



Removal of chlorophenols in aqueous solution by carbon black low-cost adsorbents. Equilibrium study and influence of operation conditions

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ARTICLE INFO

Article history:

Received 22 October 2008

Received in revised form 20 February 2009

Accepted 20 March 2009

Available online 27 March 2009

Keywords:

Chlorophenols

Organic pollutants removal

Carbon black

Adsorption in liquid phase

ABSTRACT

The adsorption process of chlorophenols (CPs) by low-cost adsorbents such as carbon blacks has been studied. The influence of different parameters such as temperature, pH, ionic strength and textural properties of the adsorbents on the adsorption process of pentachlorophenol has been analyzed. The adsorption process is exothermal and parameters such as pH and ionic strength exert a noticeable influence on the adsorption capacity of the solute. These parameters influence the adsorption capacity in an opposite manner. Thus an increase in pH seems to unfavor the adsorption process, whereas the adsorption capacity increases with increasing ionic strength. In order to analyze the influence of the number of chlorine atoms in the molecule of solute the adsorption process of different chlorophenols (i.e., 4-chlorophenol, 3,5-dichlorophenol, 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol) was analyzed. As the number of chlorine atoms (and thus the volume of the molecule) increases, the penetration of the solute through the porous texture of the adsorbent is difficult and, consequently, the adsorption capacity decreases.

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1. Introduction

Phenol and its derivatives are widely used in the chemical, petrochemical and oil refining industries as intermediates in the preparation of a number of synthetic products such as plastics, dyes, pesticides, and insecticides [1]. Because of their toxicity to human and animal life, increasingly stringent restrictions have been imposed on the concentrations of these compounds in the wastewater for safe discharge [2].

Chlorophenols are a group of phenol derivatives in which chlorines (between one and five) are included in the original phenol molecule. These chemicals possess a weak acid character and may permeate human skin. They are also readily absorbed by gastrointestinal tract, causing acute toxicity. Some symptoms of poisoning with chlorophenols are increased respiratory rate, vomiting, and nausea [3]. At concentrations as low as 0.1 mg/L chlorophenols produce a noticeable effect in drinking water. The behavior of chlorophenols in the environment has attracted considerable interest because of its potential to serve as a precursor of dioxins [4].

Several methods such as oxidation with hydrogen peroxide [5], wet oxidation [6], biological degradation [7], membrane filtration [2,8], emulsion liquid membrane processes [9], ion exchange

[10], electrochemical oxidation [11], reverse osmosis [12], photocatalytic degradation [13], adsorption [14,15] and biosorption [16] have been used for the removal of phenols. The most common disadvantage of such methods is the fact that at trace level the efficiency decreases markedly. Adsorption is usually considered the best choice due to its versatility. However, the use of relatively expensive adsorbents such as activated carbons may pose a serious problem from the economic standpoint.

Carbon black is the accepted generic name for a family of small particle size carbon pigments which are formed in the gas phase by the thermal decomposition of hydrocarbons. Approximately 80% of the worldwide market for carbon black is consumed in automotive-related rubber product applications due to its reinforcing action [17]. Thus, scrap tires constitute an important source of these adsorbents. The recovery of carbon blacks from waste tires is a very attractive alternative for the valorization of this kind of residues. In general, carbon blacks show a less developed porous texture than that corresponding to some other carbonaceous materials. Furthermore, carbon blacks are usually macro- and mesoporous materials that exhibit low micropore volume [18]. This latter makes them especially suitable as possible adsorbents of organic pollutants from the liquid phase, since this kind of pollutants are usually large molecules that are adsorbed in an at least partially solvated manner. As a consequence, the solute is not easily accessible to micropores, meso- and macropores playing the most important role in the adsorption process of this kind of pollutants. In fact, due to their sur-

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Table 1
Textural properties of the adsorbents.

Carbon black	S_{BET} (m ² /g)	V_{mi} (cm ³ /g)	W_0 (cm ³ /g)	V_{me} (cm ³ /g)	V_{ma} (cm ³ /g)	ρ_{He} (g/cm ³)	ρ_{Hg} (g/cm ³)	V_{T} (cm ³ /g)	pH _{PZC}
V3	80	0.001	0.014	0.62	1.15	2.03	0.46	1.68	8.0
V6	114	0.004	0.024	0.75	1.26	2.06	0.44	1.79	7.7
BP-880	224	0.016	0.083	0.72	1.07	2.05	0.47	1.64	7.6
BP-1300	511	0.078	0.132	0.52	0.74	2.16	0.53	1.42	4.9
BP-2000	1443	0.271	0.315	0.89	3.75	2.42	0.21	4.35	6.8

S_{BET} = specific surface area; V_{mi} = micropore volume; W_0 = micropore volume (from Dubinin-Radushkevich equation); V_{me} = mesopore volume; V_{ma} = macropore volume; ρ_{He} = helium density; ρ_{Hg} = mercury density; V_{T} = total pore volume; pH_{PZC} = pH at the point of zero charge.

face and textural properties, carbon blacks have been widely used as adsorbents of a wide range of solutes [19–21]. The most important surface groups which influence the physico-chemical properties of carbon blacks are carbon–oxygen structures [22].

