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Competitive adsorption of phenolic compounds from aqueous solution using sludge-based activated carbon

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Preparation of activated carbon from sewage sludge is a promising approach to produce cheap and efficient adsorbent for pollutants removal as well as to dispose of sewage sludge. The first objective of this study was to investigate the physical and chemical properties (BET surface area, ash and elemental content, surface functional groups by Boehm titration and weight loss by thermogravimetric analysis) of the sludge-based activated carbon (SBAC) so as to give a basic understanding of its structure and to compare to those of two commercial activated carbons, PICA S23 and F22. The second and main objective was to evaluate the performance of SBAC for single and competitive adsorption of four substituted phenols (*p*-nitrophenol, *p*-chlorophenol, *p*-hydroxy benzoic acid and phenol) from their aqueous solutions. The results indicated that, despite moderate micropore and mesopore surface areas, SBAC had remarkable adsorption capacity for phenols, though less than PICA carbons. Uptake of the phenolic compound was found to be dependent on both the porosity and surface chemistry of the carbons. Furthermore, the electronegativity and the hydrophobicity of the adsorbate have significant influence on the adsorption capacity. The Langmuir and Freundlich models were used for the mathematical description of the adsorption equilibrium for single-solute isotherms. Moreover, the Langmuir–Freundlich model gave satisfactory results for describing multicomponent system isotherms. The capacity of the studied activated carbons to adsorb phenols from a multi-solute system was in the following order: *p*-nitrophenol > *p*-chlorophenol > PHBA > phenol.

Keywords: water treatment; sludge; activated carbons; multicomponent adsorption; substituted phenols

1. Introduction

Sewage sludge is being generated in ever increasing amounts due to the rapid urbanization and higher effluent criteria implemented in recent decades. Without proper treatment and disposal, it causes a secondary pollution problem in the environment.

Sewage sludge is carbonaceous in nature and rich in organic materials. Hence, it has the potential to be converted into different kinds of activated carbon if pyrolysed under controlled conditions or with some chemical treatment. This conversion could offer the combined benefits of reducing the volume of sludge and producing a valuable adsorbent with lower cost than commercial activated carbons. Several investigations have shown the feasibility of the conversion [1–5]. Activated carbons have been widely used as adsorbents in many water treatments, especially for drinking water, due to their outstanding adsorption capacity derived from their high surface area, tailor-made pore structure and the chemical character of their surface [6–8].

The adsorption capacity of an activated carbon depends on [9]:

- the nature of the adsorbent (e.g. functional groups present, surface area and pore size distribution, ash content);
- the nature of the adsorbate (e.g. surface functional groups, polarity, hydrophobicity, molecular weight and size, solubility and pKa); and
- the solution conditions (e.g. pH, temperature and adsorbate concentration, presence of competitive solutes, polarity of solvent).

Not surprisingly, apart from some well-established facts, there are many conflicting results in the literature. The treatment of drinking water and wastewater by activated carbon sometimes involves a multitude of adsorbates competing for adsorption sites on the carbon surface. Thus, a thorough understanding of the competitive effect of various organic compounds on carbon adsorption deserves more work [10,11].

Phenolic compounds occur frequently in the aquatic environment through [12–16]:

- direct discharge of industrial wastewaters containing dyes, herbicides, surfactants, etc.;

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- effluents from oil refineries and olive mills;
- effluents from the plastics, leather, paper, paint, pharmaceutical and steel industries.

Phenolic compounds cause an unpleasant taste and odour (even at low concentrations) in drinking water, and can exert negative effects on different biological processes [17]. Most of these compounds are recognized as toxic carcinogens to humans and aquatic life and need to be eliminated for safe discharge [7]. The European Union and US Environmental Protection Agency (USEPA) have placed phenol and its derivatives (e.g. nitrophenols and chlorophenols) on their priority pollutants lists [6,18].

Adsorption appears as the best technique to remove phenols at low concentration. Especially phenol is widely taken as a reference compound for adsorption capacity determination [19]. The main drawback of the adsorption process is that, after saturation, the activated carbon is regenerated by *ex situ* high temperature processes which require long transportation high energy cost and moreover results in about 10–15% activated carbon losses.

This high adsorbent cost has limited adsorption applications to final water treatment, most often to produce drinkable water, when pollutant concentration has been very much reduced by several major processes such as biological and physicochemical treatments. In this perspective, it would be of great economic importance to develop either cheap *in situ* activated carbon regeneration processes or a cheap adsorbent to replace usual activated carbon. Our team has investigated both new *in situ* oxidative regeneration techniques [20,21] and the performance of new carbonaceous materials produced from sludge [22]. These were mainly achieved through the European project, REMOVALS (FP6-018525) with Imperial College London and GEPEA (Nantes) for the production of sludge-based activated carbons and their use in water treatment process involving both adsorption and catalytic wet air oxidation (CWAO). A previous common paper

[22] presented the first results comparing six sludge-based activated carbons when used as adsorbents and as wet air oxidation catalysts. Both adsorption and CWAO were achieved with phenol as a model pollutant.

