc} ) (fraction of organic carbon)</td>
<td>0.55</td>
</tr>
</tbody>
</table>
kinetic studies with solutions of 1 mg l$^{-1}$ PCP in a system with solid:solution ratio of 1:100 (w:w). To conduct our work we defined three regions of pH to study the behaviour of PCP in the system water–PCP–pine bark. The value of pH 2 was picked to study the sorption of the neutral species, while the pH 7 was chosen to study the sorption of anionic PCP without inducing any decomposition of the pine bark. Between these values we studied the system behaviour at pH 4.6, a value near the PCP $pK_a$, where $\phi_n$ (fraction of the neutral form) is 0.5. To study the isotherms at pH 2 and 4.6, the experiments were programmed in several groups. In each group it was maintained the same initial concentration of 100 ml PCP solution in the Erlenmyer flasks, changing the pine bark amount between 20 and 1000 mg. For the experiments at pH 7 it was preserved the same amount of pine bark (500 mg) and shifted the initial concentration of PCP to avoid variations in the pine bark amount and subsequently possible pH variations, although the solutions had been prepared in phosphate buffer. The filtered solutions were analysed for PCP by gas chromatography after solid-phase microextraction (SPME).

2.4. PCP analysis

For PCP analysis, a 85-μm PA fiber (Supelco, Cat. No. PN 57304) and the respective SPME sampling manual holder (Supelco, Cat. No. 57330-U) were employed. The fiber was previously conditioned at 300 °C for 2 h in the gas chromatograph injection port. For the extraction of PCP, 2 ml of the standard solution or sample at pH 2 saturated with Na$_2$SO$_4$ were measured into a 4 ml amber vial and the fiber was immersed in the solution for 30 min, at room temperature (25 ± 2 °C), with rapid and constant stirring. After this period, the fiber was removed and placed in the gas chromatograph (GC) injection port for 3 min.

The quantification of PCP was attained with an Agilent 6890 Series GC equipped with a 5973 N Series mass spectrophotometer (MS) selective detector in SIM mode acquiring fragments with 264, 266 and 268 atomic mass unit (amu). The interface temperature was 160 °C and the ion source (electron ionization) was set at 230 °C with electron energy of 69.9 eV, whilst the quadrupole mass filter was kept at 150 °C. The capillary column was a Hewlett-Packard 5MS (30 m × 0.25 mm × 0.25 μm) (cat. HP 19991S-433). Helium (99.999% purity) was the carrier gas, at a constant 1 ml min$^{-1}$ flow through the column. The oven was initially set at 80 °C, and then raised to 260 °C at a rate of 15 °C min$^{-1}$. The injector was in splitless mode at 250 °C, closed for 3 min before purging with helium at 20 ml min$^{-1}$. The validation parameters obtained with this analytical technique were previously reported (Brás et al., 2004).

3. Results and discussion

3.1. Sorption kinetics

3.1.1. pH effect

PCP is a hydrophobic ionizable organic compound (HIOC) and its distribution is strongly dependent of the aqueous phase pH and ionic strength ($\mu$). But this $\mu$ dependence is only reflected for pH values in the aqueous phase above 7 (Westall et al., 1985). Lee et al. (1990), working with sorption of PCP in soils, also concluded that when pH is under 3 the sorption coefficient, $K$, obtained by linear regression of the data, increased only 1.3 when $\mu$ increased 1000 times. But for pHs higher than 7, the PCP sorption coefficient increased by a factor of approximately 6 with changes in $\mu$ of 140 times. Therefore, of these two parameters the focus of our work was on the pH effect in the PCP–pine bark sorption system. PCP is the “strongest” acid of the phenols family, having a $pK_a$ of 4.70 (Crosby, 1981). The fraction of the neutral form of PCP, $\phi_n$, is dependent of the solution pH. Under pH 3 the fraction of neutral species is almost 100%, while above pH 7 the anionic PCP is predominant. Between these values, a combination of both species is present.

The first step performed in the sorption studies was the evaluation of the contact time required to reach equilibrium at different pH values. Fig. 1 shows the results of sorption kinetics and the pH influence for an initial concentration of PCP of 1 mg l$^{-1}$ and 5 g of pine bark. In fact, the solution pH has an effect in the PCP sorption on pine bark in terms of equilibrium time and extent of sorption related to the PCP species in