The aim of this work is to study the removal of pentachlorophenol and other chlorophenols by a low-cost adsorbent such as carbon black as well as the influence of the operation conditions (e.g., temperature, pH, ionic strength or porous characteristics of the adsorbent) on the adsorption process.

2. Materials and experimental procedure

2.1. Adsorbents

Different carbon blacks provided by Cabot (Suresnes, France) were used as the adsorbents throughout this study. Although in some cases carbon blacks have been considered as hard to use in field applications due to its small (nano to micron) size, the commercial carbon blacks here used exhibit larger particle sizes. For instance, a previous particle size analysis revealed that the average particle size of these adsorbents is comprised between 0.40 mm for BP-2000 and 0.82 mm for V6. Consequently, in this case the particle size does not constitute a problem from the standpoint of the applicability of the adsorbents.

The carbon blacks here used were characterized elsewhere [23] in terms of chemical composition by carrying out the proximate and elemental analyses and also texturally by gas adsorption (N₂, 77 K; CO₂, 273 K), mercury porosimetry, and helium and mercury density measurements. Information on the chemical structure of the adsorbents was obtained by FT-IR spectroscopy. Finally, in order to determine the experimental conditions when the electrical charge density on the surface of the different adsorbents is zero (i.e., the so-called point of zero charge or pH_{PZC}), an experimental procedure analogous to that described by Newcombe et al. [24] was followed. Data obtained in the referred characterization study of the carbon blacks are compiled in Table 1. From the results summarized in this table it may be concluded that the carbon blacks here used cover a wide range of surface areas (from 80 up to over 1400 m² g⁻¹) and pore volumes (micro-, meso- and macropores). Moreover, the pHs of the point of zero charge range from a clearly acidic carbonaceous adsorbent such as BP-1300 (pH_{PZC} = 4.9) to neutral or weakly basic materials such as V3, V6 or BP-880.

2.2. Chlorophenols

Pentachlorophenol (PCP) was used to perform the equilibrium experiments. In order to analyze the influence of the number of chlorine atoms present in the molecule on the adsorption process, 4-chlorophenol (4-CP), 3,5-dichlorophenol (3,5-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), and 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP) were used when necessary. All chemicals were provided by Sigma–Aldrich, Ltd. (Tres Cantos, Madrid, Spain) in analytically pure grade.

2.3. Analytical method

The concentration of solute in the supernatant liquid after contacting the adsorptive solutions with the adsorbent was determined by means of an UV–vis spectrophotometric method, with the aid of an Unicam Heλios-γ UV–vis spectrophotometer provided with a 1-cm optical pathway quartz cell. Ultrapure Milli-Q™ water was used as the reference.

Firstly, the optimal wavelength, λ_{max} (i.e., that corresponding to the maximum absorbance), was determined for each of the chlorophenols analyzed in this study. Next, different solutions of increasing solute concentration (comprised between 5 and 70 mg/L) were prepared, their absorbance being determined. By fitting the experimental measurements according to the Lambert–Beer law, the absorption coefficient, ϵ , of each solute was calculated.

2.4. Determination of the equilibrium time

In order to determine the period of time necessary to reach the equilibrium, previous kinetic experiments were performed. Fixed amounts of adsorbent (0.1 g) and volumes of adsorptive solution (90 mL of initial concentration equal to 700 mg/L) were kept in contact for different preset time intervals. The concentration of solute in the supernatant liquid was analyzed in order to test its evolution with time. The adequate dilution was performed when necessary. The period of time required to reach a constant value of concentration (i.e., the equilibrium concentration or C_e) was considered to be the equilibrium time.

2.5. Equilibrium experiments

In the equilibrium experiments, different amounts of adsorbent comprised between 0.05 and 1.5 g were placed into a series of 100-mL test tubes, fitted with Bakelite screw-on caps to avoid solvent losses by evaporation and interferences due to atmospheric carbon dioxide. Next, 90 mL of solution of known concentration (700 mg/L) were added. Then, the tubes were mounted in a thermostatic bath (Julabo SW22) containing water and maintained under steady shaking (90 rpm). Different series of experiments were carried out by varying the temperature (namely, 20, 40 and 60 °C), the pH of the solution (i.e., 7, 9, 11 and 13), the ionic strength (0.01, 0.1 and 0.5 M), the adsorbent (carbon blacks V3, V-6, BP-880, BP-1300 and BP-2000) and the adsorbate (PCP; 2,3,4,6-TeCP; 2,4,6-TCP; 3,5-DCP and 4-CP). In all cases a commercial buffer solution (provided by Panreac, Barcelona, Spain) constituted by sodium hydroxide and phosphoric acid in different proportions depending on the requested conditions was used in order to maintain pH and ionic strength constant.