The present study focuses on the performance of the best SBAC as compared with two commercial activated carbons (S23 and F22) in the case of multicomponent adsorption. Four phenolic compounds (*p*-nitrophenol, PNP; *p*-chlorophenol, PCP; *p*-hydroxy benzoic acid, PHBA; phenol, P) were used either in single or multicomponent aqueous solutions. This comparison also includes the physico-chemical properties of these three adsorbents so as to provide fundamental knowledge and basic understanding of the SBAC structure.

2. Materials and methods





2.1. Reagents

Four phenolic compounds (Aldrich Chemical) with different functional groups: phenol (-OH), *p*-chlorophenol (-Cl), *p*-hydroxybenzoic acid (-COOH) and *p*-nitrophenol (-NO₂) were used. Table 1 provides physico-chemical properties of phenol and its derivatives. All other chemicals used were analytical grade reagents.

2.2. Preparation of sludge-based activated carbon (SBAC)

According to the comparison of six SBACs in our preliminary work [22], steam-activated dewatered raw sludge prepared by Imperial College London was selected for this detailed investigation on multicomponent adsorption. Sewage sludges have been used as feedstock for the production of the carbon; municipal wastewater DRAW (dewatered, raw) originated from the UK (Little Marlow). The raw sludge used consists of 65.9% volatile contents, 41% carbon and 20.4% ash [23]. Prior to carbonization, the sludges were sterilized in steam at 122°C for 15 minutes in an autoclave, then

Table 1. Basic information concerning phenol and its derivatives [50] and comparison of its adsorption capacities in single- and multi-solute systems.

Properties	Phenol	<i>p</i> -Chlorophenol	<i>p</i> -Nitrophenol	<i>p</i> -Hydroxy benzoic acid
Symbol	P	PCP	PNP	PHBA
Molecular formula	C ₆ H ₆ O	C ₆ H ₅ OCl	C ₆ H ₅ O ₃ N	C ₇ H ₆ O ₃
Chemical structure				
pKa at 25°C	9.89	9.37	7.15	4.58/9.23
Solubility at 25°C (g L ⁻¹)	93	27	17	5
Log K _{ow}	1.5	2.39	1.91	1.37

dried to constant mass at 105–110°C and finally ground below 10 mm in size. Subsequently, ca. 210 g of sample were loaded into a quartz reactor, which was then installed within a Carbolite rotary furnace (model HTR11/150). The sample was heated at 5 or 10°C/min under a flowing (500 mL min⁻¹) nitrogen atmosphere. After the desired temperature (250–1000°C) was reached, the furnace was cooled down automatically to produce carbonized samples. When steam activation was applied, once the target temperature was reached, the equivalent of 0.7 g/min of steam was mixed with the nitrogen flow (acting as carrier) and the temperature was maintained for the whole duration of the prescribed activation period. The flow of the activation reagent was arrested and the furnace was left to cool at the end of the activation period.

The steam activation procedure was optimized using the response surface methodology [24] to establish the relationship between the textural properties of the resulting carbonaceous materials and the applied conditions. From the models, it was calculated that the maximum BET surface area was attained when the activation temperature was 838°C and dwell time was 80 min [23].

The F22 and S23 commercial activated carbons used as a reference were provided by PICA (Veolia Group) and were made from coal and oil, respectively.

2.3. Activated carbon characterization

2.3.1. Specific surface area and pore volume

Surface area was determined using nitrogen as the sorbate at 77K in a static volumetric apparatus (Micromeritics ASAP 2010 sorptometer). Specific total surface areas were calculated using the BET equation [25].

2.3.2. Boehm titration

The acid/base properties of activated carbons were determined by the classical Boehm titration method [26].

2.3.3. Thermal analysis

Thermogravimetric analysis (TGA) was performed under nitrogen flow from room temperature to 700°C with a heating rate of 10°C/min (Q600 SDT, TA Instrument).

2.3.4. Elemental analysis and ash content

Elemental analysis of the activated carbons was carried out using a Thermo Finnigan Flash EA111 for CHNSO determination and acid lixiviation (HCl:HNO₃, 3:1 v/v) followed by inductively coupled plasma atomic emission spectroscopy (Jobin Yvon – Ultima 2R) for metals.

Metals whose oxides could act as oxidation catalysts were investigated.

The ash content was determined by calcination at 650°C until constant weight according to ASTM D2866 [27].

2.4. Adsorption equilibrium studies

2.4.1. Single component isotherms

Isotherms were performed at 25°C using the batch bottle-point technique. A carbon sample of 0.5 g was placed into each bottle and 100 mL of single adsorbate aqueous solution with initial concentrations of 0.005–0.05 mol L⁻¹ for P, 0.005–0.025 mol L⁻¹ for PNP, 0.005–0.05 mol L⁻¹ for PCP and 0.005–0.025 mol L⁻¹ for PHBA were added. The initial pH was 5.6 for P, 3.8 for PHBA, 4.8 for PNP and 5.3 for PCP. Solutions were not buffered to avoid adsorption competition between organic and buffer. Bottles were shaken for three days before sampling.

