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Competitive adsorption and desorption of a bi-solute mixture: effect of activated carbon type

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Abstract This study aims to clarify the effects of carbon activation type and physical form on the extent of adsorption capacity and desorption capacity of a bi-solute mixture of phenol and 2-chlorophenol (2-CP). For this purpose, two different PACs; thermally activated Norit SA4 and chemically activated Norit CA1, and their granular countertypes with similar physical characteristics, thermally activated Norit PKDA and chemically activated Norit CAgran, were used. The thermally activated carbons were better adsorbers for phenol and 2-CP compared with chemically activated carbons, but adsorption was more reversible in the latter case. 2-CP was adsorbed preferentially by each type of activated carbon, but adsorption of phenol was strongly suppressed in the presence of 2-CP. The simplified ideal adsorbed solution (SIAS) model underestimated the 2-CP loadings and overestimated the phenol loadings. However, the improved and modified forms of the SIAS model could better predict the competitive adsorption. The type of carbon activation was decisive in the application of these models. For each activated carbon type, phenol was desorbed more readily in the bi-solute case, but desorption of 2-CP was less compared with single-solute. This was attributed to higher energies of 2-CP adsorption.

Keywords Activated carbon · Activation method · 2-chlorophenol · Competitive adsorption · Desorption · Irreversible adsorption · Phenol · SIAS model

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1 Introduction

Phenolic hydrocarbons are widely used in pharmaceutical, petrochemical, pulping industries and other chemical manufacturing processes (Chern and Chien 2002). Due to their strong toxicity, persistence in the environment and suspected carcinogenicity (Quan et al. 2005), wastewaters containing phenolic compounds should be treated before discharge into water bodies. Particularly, chlorophenols are an important class of aromatic pollutants in industrial wastewaters because of their wide use in the production of preservers, pesticides and biocides (Quan et al. 2005). Chlorinated phenols can exist up to 100–200 mg/L in contaminated environments (Sahinkaya and Dilek 2005). However, phenolic compounds are usually poorly degraded in conventional wastewater treatment systems. But, they can be effectively removed by activated carbon adsorption (Carvalho et al. 2001).

In the application of adsorption processes, reversibility of adsorption is usually as important as adsorption. There are two possible mechanisms leading to irreversible adsorption. One of them is the high energy bonding of adsorbate molecules to specific functional groups on the active sites of carbon surface resulting in covalent bonding. This phenomenon is called chemisorption. Second is the oxidative polymerization of phenolic compounds onto activated carbon due to the presence of oxygen (Aktaş 2006).

A previous study showed that carbon activation type was very important in terms of adsorption capacity of phenol (Aktaş and Çeçen 2006a). Desorption capacity, or in other words reversibility of adsorption, was also very much related to the activated carbon type, particularly to the activation method (Aktaş and Çeçen 2006a). In particular, desorption capacity was of crucial importance because bioregeneration of activated carbon in systems combined with

Table 1 Properties of activated carbons used in the experiments

Activated carbon	SA4	CA1	PKDA	CAgran
Physical form	powdered	powdered	granular	granular
Activation method	thermal	chemical	thermal	chemical
Apparent density (g/L)	545	370	295	225
Moisture (%)	2	11	2	12
Ash content (%)	8	2	8	3
Molasses number	525	180		165
Methylene Blue adsorption (g/100 g)	11	29		29
Iodine number (mg g^{-1})	700		750	
Total surface area (BET) (m^2/g)	800	1400	850	1400
Particle size distribution	$D_{10} = 3$ µm	$D_{10} = 7$ µm	0.5% >2 mm	1% > 1.7 mm
	$D_{50} = 29$ µm	$D_{50} = 28$ µm	99% > 0.59 mm	2% < 0.84 mm
	$D_{90} = 161$ µm	$D_{90} = 75$ µm		
Porosity				
Total pore volume (cm^3/g)	0.80	1.55	1.19	1.64
Micro ($\Phi < 2$ nm)	0.25	0.45	0.30	0.40
Meso (Φ 2–50 nm)	0.19	0.75	0.19	0.70
Macro ($\Phi > 50$ nm)	0.36	0.35	0.70	0.54

biological treatment was very much related to reversibility of adsorption (Aktaş and Çeçen 2006b). Studies with 2-chlorophenol (2-CP) as a single-solute (Aktaş and Çeçen 2007) were compared with single-solute phenol studies (Aktaş and Çeçen 2006a). 2-Chlorophenol was better adsorbed than phenol, but desorbed less than phenol for each type of activated carbons, which were also used in the present study.