As indicated above, a previous experiment was carried out with the aim of determining the equilibrium time. Although the equilibrium time is characteristic of each solid sorbent–solute system and varies with the nature of the solute and solid sorbent, in all cases a period of time equal to 10 days is long enough to ensure that equilibrium has been reached. Thus, when performing the equilibrium

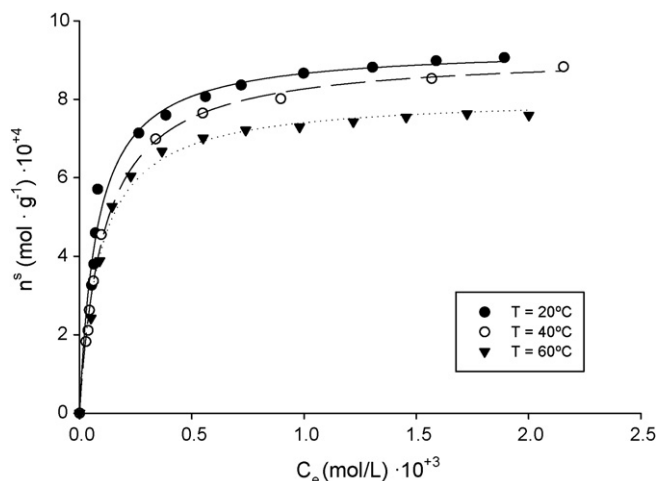


Fig. 1. Adsorption isotherms of pentachlorophenol onto the carbon black BP-1300 at different temperatures. pH = 7. $I = 0.01$ M. Stirring = 90 r.p.m.

experiments the contact time between the adsorbent and the solution was longer than that strictly required to reach the equilibrium.

On the other hand, in order to plot the adsorption isotherms it is necessary to calculate the amount of solute retained per mass unit of the adsorbent corresponding to each of the equilibrium concentrations experimentally determined. With such an aim, a mass balance relative to the solute in the liquid phase may be applied according to the following equation:

$$n^s = \frac{V}{W}(C_0 - C_e) \quad (1)$$

where n^s is the number of moles of solute retained per mass unit of the solid adsorbent, V is the volume of solution kept in contact with the adsorbent, W is the mass of solid adsorbent, C_0 is the initial concentration of solute in the liquid phase and C_e is the equilibrium concentration of solute. In this paper, the influence of the operation conditions on the removal of PCP and other chlorophenols is analyzed in detail.

3. Results and discussion

The adsorption equilibrium of pentachlorophenol (PCP) has been studied. Different operation conditions (i.e., temperature, pH, ionic strength, number of chlorine atoms in the molecule and use of different adsorbents) have been modified in order to analyze their influence on the adsorption process. The Langmuir equation has been satisfactorily used to fit the experimental results.

3.1. Influence of the operation conditions

3.1.1. Influence of temperature

Fig. 1 depicts the adsorption isotherms of PCP at different temperatures, namely 20, 40 and 60 °C. The experimental data have been satisfactorily fitted to the Langmuir isotherm:

$$n^s = \frac{n_0^s \cdot K_{ci} \cdot C_e}{1 + K_{ci} \cdot C_e} \quad (2)$$

Table 2
Adsorption capacities, n_0^s , equilibrium constants, K_{ci} , and adsorption thermodynamic functions of the adsorption process of pentachlorophenol onto the carbon black BP-1300.

T (°C)	n_0^s ($\times 10^4$ mol g $^{-1}$)	K_{ci}	R^2	ΔH° (kJ mol $^{-1}$)	ΔS° (kJ mol $^{-1}$ K $^{-1}$)	ΔG° (kJ mol $^{-1}$)
20	9.332	12,862	0.9842			-24.3
40	9.160	10,983	0.9924	-6.71	0.06	-25.5
60	8.078	9,234	0.9984			-26.7

pH = 7. $I = 0.01$ M.

where the adsorption capacity of the monolayer (n_0^s) corresponds to the asymptotic value of n^s and the value of K_{ci} is indicative of the affinity of the solute towards the active site of the adsorbent [25].