Preliminary kinetic experiments indicated that adsorption equilibrium was reached in less than three days for all the activated carbons. All the samples were filtered using a 0.25 µm filter syringe and analysed by high-performance liquid chromatography (HPLC) with an UV detector set at 254 nm for phenol and PHBA, 285 nm for PCP, and 315 nm for PNP; a ProntoSIL 120-5 AQ column (C-18, 250 mm × 4 mm, 5 µm) was used, the mobile phase being acidified distilled water (pH 2.2 using H₃PO₄):acetonitrile (60:40, v/v). The flow rate of the mobile phase was maintained at 1 mL min⁻¹. The amount of adsorbed phenolic compounds was then determined.

2.4.2. Multicomponent isotherms

The procedure for competition isotherms was the same as for the single component isotherms, with the initial solutions being composed of equimolar concentrations of the four phenolic compounds (0.007–0.025 mol L⁻¹). Bottles were shaken for seven days before sampling. From a previous adsorption kinetic study, this period had proved sufficient to ensure that adsorption equilibrium was reached. The initial pH of the mixture solution was between 3.5 and 5.

2.5. Adsorption modelling

2.5.1. Single component model

Among the wide variety of available theoretical models and empirical fitting functions used in this field, the curves for single component isotherms were evaluated according to the two parameter models of Langmuir and Freundlich. The most extensively used isotherm equation

for modelling the adsorption data is the Langmuir equation, which is suitable for monolayer adsorption onto a surface with a fixed number of identical sites and is given by the following equation:

$$q_e = \frac{q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}, \quad (1)$$

where q_e is the amount of adsorbate fixed on adsorbent at equilibrium (mol g⁻¹), C_e is the equilibrium concentration of the adsorbate in aqueous solution (mol L⁻¹), and q_{\max} and K_L are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively. A high K_L value reveals a strong interaction between the pollutant and the surface of the adsorbent. The Langmuir parameters were evaluated by linearization of C_e/q_e versus C_e .

The Freundlich model is an empirical equation based on adsorption on a heterogeneous surface [28]. It is given by the following equation:

$$q_e = K_F \cdot C_e^{1/n}, \quad (2)$$

where K_F is the Freundlich constant for a heterogeneous adsorbent, and n is related to the magnitude of the adsorption driving force and to the adsorbent site energy distribution. The value of n indicates favourable adsorption when $1 < n < 10$; the more favourable, the lower its value within this range [29]. The Freundlich parameters were determined by linearization of $\log q_e$ versus $\log C_e$. The adsorption models constants, the values of which express the surface properties and affinity of the adsorbent, can be used to compare the adsorption capacity of adsorbents for different adsorbates.

2.5.2. Competitive adsorption models

Because of the limited success of the generalized Langmuir model in predicting multicomponent adsorption equilibria, several authors have modified the equations by the introduction of a power law expression of Freundlich form [30]. In this work, the competitive isotherms were evaluated according to the Langmuir–Freundlich model as shown in the following equation [31]:

$$q_{e,j} = \frac{q_{\max} \cdot (K_{L,j} \cdot C_{e,i})^{ni}}{1 + \sum_j (K_{L,j} \cdot C_{e,j})^{nj}}, \quad (3)$$

where $q_{e,i}$ is the amount of component i adsorbed per unit weight of adsorbent, $C_{e,i}$ the equilibrium concentration of the component i and $C_{e,j}$ the equilibrium concentration of the other component j , q_{\max} , n and K_L are

parameters obtained from the Langmuir model and the Freundlich model for each single component.

The values of the Optimized Extend Langmuir–Freundlich model parameters were obtained from non-linear regression. Identification was made by using the generalized reduced gradient method (Solver Microsoft Excel) to minimize the residual sum of squares (RSS), as shown in Equation (4):

$$RSS = \sum_{i=1}^n (q_{\text{exp},i} - q_{t,i})^2, \quad (4)$$

where $q_{\text{exp},i}$ are the elements of the vector $q_{\text{exp},i}$ containing the given experimental adsorbed phase concentrations, n is the data points and $q_{t,i}$ are the corresponding theoretical values calculated by model being studied.

Based on the objective function values (F_{OBJ}), relative average deviation (RAD) and a correlation coefficient (R^2) between the measured and the model-predicted values, statistical analysis was carried through to evaluate the model's behaviour. The objective function (F_{OBJ}) and the relative average deviation (RAD) were calculated using the equations:

$$F_{\text{OBJ}} = \sum_{i=j}^n \left(\frac{q_{\text{exp},i} - q_{t,i}}{q_{\text{exp},i}} \right)^2, \quad (5)$$

$$RAD = \frac{100}{N} \sum_{i=j}^n \left(\frac{q_{\text{exp},i} - q_{t,i}}{q_{\text{exp},i}} \right)^2, \quad (6)$$

where $q_{\text{exp},i}$ and $q_{t,i}$ are the experimental and calculated values for each data point, respectively, and n is the number of experimental data.

3. Results and discussion

3.1. Characterization of the studied carbons

Table 2 shows that the total mesopore volume and micropore volume of the SBAC are 0.17 and 0.11 cm³ g⁻¹, respectively; the two commercial activated carbons exhibited much more microporosity. The BET surface area of the sludge-based carbon was about 265 m² g⁻¹ which was nearly four times lower than that of the commercial activated carbons. The lower specific surface area of the SBAC is related to its lower microporosity, which is primarily attributed to the properties of the precursor.