The competitive adsorption of aromatic compounds from a multi-component mixture on activated carbon has been extensively investigated in literature (DiGiano et al. 1980; Fritz et al. 1980; Singer and Yen 1980; Knettig et al. 1986; Yonge and Keinath 1986; Garner et al. 2001; Garcia-Araya et al. 2003). However, there is a lack of knowledge in literature about the effect of both carbon activation type and physical form (PAC or GAC) on adsorption of bi-solute mixtures and reversibility of adsorption. Hence, this study aims to clarify the effect of activated carbon type and physical form of carbon on the extent of adsorption capacity and desorption capacity of a bi-solute mixture of phenol and 2-chlorophenol. For this purpose, two different PACs; thermally activated Norit SA4 and chemically activated Norit CA1, and their granular countertypes with similar physical characteristics, thermally activated Norit PKDA and chemically activated Norit CAgran, were used for determination of the extent of adsorption capacity and reversibility of adsorption. As model compounds phenol and 2-chlorophenol were used in combination and the results were compared with the previous single-solute studies with phenol and 2-CP (Aktaş and Çeçen, 2006a, 2007).

2 Materials and methods

2.1 Activated carbon characteristics

Norit SA4 and its granular countertype PKDA are peat-based carbons steam activated at 850–1000 °C. Norit CA1 and its granular countertype CAgran are wood-based carbons produced by chemical activation using the phosphoric acid process at a temperature of 500 °C. After the activation process, the bulk of the acid is recovered through water washing. The characteristics of the four commercial carbon types can be seen in Table 1. All activated carbon samples were obtained from the Norit Company, the Netherlands. The surface area of the carbons were determined by the Norit Company from the N_2 isotherm according to the BET 3 parameters method. Following IUPAC recommendations, the pore size distribution was determined by the Norit Company according to the volume distribution method, which was based on analytical data consisting of the bulk density (ASTM), the density in mercury, mercury porosimetry, density in benzene and benzene adsorption isotherm. The macropore volume was taken from the standard listing of porosimetry results as the difference between the volumes at $\Phi = 50$ nm and $\Phi = 15000$ nm. The mesopore and micropore volumes were calculated by the Norit Company from the benzene isotherms using the Kelvin method. The micro- and mesopore volumes, dominating the adsorptive capacities, do not differ very much between the powdered and granular countertypes. However, in the production of powdered carbons, the larger macropores are milled away, resulting in significant differences compared to the granules.

2.2 Adsorption experiments

The first step in the experimental work consisted of the determination of bi-solute phenol and 2-CP adsorption capacities for each activated carbon type in batch adsorption tests. Adsorption studies were performed in 100 mL flasks shaken at 140 RPM and 25 °C. For determination of the adsorption isotherms, different masses of activated carbon (200–4000 mg/L) were contacted with fixed concentrations of phenol and 2-CP (200 mg/L of each). KH_2PO_4 (1000 mg/L) and K_2HPO_4 (1000 mg/L) were dissolved in the mixture to adjust pH to 7 and the mixture was agitated until reaching equilibrium. Adjustment of pH to 7 prevented dissociation of phenol and 2-CP, which have pK_a (dissociation constant) values of 9.99 and 8.48, respectively. The equilibrium time was determined to be less than 7 days in previous single-solute adsorption studies (Aktaş and Çeçen, 2006a, 2007). Hence, agitation time was set as 7 days for each carbon type. Finally, initial and final equilibrium concentrations in the adsorption flasks were measured and used for the construction of adsorption isotherms.