The values of n_0^s and K_{ci} corresponding to the fitting of the experimental data to Eq. (2) are summarized in Table 2. The solid lines in the plots of the adsorption isotherms in solution (Fig. 1) represent the theoretical values calculated using the fitting parameters obtained from Eq. (2). It may hence be concluded that there is a very good agreement between the predicted values and the experimental data. Furthermore, an increase in temperature leads to a decrease in the adsorption capacity of the monolayer (n_0^s). This fact is attributable to an increase of the solubility of PCP in the liquid phase as temperature rises. Consequently, the tendency of the solute to be adsorbed is less remarkable and the adsorption capacity decreases. On the other hand, the values of K_{ci} are in the range comprised between 9.2×10^3 and 1.3×10^4 (see Table 2), although such values decrease as well at higher operation temperatures. This trend suggests that the affinity of the solute towards the active sites of the adsorbent is remarkable and the reversibility of the adsorption process is very limited.

Kao et al. [26] have studied the adsorption process of chlorophenols in aqueous solution. The same variation pattern of the adsorption capacity of the monolayer and affinity with temperature has been reported by these authors. In the first case, the referred researchers use fly ash as the adsorbent. Since the specific surface area and textural properties of this kind of materials is developed to a very limited extent, the values of affinity and adsorption capacity reported by Kao et al. are lower than those obtained in this study. The same trend (i.e., decrease of the affinity and retention capacity with increasing temperature) has been reported by Radhika and Palanivelu [27] when studying the adsorption of PCP by a commercial activated carbon and another activated carbon prepared by chemical activation of coconut shell.

From the values of K_{ci} , the standard average adsorption enthalpy (ΔH°) and entropy (ΔS°) have been obtained, taking into account that

$$K_{ci} = \exp\left(\frac{-\Delta G^\circ}{R \cdot T}\right) = \exp\left(\frac{\Delta S^\circ}{R}\right) \cdot \exp\left(\frac{-\Delta H^\circ}{R \cdot T}\right) \quad (3)$$

Consequently, the plot of $\ln K_{ci}$ vs $1/T$ leads to the values of ΔH° and ΔS° shown in Table 2.

From the values of ΔH° and ΔS° included in Table 2 it may be concluded that, as expected, the adsorption process is exothermic. On the other hand, the entropic term is positive, which is indicative of an increase in the disorder of the system as the adsorption of PCP takes place. This could be attributable to a remarkable desolvation of the molecules of solute passing from the solution to the adsorbed phase. Finally, the values of Gibbs free energy are negative along the temperature range here studied. Thus, it may be stated that the adsorption process occurs in a spontaneous manner regardless what the temperature is.

3.1.2. Influence of pH and ionic strength

In order to test the influence of both factors on the adsorption process of PCP, different adsorption experiments were carried out using the carbon black BP-1300 as the adsorbent and at constant temperature (20 °C). Fig. 2 (left) shows the influence of pH whereas

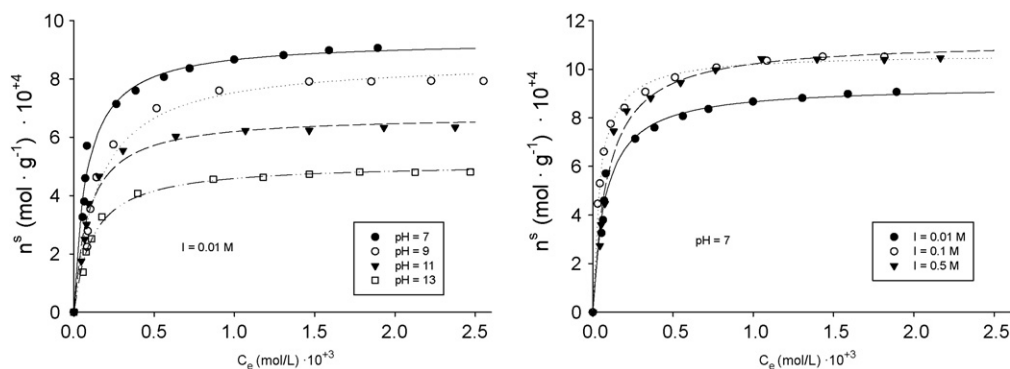


Fig. 2. Adsorption isotherms of pentachlorophenol onto the carbon black BP-1300 at different values of pH (left) and ionic strength (right). $T = 20^\circ\text{C}$. Stirring = 90 r.p.m.

Fig. 2(right) illustrates the effect of ionic strength on the adsorption of PCP onto the solid sorbent. The fitting parameters of the experimental data to the Langmuir equation are summarized in Table 3. From this figure and from the values included in Table 3 it may be concluded that the model is able to fit reasonably well the adsorption of PCP onto the adsorbent when the pH or ionic strength are modified.