Table 3 gives the contents of oxygen-containing surface functional groups of the activated carbons. The total acidic groups content of the SBAC (1.1 mmol g⁻¹) was found to be higher than those of commercial activated carbons, 0.2 and 0.65 mmol g⁻¹ for S23 and F22,

Table 2. Characterization of activated carbons.

Activated carbon	BET surface ($\text{m}^2 \text{g}^{-1}$)	Mesoporous volume ($\text{cm}^3 \text{g}^{-1}$)	Microporous volume ($\text{cm}^3 \text{g}^{-1}$)	Pore diameter (\AA)	Apparent density (kg m^{-3})
S23	1230	0.04	0.49	17	1013
F22	985	0.12	0.40	20	993
SBAC	265	0.17	0.11	35	1471

Table 3. Results of Boehm titration.

Activated carbon	Carboxylic group (mmol g^{-1})	Lactonic group (mmol g^{-1})	Phenolic group (mmol g^{-1})	Total acidic sites (mmol g^{-1})	Total basic sites (mmol g^{-1})	pH PZC
S23	0.00	0.09	0.21	0.30	0.98	9.8
F22	0.05	0.01	0.18	0.24	0.51	9
SBAC	0.15	0.15	0.80	1.10	0.64	6.3

respectively, while S23 has the greatest content of basic groups (0.98 mmol g^{-1}). However, it is important to note that Boehm titration is not convenient for the SBAC due to the release of either carbonates in basic solutions or phosphates and ferric ions in acidic solutions. The presence of basic groups enhances the adsorption of aromatic compounds through the formation of an electron acceptor–donor complex [32].

Thermogravimetric analysis of the three activated carbons reveals the same global behaviour (Figure 1). The higher difference between the three activated

carbons is observed during the first mass loss ($<273^\circ\text{C}$) and mainly represents the degree of humidity and small adsorbed molecules. During the thermal decomposition of the oxygenated surface groups of the activated carbons studied, the loss of mass at temperatures ranging from 200 to 500°C is essentially attributed to the decomposition of carboxylic acid groups to CO_2 , while the loss of mass observed at higher temperatures, from 500 to 700°C , is mainly due to the decomposition of the lactonic and phenolic groups [33].

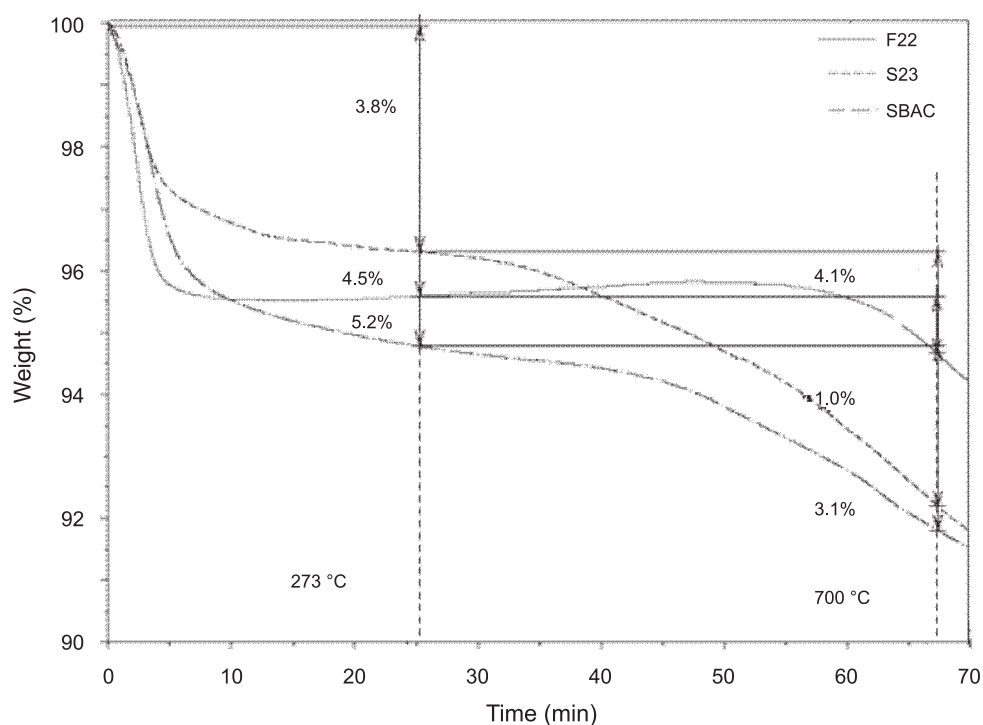


Figure 1. Thermogravimetric analysis (TGA) of commercial activated carbons and SBAC.

Table 4 shows that SBAC has a higher ash content compared with the commercial activated carbons. This is in accordance with Smith *et al.* [34] for the production of SBAC by carbonization and steam activation where the lower BET surface area was related to the lower carbon content of the parent sludge. It was also characterized by the presence of a large amount of iron, about 100 times more than that found in the commercial activated carbons.

Moreover, SBAC contained a rather high percentage of oxygen (Table 5) suggesting the presence of acidic surface functional groups and even more of inorganic salts and oxides. From Tables 4 and 5, it was found that the ash content and the elemental analysis cannot be merged in a consistent mass balance due to other elements not analysed by these two methods.