2.3 Desorption experiments

The second step consisted of the determination of phenol and 2-CP desorption capacity for each activated carbon type in batch desorption tests. Desorption studies were performed in 250 mL flasks shaken at 140 RPM and 25 °C. Desorption of the target compounds was conducted to determine the degree of reversibility of adsorption for each activated carbon. Desorption isotherms were constructed according to a batch-displacement technique. Activated carbon (2000 mg/L) was initially contacted with an excess amount of phenol (500 mg/L) and 2-CP (250 mg/L) and was agitated for 7 days until equilibrium was reached as in adsorption batches. KH_2PO_4 (1000 mg/L) and K_2HPO_4 (1000 mg/L) were also added to mixture both at initial loading of carbons and at each desorption step to adjust pH to 7. After initial adsorption equilibration, the supernatant was removed by centrifugation and the sorbate concentration in the supernatant was measured. The supernatant was replaced by distilled water buffered with phosphate. Desorption equilibrium was previously determined as 24 hours both for phenol and 2-CP (Aktaş and Çeçen, 2006a, 2007). Upon equilibration, the concentrations in the liquid phase were measured. Desorption was conducted successively until the phenol or 2-CP concentrations in the supernatant were under the detection limit of about 0.2 mg/L. A succession of desorption steps produced a desorption isotherm. After each successive desorption step, the new hypothetical activated carbon loading remaining for the following desorption step (q_i) was calculated by subtracting the amount of desorbed phenol from the activated carbon loading at the beginning of the desorption step as shown by (1).

$$q_i = \frac{X_a - \sum (X_d)_i}{M} \tag{1}$$

where X_a is the initial phenol loading on the carbon (mg), X_d is the mass of phenol desorbed after each ith desorption step (mg) and M is the mass of activated carbon used in each desorption experiment (g).

2.4 Analyses

Phenol and 2-CP concentrations were determined with an Agilent 6890N gas chromatograph equipped with an FID (Flame Ionization detector) and HP-5 column (length 30 m, ID 0.32 mm, film thickness 0.25 µm). Helium was used as the carrier gas at the splittless mode with a flow rate of 25 cm/sec. The inlet temperature was 240 °C and detector temperature was 300 °C. The oven temperature was held at 40 °C for 1 min, increased to 140 °C at 10 °C/min and then increased to 260 °C at 20 °C/min. 1 mL sample was extracted with 0.5 mL methylene chloride in 2 mL closed vials for 3 minutes and 2 µL of the methylene chloride phase was injected with an auto-injector.

3 Results and discussion

3.1 Adsorption studies

The isotherm data for the competitive adsorption of phenol and 2-chlorophenol on each activated carbon type are plotted in Fig. 1 as closed data points. In order to compare competitive adsorption with single-solute adsorption, the previously obtained single-solute adsorption data (Aktaş and Çeçen, 2006a, 2007) were also included in Fig. 1 as open data points. Figure 1 also contains the model lines, which will be investigated in the succeeding section. The competitive adsorption data for phenol did not fit the Freundlich equation for any of the activated carbon types although the previous single-solute data had satisfied this condition (Aktaş and Çeçen 2006a). The competitive adsorption data for 2-CP fitted the Freundlich equation below, as in the previous single-solute adsorption isotherms with this compound (Aktaş and Çeçen 2007). The Freundlich adsorption isotherm constants for 2-chlorophenol are shown in Table 2.

$$q = \mathrm{K}C^n \tag{2}$$

q = adsorption capacity of the activated carbon (mg adsorbate adsorbed/g carbon), C = the equilibrium adsorbate concentration (mg/L). K and n are the Freundlich constants (Freundlich exponent and slope).