On the one hand, it may be observed that, as pH increases, both the adsorption capacity of the monolayer and the affinity of the solute towards the active sites of the adsorbent decrease. Since the pK_a value corresponding to pentachlorophenol is equal to 4.7, in all the experiments performed at different pH values (i.e., from 7 up to 13) the compound will be present in anionic form (pentachlorophenolate ion). Hence, the differences observed in the adsorption capacity of the monolayer (n_0^s) and the affinity of the solute towards the active sites of the adsorbent (K_{ci}) must be justified taking into account the effect of pH on the ionization of the active sites of the adsorbent. In this connection, it must be born in mind that the pH of the point of zero charge corresponding to the carbon black BP-1300 is as low as 4.9 (see Table 1) and this adsorbent can be regarded as moderately acidic. Thus, under the operating conditions the net charge of the adsorptive surface is negative. According to the pioneering work by Coughlin and Ezra [28] dispersion forces between the phenol π -electron system and the π -band of the graphitic planes of the carbonaceous adsorbent appear to play an essential role in the adsorption process. Additionally, the presence of five markedly electronegative chlorine atoms in the structure of PCP results in the removal of π -electrons from the aromatic ring of this latter molecule. As a consequence, the interaction between the adsorbent and PCP becomes weaker and, thus, the affinity of the solute towards the active sites of the adsorbent decreases. Moreover, as pH increases the formation of anionic species in the surface and pores of the carbon black is favored.

A similar explanation is provided by Mattson et al. [29]. According to the referred authors, the interaction of the aromatic ring with

the surface of the carbonaceous adsorbent is the main factor governing the adsorption process of phenolic compounds. Such process involves the interaction through the corresponding π -electron systems and the subsequent formation of donor–acceptor complexes. Thus, both the availability of electron density in the donor as well as the electron affinity of the acceptor markedly influence the stability of such complexes. In the particular case of PCP, the five chlorine substituents act as strong electron withdrawing groups. Thus, the overall electron density in the π -system of the ring decreases and the chlorine-substituted aromatic compound may act to some extent as an acceptor of the electrons provided by the negatively charged surface of the adsorbent. Anyhow, as pH increases such a surface becomes more and more negatively charged due to a more remarkable ionization of the surface groups. Consequently, the repulsive effects between the chlorophenolate anions and the negatively charged active sites of the adsorbent will unfavor the adsorption, mainly at higher values of pH. The same behavior has been previously reported by other authors [26,30,31].

On the other hand, an increase of ionic strength, I , from 0.01 M up to 0.1 M at constant pH equal to 7 leads to a remarkable increase in the polarity of the liquid phase. Thus, despite the surface of the adsorbent is partially negatively charged at the operation pH, the occurrence of a massive amount of both positively and negatively charged ions in the bulk solution favors the migration of the solute molecules towards the more apolar environment inside the porous texture of the adsorbent, thus favoring the migration of the solute to a more apolar environment inside the porous texture of the carbon black. However, a further increase of I up to 0.5 M has no noticeable effect on the adsorption process.

3.1.3. Influence of the number of chlorine atoms of the solute

The adsorption isotherms of four more chlorophenols (in addition to PCP) were determined in order to analyze the influence of the number of chlorine atoms on the adsorption behavior of this kind of chemicals. Such chlorophenols are 4-CP; 3,5-DCP; 2,4,6-TCP and 2,3,4,6-TeCP.

All the adsorption experiments were performed using carbon black BP-1300 as the adsorbent and at constant temperature (20°C), ionic strength (0.01 M) and pH (7).

Fig. 3 depicts the adsorption isotherms of the different chlorophenols on the referred adsorbent. The fitting parameters to the Langmuir equation are summarized in Table 4. From Fig. 3 as well as from the values included in this latter table, it may be concluded that the experimental data fit reasonably well to the Langmuir equation. Furthermore, it may be observed that as the number of chlorine atoms increases the adsorption capacity of the monolayer decreases. However, the affinity of the different solutes towards the active sites of the solid (and, consequently, the value of K_{ci}) increases with an increasing number of chlorine atoms present in the molecule.

Table 3

Fitting parameters to the Langmuir's equation for experiments carried out at different pH and ionic strength (I).

pH	n_0^s ($\times 10^4 \text{ mol g}^{-1}$)	K_{ci}	R^2
7	9.332	12,862	0.9842
9	8.668	11,605	0.9834
11	6.758	11,031	0.9831
13	5.113	8,705	0.9945
I (mol/L)	n_0^s ($\times 10^4 \text{ mol g}^{-1}$)	K_{ci}	R^2
0.01	9.332	12,862	0.9842
0.1	10.64	22,746	0.9972
0.5	11.03	20,010	0.9822