Table 4. Metal composition analysis of the activated carbons.

Carbon	Zn	Ni	Co	Mn	Fe	Cu	Ash (wt%)
	(ppm)						
PICA S23	13	3	0	5	116	74	3.2
PICA F22	13	24	0	6	578	28	12.0
SBAC	613	28	1	149	$4.79 \cdot 10^4$	672	65.0

Table 5. Elemental analysis of activated carbons.

Carbon	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt%)
PICA S23	92.3	0.6	0.3	–	2.3
PICA F22	84.4	0.5	0.5	0.7	1.1
SBAC	27.9	0.6	1.4	0.8	10.3

Table 6. Parameters of Langmuir and Freundlich models for the adsorption of single solute of P, PCP, PNP and PHBA on three types of activated carbons at 25°C.

ACs	Phenol	Langmuir model			Freundlich model		
		q_{\max} mol g ⁻¹	K_L L mol ⁻¹	R^2	n	K_F (mol g ⁻¹ (L mol ⁻¹) ^{1/n})	R^2
S23	P	0.0037	2941	0.9988	0.161	0.007	0.9296
	PCP	0.0084	15151	0.9977	0.178	0.015	0.7711
	PNP	0.0041	2777	0.9989	0.269	0.016	0.9413
	PHBA	0.0039	476	0.9886	0.443	0.031	0.9672
F22	P	0.0033	500	0.9917	0.212	0.007	0.9097
	PCP	0.0063	3333	0.9959	0.208	0.016	0.9763
	PNP	0.0031	2829	0.9934	0.639	0.191	0.7190
	PHBA	0.0021	4224	0.9935	0.444	0.041	0.6291
SBAC	P	0.0026	74	0.9726	0.469	0.009	0.9926
	PCP	0.0023	909	0.9908	0.144	0.004	0.8794
	PNP	0.0025	43	0.5595	1.354	0.841	0.9253
	PHBA	0.0016	90	0.1759	0.741	0.031	0.8896

3.2. Single component adsorption

3.2.1. Effect of carbon surface chemistry

Figure 2(a), (b) and (c) shows the single component adsorption isotherms for the four substituted phenols in aqueous solution onto SBAC, S23 and F22, respectively. The results show that the phenols adsorption capacity of the sludge-based activated carbon (SBAC) is lower than that obtained by the two commercial activated carbons (S23 and F22) investigated for comparison (Table 6). This lower performance could be due to the much lower BET surface area ($265 \text{ m}^2 \text{ g}^{-1}$) and the less developed microporous structure of SBAC (Table 2). Phenol molecules, due to their molecular size, are mainly adsorbed in pores with diameter greater than 1 nm, i.e. within the microporous range.

It can be noted that the maximum adsorption capacity of SBAC for phenol as a reference compound is half that of F22 and S23, while the ratio of their surface areas is nearly 1:4 for F22 and about 1:5 for S23. The adsorption capacity of SBAC is therefore higher than expected from the BET surface area. This would suggest an economically attractive utilisation of SBAC as a preliminary adsorbent in water treatment.

Due to competition between water and phenol compounds, the acidic nature of SBAC also plays an unfavourable role in its adsorption capacity. Water molecules adsorbed on oxygen groups become secondary adsorption centres, retaining other water molecules by means of hydrogen bonds. The adsorbed water molecules block the entry of organic molecules to significant parts of the surface; this effect is generally called 'solvent effect' [35]. Moreover, the acidic surface oxygen groups, located at the edge of the graphite