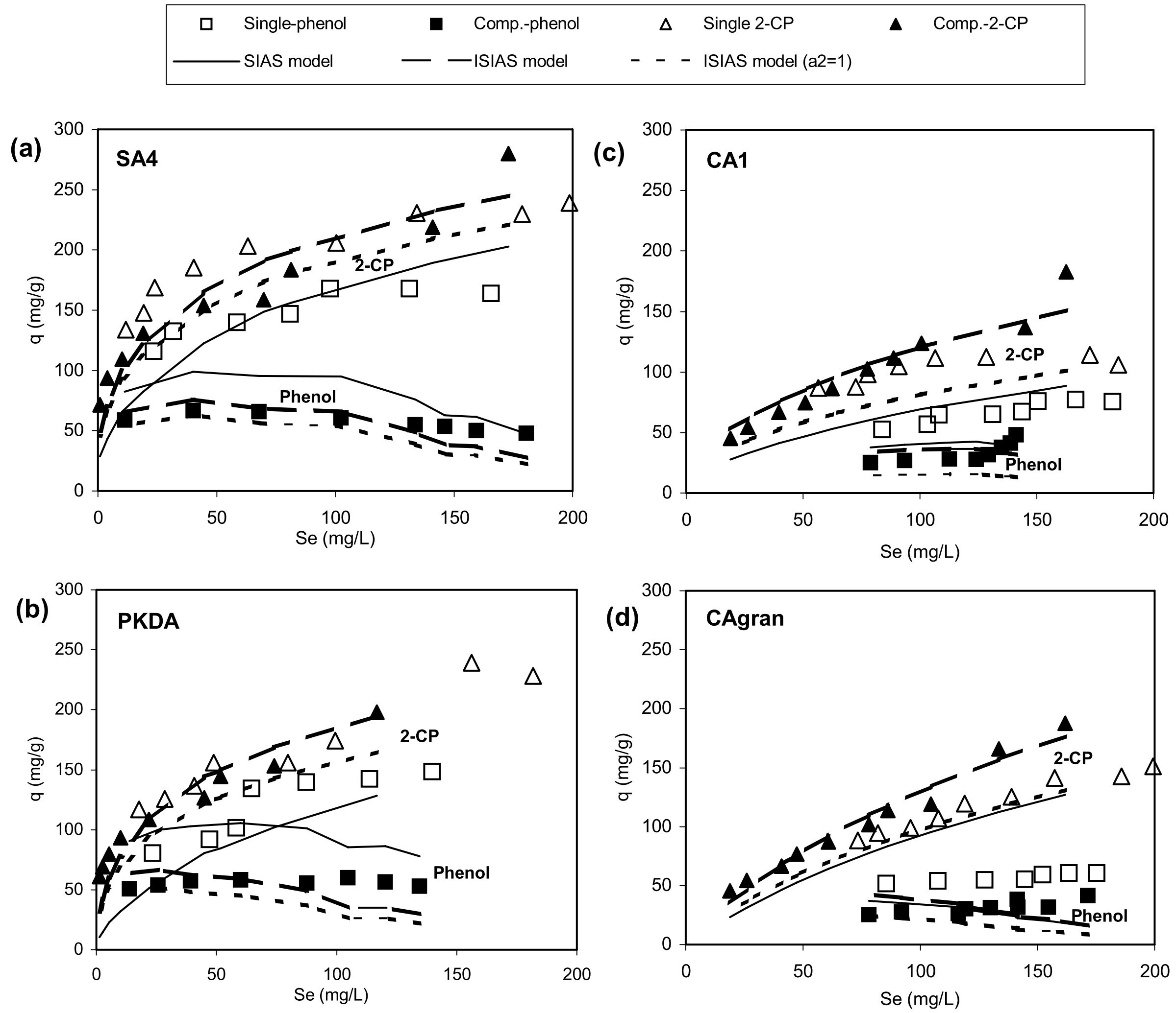


Fig. 1 Competitive bi-solute and single-solute adsorption isotherms for phenol and 2-CP with their Simplified Ideal Adsorbed Solution (SIAS) and Improved SIAS (ISIAS) model fits for (**a**) SA4, (**b**) PKDA, (**c**) CA1, (**d**) CAgran (*open data points* refer to single-solute adsorption, *closed data points* refer to bi-solute adsorption, *full lines* refer to SIAS model fits, *dashed lines* refer to ISIAS model fits)

Table 2 Freundlich isotherm constants for 2-chlorophenol in the presence of phenol (bi-solute case) and in the absence of phenol (single-solute case)