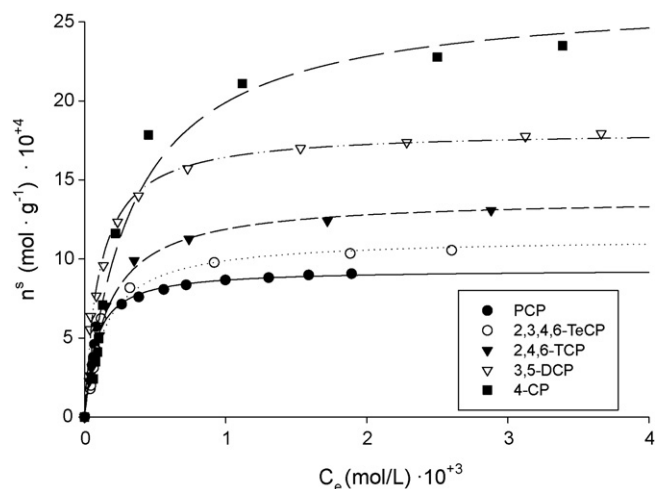


Fig. 3. Adsorption isotherms of different chlorophenols onto the carbon black BP-1300. $T = 20^\circ\text{C}$. $\text{pH} = 7$. $I = 0.01\text{ M}$. Stirring = 90 r.p.m.

This fact may be attributable to different factors. Firstly, as the number of chlorine atoms increase, the molecular size increases as well, and the penetration of the solute through the porous texture of the adsorbents is more handicapped. In addition, as the number of chlorine atoms increases each of the adsorbed molecules cover a wider area on the surface of the solid, hence impairing the adsorption of further molecules of solute. Moreover, it must be born in mind that the experiments were performed at $\text{pH} = 7$ and that the pK_a values corresponding to PCP, 2,3,4,6-TeCP, 2,4,6-TCP, 3,5-DCP and 4-CP are 4.7, 5.5, 6.15, 7.85 and 9.30, respectively. Thus, PCP, 2,3,4,6-TeCP, and 2,4,6-TCP will be in their anionic (chlorophenolate) form at $\text{pH} = 7$. In addition, the anionic form tends to be more extensively hydrated, thus increasing even more its molecular size. As a consequence, the adsorption of PCP, 2,3,4,6-TeCP, and 2,4,6-TCP will be sterically and electrostatically difficult. On the contrary, 3,5-DCP and 4-CP will be present in solution as relatively poorly hydrated, neutral molecules at $\text{pH} = 7$. Hence, the adsorption of these latter molecules is easier than those of the negatively charged, large molecules of PCP, 2,3,4,6-TeCP, and 2,4,6-TCP. All these factors contribute to a decrease of the adsorption capacity (n_0^s) as the number of chlorine atoms increases.

On the other hand, it must be born in mind that, since the pH at which the experiments have been carried out is equal to 7 and the pH_{PZC} is 4.9, the surface of carbon black BP-1300 is negatively charged under the operation conditions. Nevertheless, as indicated above, the chlorine atoms act as strong π -electron withdrawing groups. Consequently, the larger the number of chlorine atoms the more noticeable is the electron withdraw. Thus, PCP shows a much more remarkable negative charge deficiency in the π -ring than 4-CP does. As a consequence, PCP molecules are more strongly retained than those with less chlorine atoms in their respective structures.

To sum up, the adsorption of bigger molecules with more chlorine atoms is sterically handicapped and consequently the

Table 4

Fitting parameters to the Langmuir's equation for experiments carried out with different chlorophenols.

Chlorophenol	$n_0^s (\times 10^4)$	K_{ci}	R^2
PCP	9.332	12,862	0.9842
2,3,4,6-TeCP	11.34	6,802	0.9806
2,4,6-TCP	13.86	5,986	0.9967
3,5-DCP	18.14	5,994	0.9940
4-CP	26.72	2,916	0.9768

Table 5

Fitting parameters to the Langmuir's equation for experiments carried out using different carbon blacks as the adsorbent

Adsorbent	$n_0^s (\times 10^4 \text{ mol g}^{-1})$	K_{ci}	R^2
V3	1.918	35,697	0.9974
V6	2.653	20,848	0.9818
BP-880	4.511	14,920	0.9953
BP-1300	9.332	12,862	0.9842
BP-2000	32.82	20,855	0.9403

adsorption capacity decreases. Nevertheless, once these molecules have reached the active sites present in the solid surface, they are adsorbed in a stronger manner than those with less chlorine atoms and the value of K_{ci} thus increases.

3.1.4. Influence of the adsorbent

As indicated above, in order to test the influence of the adsorbent, different carbon blacks have been used as the adsorbents of PCP. The most remarkable properties of such adsorbents are summarized in Table 1.