![Fig. 1. Sorption kinetics of PCP on pine bark at different solution pH: (•) pH 7; (○) pH 4.6 and (∗) pH 2.](image-url)
solution and its properties. Although it was expected that at pH 4.6 (where \( \phi_n \) is 0.5) the data would be somewhere in the middle between the data accomplished for the higher and the lower pH tested, the results show a sorption well above the expected. This is probably because the two species are in equilibrium and the rapid sorption of the neutral form promotes the equilibrium to move to the formation of more molecular PCP, until a thermodynamic equilibrium between the two species is reached. Peuravuori et al. (2002) studying PCP sorption in lake aquatic humic matter at pH 3, 5.5 and 7 achieved a similar development and also proposed the equilibrium theory. These results can also be explained taking into consideration that pH is a key factor controlling the solubility and the octanol–water partitioning coefficient, \( K_{ow} \). This partitioning coefficient is an important physicochemical parameter used in prediction of environmental fate of organic contaminants, once it quantifies the hydrophobicity of the organic molecule (Nowosielski and Fein, 1998). It was shown by Westall et al. (1985) that for pH values under \( pK_a \) the PCP distribution between the octanol and water phases do not change (\( \log K_{ow} \sim 5 \)), while for higher pHs the \( K_{ow} \) value decreases with the pH, reaching a constant solubility above pH 9 (\( \log K_{ow} \sim 1.8 \)). Wightman and Fein (1999) studied the changes in solubility with the pH and concluded that below the \( pK_a \) the solubility stays almost unchangeable, increasing afterwards with a linear shape, probably due to the formation of sodium chlorophenolate aqueous complexes or to the ions activities, which increase the total chlorophenol solubility.

Other sorption studies in pine bark carried out with pesticides and hydrocarbons in aqueous matrix and with vapor toluene also reported fast kinetics, with the equilibrium being reached in less than 2 h (Chiu et al., 2003; Haussard et al., 2003; Ratola et al., 2003).

3.1.2. Particle diameter effect

The equilibrium time attained by molecular PCP is in agreement with the extremely low specific surface area and pore volume of the pine bark, suggesting that only the external particle surface is available for sorption (Table 1). As consequence, the smaller the particle is, higher extension of sorption is expected. In fact, the experiments conducted with different diameter particles of pine bark, at pH 2, showed that particles with higher size have poor capacity for sorbing the PCP (Fig. 2).

The same trend is observed for both pine bark sizes, but when evaluating the change in the concentration normalized by the geometrical surface area (data not shown) it is clear that higher particles attain the equilibrium faster than the smaller ones, but reaching a similar final sorption capacity.

3.1.3. Effect of PCP initial concentration

The PCP uptake by pine bark over time at different initial PCP concentrations is shown in Fig. 3. For the same amount of sorbent, the sorption efficiencies decrease with the increase of PCP in solution, while the amount of PCP sorbed increased from 0.11, 0.97 and 7.65 mg g\(^{-1}\) for the initial values of PCP:sorbent ratio of 0.12, 1.33 and 11.6 mg g\(^{-1}\), respectively. The time necessary to reach the equilibrium is affected by the increase of PCP initial concentration, increasing as PCP increases in solution. Nevertheless, a contact time of 24 h was considered to be enough to ensure the equilibrium between the solid and liquid phases.
3.2. Sorption isotherms

The sorption isotherm is a mathematical model for characterizing the equilibrium distribution of a solute between the solid and liquid phases within the system at constant temperature. The model relates the amount of solute sorbed per weight of sorbing phase, \( q_e \), with the amount of solute retained in the solvent phase, \( C_e \). The simplest is the linear model, which states that the amount of solute retained by the solid phase is directly proportional to the solution concentration (Eq. (1)).

\[
q_e = K_d \cdot C_e
\]  

The constant \( K_d \) is often referred as the distribution coefficient. The Freundlich isotherm is another model widely used in wastewater adsorption systems representing a nonlinear equilibrium between the phases (Eq. (2)).

\[
q_e = K_F \cdot C_e^{1/n}
\]

The parameter \( K_F \) is linked to the sorption capacity and \( 1/n \) to sorption intensity.

The sorption isotherms determined for PCP sorption in pine bark, at different pH values (Fig. 4) show, within the error of the quantification method, a reasonable linearity over the range of the studied concentrations, with good correlation factors (Table 2). Weber et al. (1991) suggested that the linear isotherm is appropriate for sorption in which the energies involved in the sorption process are uniform with the increase of solute concentration and the loading of sorbate is low, being associated with very low solute concentrations and solids with low sorption potential.