	Carbon type	Physical form	Activation method	K [(mg/g) (L/mg)^n]	n	R^2
Bi-solute	SA4	Powdered	Thermal	66.30	0.2387	0.95
	CA1	Powdered	Chemical	7.18	0.6113	0.98
	PKDA	Granular	Thermal	54.59	0.2435	0.97
	CAgran	Granular	Chemical	6.25	0.6528	0.98
Single-solute	SA4	Powdered	Thermal	86.51	0.1947	0.96
	CA1	Powdered	Chemical	13.58	0.4064	0.97
	PKDA	Granular	Thermal	60.40	0.2265	0.93
	CAgran	Granular	Chemical	8.20	0.5526	0.98

The K value, which is an indicator of adsorption capacity, was lower for the competitive adsorption of 2-CP compared with the single-solute adsorption for each type of activated carbon. Previous single-solute 2-CP adsorption studies (Aktaş and Çeçen 2007) had resulted in higher K values compared with the bi-solute K values obtained in the present study (Table 2). The adsorption intensity, n, was shown by the slope of the adsorption isotherm curves (Fig. 1). In competitive adsorption, n values were higher (Table 2) compared with the previous single-solute values. In both single-solute and bi-solute adsorption, the thermally activated carbons were obviously better adsorbers for 2-chlorophenol as shown by higher K and lower n values (Table 2). This was attributed mainly to the changes in surface chemical properties, which were related to the type of activation method in previous studies (Aktaş and Çeçen, 2006a, 2007). Chemical treatment of carbons CA1 and CAgran with phosphoric acid resulted in an acidic surface. When the solution was not buffered with phosphate salts, pH decreased to a value as low as 3.2 in the presence of chemically activated carbons due to the acidic surface functional groups. Acidic surface properties are associated with the formation of oxygen-containing surface functional groups and higher polarity of the activated carbon. This leads to water adsorption by means of hydrogen bonding on oxygen-containing functional groups, and clustering of additional water molecules around adsorbed water molecules. Such water clusters can prevent pollutant access to hydrophobic regions on the carbon surface, reduce interaction energy between the pollutant and carbon surface and block pollutant access to micropores (Knappe et al. 2003; Puri 1980). The negative influence of surface oxides has been also attributed to the depletion of the electronic π-band of graphite-like layers resulting in consequent lowering of van der Waals forces of interaction (Puri 1980) and also reduced oxidative polymerization of phenols (Garcia-Araya et al. 2003).

For each carbon type, 2-CP adsorption was not negatively affected by the presence of phenol. However, phenol adsorption was suppressed to a great extent in the competitive presence of 2-CP (Fig. 1). Similar adsorption of 2-CP in bi-solute and single-solute systems showed that 2-CP was adsorbed preferentially, but phenol was adsorbed competitively. According to Sontheimer et al. (1985) also, the better adsorbable compound influences the adsorption capacity of the weakly adsorbable one more than the opposite. In such a case, adsorption data of the weakly adsorbable compound takes a curved shape (Sontheimer et al. 1985), as seen in the case of phenol in this study (Fig. 1). This points out the presence of a preferentially adsorbed compound, which is 2-CP in this case. The shape of 2-CP data was not curved, which showed preferential adsorption. According to Sontheimer et al. (1985), the higher n values for 2-CP in the bi-solute case also show that there was still competition between phenol and 2-CP although 2-CP was adsorbed preferentially.

According to the Polanyi-Manes adsorption potential theory, the conditions for adsorption were satisfied only for one adsorbate (Knettig et al. 1986), which was 2-CP in this study. Moreover, at low carbon dosages resulting in higher 2-CP equilibrium concentrations, the bi-solute adsorption of 2-CP exceeded single-solute adsorption, best seen for CA1 and CAgran (Fig. 1). These experimental results suggested that adsorption of 2-CP was favoured, similar to other phenolic adsorbates where adsorption of one component was favoured (Garcia-Araya et al. 2003). Similar results were also reported in a previous study (Fritz et al. 1980) for the p-nitrophenol and phenol couple, where p-nitrophenol was preferentially adsorbed. Also in that study, there was only a weak reduction in p-nitrophenol adsorption capacity, whereas phenol adsorption was very much reduced due to competition (Fritz et al. 1980). However, Knettig et al. (1986) had previously reported non-competitive adsorption for both phenol and 2-CP, probably due to the carbon type and concentration range studied.