Fig. 4 (left) illustrates the influence of the specific surface area (S_{BET}) and mesopore volume (V_{me}) on the adsorption capacity (n_0^s) of PCP onto the different carbon blacks. As usual, the remaining variables (i.e., pH , ionic strength and temperature) have been kept constant. The adsorption isotherms plots have been omitted for the sake of brevity. Nevertheless, the fitting parameters to Langmuir equation are summarized in Table 5. From such parameters, as well as from the plot depicted in Fig. 4(left), it may be concluded that as the specific surface area of the adsorbent increases the adsorption capacity of the monolayer increases as well. This fact is particularly noticeable for sample BP-2000, the adsorbent that shows a more developed surface area (up to $1443 \text{ m}^2 \text{ g}^{-1}$). An increase in the mesopore volume also leads to a more remarkable adsorption capacity of PCP.

Furthermore, in Fig. 4(right) the adsorption capacity has been plotted versus the micropore (W_0) and total (V_T) pore volume. It may be concluded that, whereas W_0 exerts an important influence on the maximum amount of PCP adsorbed by the different carbon blacks, V_T appears to be a minor factor conditioning the adsorption of PCP. This latter may be due to a relatively important contribution of the macropore volume to V_T . This kind of pores play an important role as channels that guide the PCP towards the active sites of the adsorbent – mainly located in mesopores and wide micropores – but do not contribute noticeably to the total amount of solute retained by the adsorbent.

Finally, the pH_{PZC} appears to exert a noticeable influence on both, the adsorption capacity and the affinity of PCP towards the active sites of the different adsorbents. On the one hand, Fig. 5 clearly shows that a maximum in the adsorption capacity is reached for the sample that exhibits a value of pH_{PZC} more similar to that used in these experiments (again, BP-2000). On the other hand, values of K_{ci} summarized in Table 5 suggest that, as a rule (excepting for sample BP-880), as pH_{PZC} increases PCP is more strongly retained. Since the net surface charge of those samples showing larger values of pH_{PZC} remains either neutral or positive at the experimental pH (i.e., 7), the interactions between these samples and the negatively charged pentachlorophenolate ions are expected to be stronger.

From all the above exposed, it may be concluded that, under the experimental conditions here used, BP-2000 is the best adsorbent in terms of adsorption capacity of the monolayer (n_0^s). This fact is attributable to its large values of S_{BET} ($1443 \text{ m}^2/\text{g}$) and pore volumes (see Table 1) as well as to its pH_{PZC} . For the remaining adsorbents, the adsorption capacity decreases as the surface and porous texture do. Thus, the carbon black BP-2000 could be suggested as the best

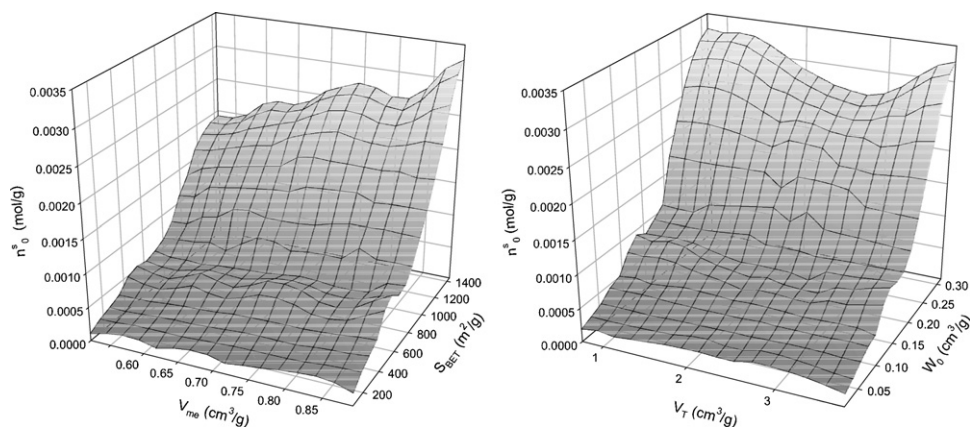


Fig. 4. Influence of the surface and porosity of the carbon blacks on the adsorption capacity of pentachlorophenol. Specific surface area and mesopore volume (left) and micropore and total pore volumes (right). $T = 20^\circ\text{C}$. $\text{pH} = 7$. $I = 0.01\text{ M}$. Stirring = 90 r.p.m.