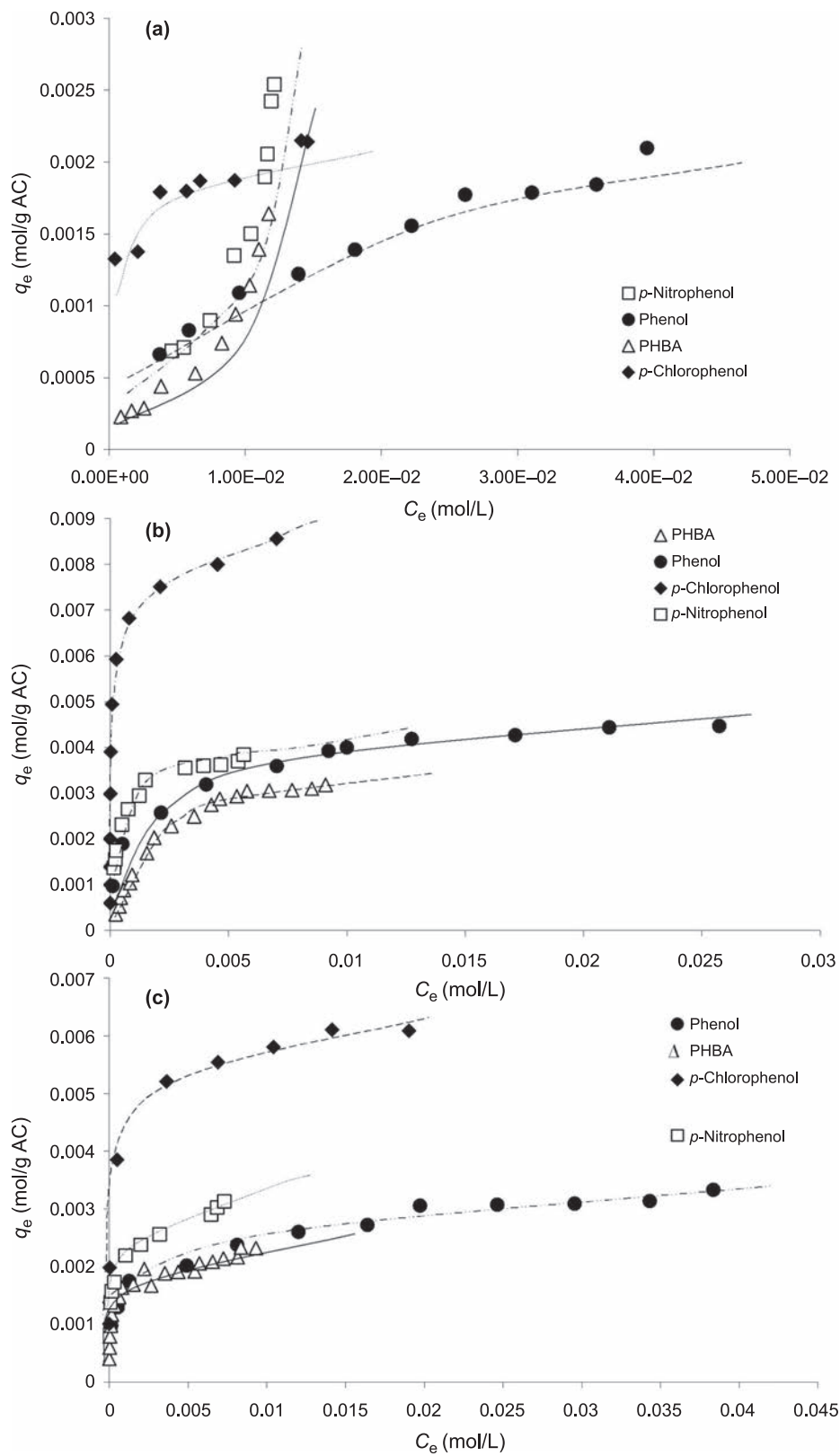


Figure 2. Adsorption isotherms at 25°C of single component of phenol, PHBA, *p*-nitrophenol and *p*-chlorophenol onto activated carbons (a) SBAC, (b) S23 and (c) F22.

layers, remove electrons from the π -electron system, so creating positive holes in the conducting π -band of the graphite layer, and weakening interaction between the π -electron of the phenol aromatic ring and π -electron of the graphite layer leading to reduce the phenols uptake [36].

The sludge-made activated carbon also displayed a distinctive chemical composition; its carbon content was much lower whereas its ash, oxygen and nitrogen contents were higher than in commercial activated carbons.

While S23 and F22 have nearly the same surface area, S23 exhibits the greatest adsorption capacities. This seems to be related to the basic nature of this activated carbon where the basic functional group present on carbon surface acts as an electron-donor and interacts with the aromatic ring of phenols as electron-acceptor in a complex donor-acceptor mechanism [32].

3.2.2. Effect of the adsorbate nature

Prior to analysis of the competitive effect on the equilibrium adsorption of different substituted phenols, it was necessary to obtain the single adsorption isotherm for each compound in aqueous solution.

The single component isotherms revealed the strongest adsorption capacity for PCP whichever activated carbon was used, followed by PNP, P and PHBA (Figure 2). Different behaviour was observed in the case of SBAC at higher concentrations; the adsorption capacities were increased strongly for PNP and PHBA, and the isotherms of these two compounds were represented by type II isotherm, whereas type I is convenient for all the other adsorption isotherms [37]. A type II isotherm indicates a multilayer adsorption consecutive to additional interactions between the molecules. The possibility of the formation of these adsorbates is due to the mesoporous nature of SBAC (Table 2); it is not observed for the other microporous activated carbons.

The activated carbons are mainly hydrophobic and display a strong affinity for organic molecules with a limited solubility in water. Hydrophobic compounds tend to be pushed to the adsorbent surface and hence they are more adsorbed than hydrophilic compounds [7]. The higher capacity for PCP may be essentially explained according to the hydrophobicity of the adsorbed molecules. Among these four phenols, PCP is more hydrophobic than PNP, P and PHBA, as expected from the magnitude of the octanol-water partition coefficient; $\log K_{ow,PCP} < \log K_{ow,PNP} < \log K_{ow,P} < \log K_{ow,PHBA}$ (Table 1).

On the other hand, the adsorption capacities are known to depend on the solubility of the phenols

compounds in water. Moreno-Castilla *et al.* [38] reported that the adsorption capacity increased with decreased water solubility of the phenolic compounds. In the present study, this parameter seems to be secondary since PHBA is the less adsorbed although it is the less soluble compound (Table 1).

Another parameter generally taken into account is the dispersive interactions between the activated carbon (electron donating) and the aromatic molecules (electron accepting). The functional groups present at the surface of the activated carbon can decrease or increase the electronic density of the graphitic planes [39]. At the same time, the chemical structure of the molecule can also play an important role in the adsorption, where the nature of substituents could increase (electron donating effect) or decrease (electron withdrawing effect) the electron density of the aromatic ring and influence the interactions between the surface groups and the aromatic ring [32,38].