The difference between single-solute and bi-solute adsorption of phenol was much more obvious in the case of thermally activated carbons SA4 and PKDA. These carbons adsorbed phenol much better than the chemically activated ones in the case of single-solute (Aktaş and Çeçen 2006a). The preferential adsorption of 2-CP by the thermally activated carbons resulted in a drastic decrease in phenol adsorption.

Although 2-CP adsorption did not decrease much in the presence of phenol, the total amount of adsorbed phenol and 2-CP increased in bi-solute adsorption. This was because in addition to 2-CP adsorption, some phenol was also adsorbed. The amounts of phenol adsorbed in addition to 2-CP were as high as 57.4 ± 6.9 mg/g for SA4, 33.3 ± 8.1 mg/g for CA1, 55.7 ± 3.0 mg/g for PKDA and 31.5 ± 5.3 mg/g for CAgran. In the case of competitive adsorption, phenol loadings were still higher for thermally activated carbons than chemically activated ones. This enhancement of cumulative adsorption for bi-solute mixtures of aromatic compounds was also observed in other studies, generally for phenol and substituted phenols. It was mainly attributed to the influence of differences in molecular size (Garner et al. 2001). However, there are also studies in literature reporting that cumulative adsorption capacities for a mixture of phenolic compounds were lower than those for individual compounds (Knettig et al. 1986).

3.2 Description of competitive adsorption using models

The loadings on activated carbon (q) in the case of competitive adsorption can be modelled by using the single-solute adsorption parameters. The Ideal Adsorbed Solution (IAS)

Table 3 ISIAS model competition factors for phenol and 2-CP

Carbon type	a_1 (phenol)	a_2 (2-CP)	RSS/data points (mg^2/g^2)	a_1 ($a_2 = 1$)	RSS/data points ($a_2 = 1$) (mg^2/g^2)
SA4	1.030	0.894	300	1.179	469
CA1	0.900	0.645	118	n.a.	n.a.
PKDA	1.132	0.836	286	1.392	525
CAgran	0.817	0.732	116	n.a.	n.a.

a_1 a_2: competition factors in (6) for phenol and 2-CP, respectively

n.a.: not applicable

model originally developed to describe competitive adsorption of gases was extended by Radke and Prausnitz (1972) to aqueous mixtures of solutes. DiGiano et al. (1980) provided a Simplified Ideal Adsorbed Solution (SIAS) model to simplify the handling of mathematical equations. According to the SIAS model, the individual loadings in the mixture can be calculated from the equation below;

$$q_i = K'^{\left(\frac{n'-1}{n'}\right)} \left[K_i C_i^{n_i}\right]^{1/n'} \left[\sum_N \left(\frac{K_i}{K'} C_i^{n_i}\right)^{1/n'}\right]^{(n'-1)} \tag{3}$$

where q_i = solid-phase equilibrium concentration of solute i, K_i, n_i = single-solute empirical Freundlich constants for solute i, C_i = liquid-phase equilibrium concentration of solute i, n' = average value of n_i, and K' = average value of K_i.

The SIAS model was modified by Yonge and Keinath (1986) and the Improved Simplified Ideal Adsorbed Solution (ISIAS) model was developed in order to account for non-ideal competition for adsorption sites by adding a competition factor, a. This model equation can be seen in (4).