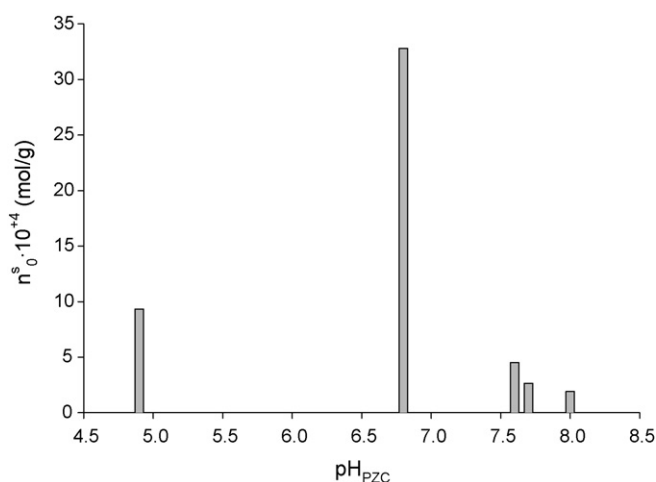


Fig. 5. Variation of the adsorption capacity with the pH of the point of zero charge. $T = 20^\circ\text{C}$. $\text{pH} = 7$. $I = 0.01\text{ M}$. Stirring = 90 r.p.m.

choice to remove PCP at the industrial scale, since the amount of adsorbent requested to remove a given amount of pollutant would be minimized.

4. Conclusions

The adsorption process of pentachlorophenol and four more chlorophenols onto low-cost adsorbents such as carbon blacks been investigated. The influence of different parameters (namely, temperature, pH, ionic strength, number of chlorine atoms in the molecule and use of different adsorbents) on such process has been analyzed. From the results obtained in the present study, it may be concluded that as usual, the adsorption process is exothermal. Furthermore, as temperature grows the amount of solute retained per gram of adsorbent becomes smaller. This process is more favored at neutral pH, probably due to the fact that, as pH increases the surface of the adsorbent becomes more and more negatively charged due to a more remarkable ionization of the surface groups (note that the pH_{PZC} is equal to 4.9). Consequently, the repulsive effects between the chlorophenolate anions and the negatively charged active sites of the adsorbent will unfavor the adsorption, mainly at higher values of pH. With respect to the ionic strength, the presence of a large amount of ions tends to favor the migration of the pentachlorophenolate ions to the more apolar environment inside the porous texture of the adsorbent, thus increasing the adsorption capacity when I rises from 0.01 M up to 0.1 M. The influence of the number

of chlorine atoms in the molecule of solute has also been studied. The adsorption of bigger molecules with more chlorine atoms is sterically handicapped and consequently the adsorption capacity decreases. Nevertheless, once these molecules have reached the active sites present in the solid surface, they are adsorbed in a stronger manner than those with less chlorine atoms and the value of K_{Ci} increases. Finally, different carbon blacks showing a wide variety of textural and surface properties have been used as the adsorbents for the removal of pentachlorophenol. A positive influence of large values of S_{BET} , V_{mi} and V_{me} on the adsorption capacity has been found, whereas samples showing neutral or weakly basic values of pH_{PZC} appear to retain the PCP molecules in a stronger and less reversible manner.

5. Nomenclature

C_e	equilibrium concentration of the solute in the supernatant liquid (mol L^{-1})
C_0	initial concentration of solute in the liquid phase (mol L^{-1})
I	ionic strength (mol L^{-1})
K_{Ci}	equilibrium constant in the Langmuir isotherm
n^s	number of moles of solute retained per mass unit of the solid adsorbent (mol g^{-1})
n_0^s	adsorption capacity of the monolayer (mol g^{-1})
PCP	pentachlorophenol
R	molar gas constant ($\text{J mol}^{-1}\text{K}^{-1}$)
S_{BET}	specific surface area (m^2g^{-1})
T	temperature ($^\circ\text{C}$)
V	volume of solution kept in contact with the adsorbent (L)
V_{ma}	macropore volume (cm^3g^{-1})
V_{me}	mesopore volume (cm^3g^{-1})
V_{mi}	micropore volume (cm^3g^{-1})
V_T	total pore volume (cm^3g^{-1})
W	mass of solid adsorbent (g)
W_0	micropore volume (from Dubinin-Radushkevich equation)
ΔG°	standard average adsorption Gibbs free energy (kJ mol^{-1})
ΔH°	standard average adsorption enthalpy (kJ mol^{-1})
ΔS°	standard average adsorption entropy ($\text{kJ mol}^{-1}\text{K}^{-1}$)
ϵ	molar absorption coefficient of the solute
λ_{max}	wavelength corresponding to the maximum absorbance of the solute
ρ_{He}	helium density (g cm^{-3})
ρ_{Hg}	mercury density (g cm^{-3})
2,3,4,6-TeCP	2,3,4,6-tetrachlorophenol
2,4,6-TCP	2,4,6-trichlorophenol

3,5-DCP 3,5-dichlorophenol
4-CP 4-chlorophenol

Acknowledgements

Financial support of this work by Spanish CICYT (project CTQ2007-60255/PPQ) and by the Junta de Extremadura (project PRI-07A031) is gratefully acknowledged.

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