At a value $\text{pH} < \text{pKa}$, the phenol compounds are in the non-ionized forms and the electrostatic interactions do not play an important role in the adsorption phenomenon. The interaction between the carbon surface and the phenols in this case can be attributed to dispersion effects. The enhanced interaction in the case of PNP and PCP is due to the electron-withdrawal effect of their $-\text{NO}_2$ and the $-\text{Cl}$ substituents, respectively, as they reduce the overall electron density of the aromatic ring, increasing its ability to accept the electron of the graphite layers of the activated carbon [17,38,40].

For a comparison of single solute isotherm results in a quantitative manner, the isotherms were described by the Langmuir and Freundlich models; the constants obtained according to these two models are listed in Table 6. The correlation coefficients square (R^2) for both models at 25°C suggested that the empirical Langmuir equation was more convenient than Freundlich equation in describing the behaviour of PCP, PNP, P and PHBA adsorption onto the two commercial activated carbons (S23 and F22). However, for SBAC, the Freundlich model was found to better represent the adsorption data for PNP, P and PHBA, while the Langmuir model described well the data of PCP.

The convenience of the Langmuir equation for the two commercial activated carbons clearly indicates that S23 provides the highest maximum adsorption capacity (q_{max}) for the four phenols, and the best adsorption equilibrium constant (K_L) for P and PCP. The higher value for PCP proves its high affinity with this carbon surface compared with the other phenols studied in this work. For F22, the values of K_L are nearly the same for PCP, PNP and PHBA, and the higher value of q_{max} again indicates more affinity of PCP with the carbon surface.

3.3. Competitive adsorption isotherms

The studies of such competitive systems, especially those containing a large number of solutes, are very complex and rarely detailed. Many factors influence adsorption equilibria such as the structural and energetic heterogeneity of the adsorbent and the differences in physicochemical properties of adsorbates, which makes it a very difficult problem [7].

The results of competitive adsorption of an equimolar mixture of four phenols onto SBAC, S23 and F22 are shown in Figures 3(a), (b) and (c), respectively.

Whichever the activated carbon, the adsorption isotherms of these phenols range in the following order: PNP > PCP > PHAB or P (Table 1). For these two last phenols, the order depends on the activated carbon and the phenols' concentrations. At high concentrations, an inversion of selectivity between PHBA and P onto SBAC and S23 was observed. This result was in agreement with that obtained by Monneyron *et al.* [41] who reported that, as the concentration increases, solubility is considered the critical factor for the adsorption of phenols.