$$q_i = K'^{\left(\frac{n'-1}{n'}\right)} \left[\frac{K_i}{a_i} C_i^{n_i}\right]^{1/n'} \left[\sum_N \left(\frac{K_i/a_i}{K'} C_i^{n_i}\right)^{1/n'}\right]^{(n'-1)} \tag{4}$$

where

$$K' = \frac{\sum (K_i/a_i)}{N}.$$

The single-solute Freundlich parameters obtained in previous studies (Aktaş and Çeçen 2006a, 2007) were used to predict the competitive bi-solute loadings using both the SIAS and ISIAS models. The SIAS model could not predict the experimentally measured loadings for each activated carbon type although it could roughly estimate the trend of the actual curve (Fig. 1). The SIAS model underestimated 2-CP loadings on each type of activated carbon. However, the model overestimated phenol loadings, particularly those on thermally activated carbons SA4 and PKDA (Fig. 1a, b), whereas overestimation was not clear for chemically activated carbons CA1 and CAgran (Fig. 1c, d). The results obtained with the SIAS model showed that ideal adsorbed solution theory (IAST) failed to describe the bi-solute data. Competition between phenol and 2-CP was non- ideal, but in the direction to favor 2-CP adsorption. Although the single-solute adsorption data had indicated higher adsorption capacity of 2-CP compared with phenol, much more adsorption of 2-CP took place in bi-solute mixture than predicted from single-solute adsorption. Besides the ideal adsorbed solution theory, the bi-solute data was also investigated using the Langmuir competitive model as described by Singer and Yen (1980). The Langmuir model also could not predict the actual bi-solute data and resulted in overestimation of phenol and underestimation of 2-CP adsorption (data not shown here). This was attributed to the fact that the competitive Langmuir model does not have a thermodynamic basis, and the assumptions of a homogeneous surface and uniform adsorption are not valid for activated carbon (Singer and Yen 1980).

The non-ideal competition between phenol and 2-CP necessitated the use of the ISIAS model. The ISIAS model requires the determination of optimum a_i values in (4), where a_1 and a_2 refer to the competition factors for phenol and 2-CP, respectively. The optimum a_1 and a_2 values were determined by nonlinear programming which provides the lowest residual sum of squares (RSS) of competitive bi-solute data. RSS is the sum of squares of the error (difference between the experimental and model q values). The optimum a_1 and a_2 values and corresponding lowest RSS values for each type of carbon are presented in Table 3.

The ideal adsorbed solution theory (IAST) assumes that adsorption sites are equally accessible to both solutes and adsorption is reversible (Knappe et al. 2003). The competition factors reported as a_i values in Table 3 denote deviations from IAST. The a_i values distant from 1 indicate that the competitive adsorption becomes more distant from ideal competition. Particularly, a_2 values of 2-CP adsorption were much smaller for chemically activated carbons (CA1 and CAgran) compared with thermally activated carbons (SA4 and PKDA). This showed that competitive adsorption of 2-CP on chemically activated carbons was more distant from ideality in favor of 2-CP adsorption.

Different degrees of irreversible adsorption were previously reported both for phenol and 2-CP as single-solutes (Aktaş and Çeçen, 2006a, 2007) and also for bi-solute adsorption in this study (see Sect. 3.3). This irreversible adsorption is a reason for the failure of the IAST as well as the unequal competition for adsorption sites (Yonge and Keinath 1986). The best fit of SIAS model was seen in the case of phenol adsorption on chemically activated carbons (Fig. 1) due to highly reversible adsorption (see Desorption Studies).

Although the ISIAS model provided a reasonable fit for the bi-solute data, the improvement in the IAST obtained by the ISIAS model was the result of parameters that were determined from the bi-solute data itself. In determination of optimum a_1 and a_2 values in (4), bi-solute adsorption data were also required besides the single-solute adsorption parameters. Yonge and Keinath (1986) suggested a correlation between competition factors and the solubility of competing solutes in order to make the model truly predictive without the use of bi-solute data. They stated that the term associated with the low solubility sorbate (a_2 of 2-CP in this case) was not significant and should be taken as equal to 1, and the term associated with the higher solubility sorbate (a_1 of phenol in this case) resulted in a significant improvement in data description. Based on the inverse relationship between solubility and adsorption capacity, the authors developed a correlation between a_1 and $(\delta_1 - \delta_2)/\delta_1$, where $\delta =$ sorbate solubility and $\delta_1 > \delta_2$.