Looking to the Freundlich parameters and correlation factors it can be concluded that this model is also suitable for describing the experimental data, with the exponent, \( 1/n \), at pH 2, close to the unity, enforcing the idea of the linear behaviour of this system. Lee et al. (1990) reached the same conclusion in systems consisting in water–PCP–soil at different pHs with concentrations lower than 5 \( \mu g \) ml\(^{-1}\), while DiVicenzo and Sparks (2001) attended the same situation only for pH 4 but for pH 8 the isotherm became nonlinear. Shimizu et al. (1992) referred that the isotherms are linear if the equilibrium aqueous organic compound concentration is below \( 10^{-5} \) M or below one half of the aqueous phase solubility (whichever is lower). For pH 4.6 and 7.0, the adjustment of the Freundlich isotherm offer slightly better correlation factors than the linear model with the concentration exponent moving away from one. This behaviour may reflect that different PCP species have different mechanisms of interaction with the pine surface during the sorption process.

In the literature some other sorption materials are indicated for PCP sorption (see Table 3). Evaluating the sorption in natural organic materials, like pine bark and peat, a similar affinity of the sorption capacity and the same linear behaviour at acidic pH can be found, once the \( 1/n \) constant reported by Tanjore and Viraraghavan (1997) is very close to the unity. When comparing with biomass, the sorption capacity of pine bark is much lower and the biomass presents an obvious withdrawal from the linearity, showing that the sorption is more favourable probably because it has functional groups highly reactive at the surface and electrostatic interactions can be promoted at the mentioned pH (Jianlong et al., 2000). In this table it is also noticeable the decrease of the sorbent capacity with the increased pH and, most important of all, the ability of the Freundlich isotherm to fit the experimental data for higher pHs.

Several authors suggest that the linear behaviour of the isotherm is a feature of a system where a partitioning mechanism between the organic and the aqueous phases takes place, like the sorption of organic solutes in water by the organic matter of the soil (Lee et al., 1990). In systems where the soil is the sorbent, the partitioning process...
A study performed by Brás et al. (1999) with pine bark as sorbent of lindane (log $K_{ow} = 4.8$) and other organochlorine pesticides suggested that indeed the particle diameter was a key parameter in the sorption process due to the low specific surface area of the pine bark.
Temperature is another environmental parameter that can act in the sorption equilibrium. Our intent was to verify the system behaviour with the temperature for pH 2, which presented the greatest sorption capacity. Three series of batch experiments were conducted at 10, 25 and 35 °C, with a PCP initial concentration of 0.5 mg l⁻¹. The \( K_d \) values obtained for the temperatures tested are presented in Table 4, showing no significant changes in the sorption equilibrium with temperature because the solubility of the neutral species of PCP and the hydrophobic interactions between solute and sorbent remain unchangeable. Wightman and Fein (1999) showed that the solubility increases with temperature, rising by a factor of 2.4 from 25 °C to 55 °C, only in the pH range higher than the \( pK_a \). This could be a result of the temperature effect on the polarity of the water molecule, which decreases with the temperature rising, endorsing solvata-
tion of neutral aqueous species. Another fact illustrated by these authors was that the \( pK_a \) tends to displace to lower values as the temperature increases.

The effect of temperature can be predicted based on its effect on the solute aqueous activity coefficients. Sev-

erstone and Banerjee (1996) sustain that the temperature effects can be predicted by the solubility information but they also reported that the distribution coefficient has only a weak temperature dependency that can be offset by the organic acid \( pK_a \), which for chlorophenols may increase or decrease with the temperature. But even with the same chlorophenol and in the same temperature range, slight sorbent differences can behave in different manner as function of temperature. Zheng et al. (2004) showed that for Chitosan flake-type the \( K_f \) and \( 1/n \) decreased with the temperature increase, while for Chitosan bead-type no evident trend was found.

4. Conclusions

The following conclusions can be drawn from the present work:

1. Pine bark can act as an important sorbent for the sorption of the neutral species of hydrophobic ionizable organic compounds, and its surface acidity is helpful in decreasing the pH of the contact solutions, promoting the increase of the hydrophobic species in solution.

2. The pH of the water–PCP system is a main factor controlling the extent of sorption by pine bark, once it determines the PCP species in solution. At lower pH, where only the neutral species exists, the sorption is higher and the distribution coefficient is 40 times greater than at pH 7, where only anionic PCP is present. At pH around the PCP \( pK_a \), the distribution coefficient is only 1.3 times lower than in the pH range where only exists the neutral PCP.

3. Lower particle sizes showed to have higher sorption capacity with the distribution coefficient increasing by a factor of 2 relatively to the larger particle size tested, enforcing the idea that only the geometrical surface area is available for the sorption process.

4. The temperature does not seem to have a significant role in controlling the sorption of PCP by pine bark.

5. Although in the range of pH studied the PCP sorption can be well described by the linear isotherm, there are some evidences that for higher pHs nonlinear models could be more adequate to describe the experimental data.

References