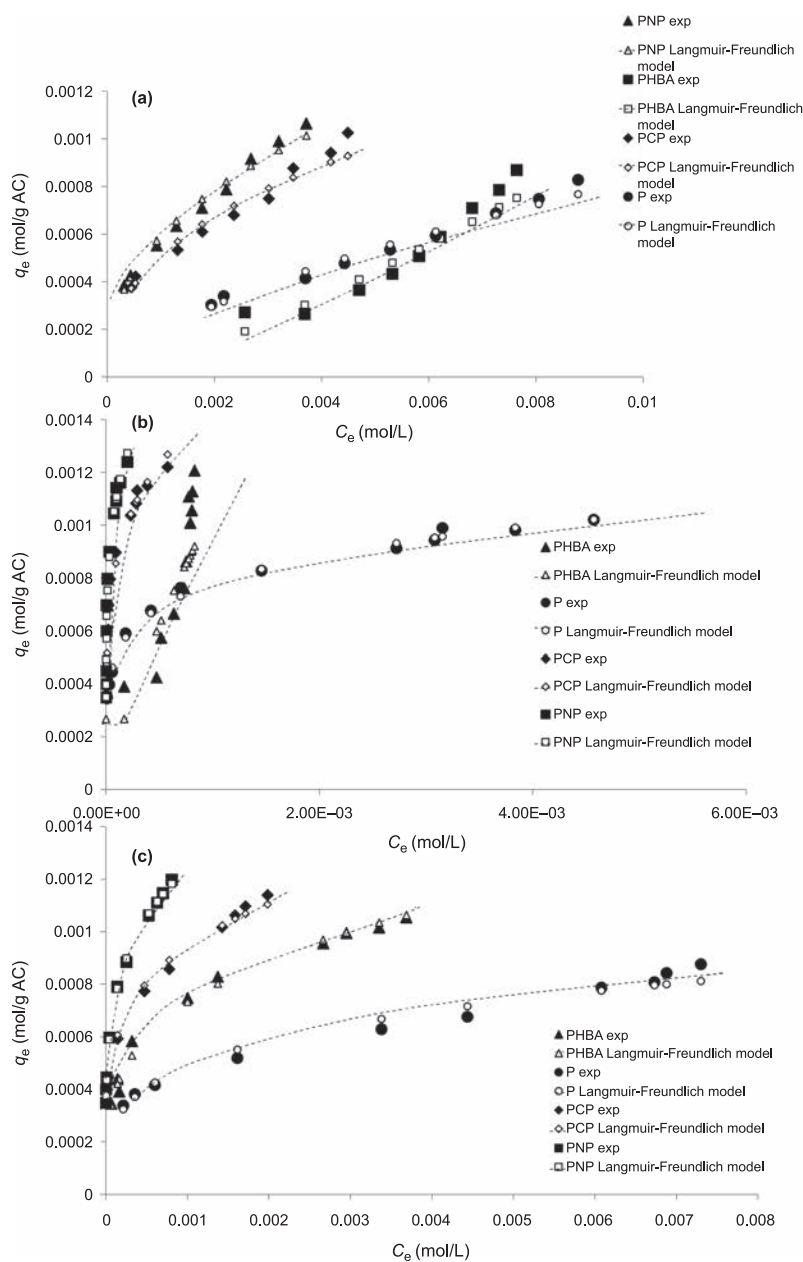


Figure 3. Comparison of experimental data of adsorption isotherms at 25°C with the calculated data by the Langmuir-Freundlich model for an equimolar mixture of phenol, PHBA, *p*-nitrophenol and *p*-chlorophenol onto (a) SBAC, (b) S23 and (c) F22.

Different authors have reported that the order of adsorption affinity may be interpreted on the basis of the chemical and physical characteristics of molecules and the nature of the different groups located on the aromatic ring [42–47]. Among the four phenols investigated here, the order of decreasing solubility is PHBA < PNP < PCP < P which does not at all correspond to the order of single adsorption. However, the hydrophobic nature of the adsorbate could be taken into account; PNP and PCP, which have hydrophobic characteristics, are adsorbed to a greater extent than P and PHBA, which have hydrophilic groups [17]. Finally, it appears that various chemical characteristics of the phenols are involved in the competition.

As shown previously among the four substituted phenols used in this work, PNP is the most strongly adsorbed followed by PCP, whereas phenol is the least adsorbable. This is in accordance with Srivastava and Tyagi [10] who reported that PNP is preferentially adsorbed in PNP–PCP mixtures. It is in agreement with the well-known theory of the formation of π – π bonds, where activated carbon acts as an electron donor and the solute benzene ring has an electron-withdrawing character [48]. The nitro-group of nitrophenol is electron withdrawing, thereby causing a decrease in electron density of the π -electrons of the benzene ring. Therefore, dispersion forces between the carbon surface and the phenolic compound are expected to be the strongest for PNP. In the order of preferential adsorption, PCP is the second adsorbable compound owing to the withdrawing effect of its -Cl group [49].

In the field of competitive adsorption, several complex models have been formulated in the literature. In this study, the modified three parameters Langmuir–Freundlich model was applied. The simple formula makes this model very attractive. Although not thermodynamically consistent, this expression (Equation (3)) has been shown to provide a reasonably good empirical correlation of multicomponent equilibrium data on the adsorbent. Moreover, the parameter n characterizes the heterogeneity of the adsorbent surface with respect to the adsorbing molecules [17]. The Langmuir–Freundlich model was initialized with the parameters obtained from the Langmuir and Freundlich models of single solute isotherms. The values of the Optimized Extend Langmuir–Freundlich model parameters were then calculated minimizing the residual sum of squares (RSS) expressed by Equation (4).

Statistical analysis of the multicomponent isotherms data obtained at 25°C shows that the equilibrium data for all the pollutants fitted well to the Langmuir–Freundlich model (Table 7). For the three activated carbons, the higher values of correlation

Table 7. Correlation coefficient (R^2) residual sum of squares (RSS) objective function values (F_{OBJ}) and the relative average deviation (RAD) for multicomponent system using the Langmuir–Freundlich model.

ACs	Phenol	R^2	RSS	F_{OBJ}	$RAD\%$
S23	P	0.9945	2.88E-07	0.7765	6.4708
	PCP	0.9623			
	PNP	0.9923			
	PHBA	0.7897			
F22	P	0.9730	2.39E-08	0.0676	0.6756
	PCP	0.9949			
	PNP	0.9981			
	PHBA	0.9902			
SBAC	P	0.9782	6.92E-08	0.2340	2.6002
	PCP	0.9606			
	PNP	0.9846			
	PHBA	0.9335			

coefficient (R^2) and the lower values of residual sum of squares (RSS), the objective function values (F_{OBJ}) and the relative average deviation (RAD) obtained with this model confirm the good agreement between the experimental and calculated data for the four-component system.

4. Conclusions

Despite the rather low surface area, it may be concluded that the dried activated carbon resulting from sludge treatment (SBAC) shows an adsorption capacity of about half those of high-performance commercial activated carbons. As it may still be improved, it should be considered as a convenient low-cost material for the removal of phenol and substituted phenols from polluted water. Production of SBAC from sludge thus constitutes a possible way of valorisation of this abundant waste.

Concerning adsorption features of four phenols on various activated carbons, it may be concluded that for single-solute adsorption, hydrophobicity is the main factor to explain the higher capacity of adsorption of PCP.

Studies on competitive adsorption have been performed to give an insight into some of the factors affecting selective uptake of various phenols on activated carbon from multi-solute aqueous solutions. The preferential adsorption of PNP followed by PCP could be explained by the electron-withdrawing effect of the -NO₂ group and -Cl group. The simple Langmuir–Freundlich model gives satisfactory results for describing the four component experimental data.

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