However, the results of our present study showed that this modification of the ISIAS model was not successful in describing the bi-solute data for the chemically activated carbons used in this study (Fig. 1c, d). Calculated a_1 values were not reliable and therefore were not tabulated in Table 3 for the chemically activated carbons CA1 and CAgran. This showed that this modification of the ISIAS model is not suitable for every type of activated carbon. The modified ISIAS model gave a better fit for the thermally activated carbons SA4 and PKDA (Fig. 1a, b), but a_1 values with the assumption of $a_2 = 1$ were not actually the same for SA4 and its granular countertype PKDA (Table 3). The numerical value of $(\delta_1 - \delta_2)/\delta_1$ was approximately equal to 0.67 for the phenol ($\delta_1 = 8.45\%$) and 2-CP couple ($\delta_2 = 2.8\%$). The empirical relationship between a_1 and $(\delta_1 - \delta_2)/\delta_1$ as shown by Yonge and Keinath (1986) was a very rough estimate and was generalized for aromatic compounds. Data presented by Yonge and Keinath (1986) can be used to develop an empirical equation (5) for a very rough calculation of a_1.

$$a_1 \cong 0.69 * (((\delta_1 - \delta_2)/\delta_1) - 0.26) + 1.035. \tag{5}$$

Using the empirical equation above, a_1 was calculated to be 1.317 for the phenol and 2-CP couple. This value was not equal to the a_1 values obtained in our study, but also was not very distinct from them. Thus, such an empirical relationship between the competition factor and solubilities of solutes may not result in perfect estimations of the competitive data, but can only give a rough idea about it. As also evidenced from Fig. 1 and lower RSS values reported in Table 3, a_1 and a_2 values calculated according to the ISIAS model could give better predictions compared with the modified ISIAS model for the concentration ranges used in this study. However, the differences in a values in Table 3 showed that these should be calculated for each type of carbon. This is necessary because of different activation methods, surface chemical properties, and porosities etc. of every carbon type.

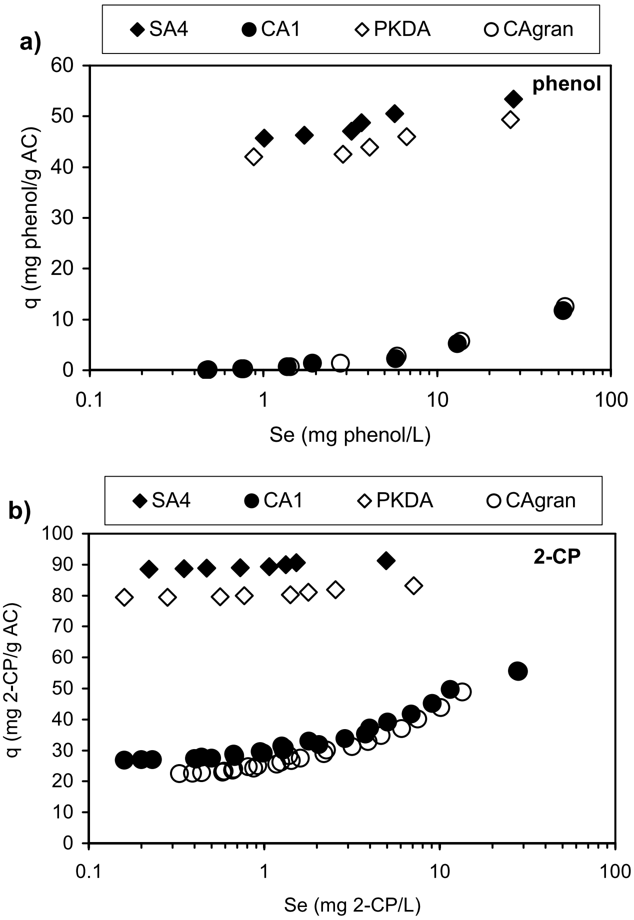


Fig. 2 Competitive desorption isotherms of each activated carbon type for (**a**) phenol and (**b**) 2-CP

3.3 Desorption studies

Bi-solute desorption data for each carbon type were fitted into the Freundlich type isotherm equation with satisfactory correlations. However, desorption data did not fit the Langmuir equation (Aktaş 2006). Desorption isotherms are

Table 4 Freundlich desorption isotherm constants for phenol and 2-CP in the bi-solute and single-solute cases

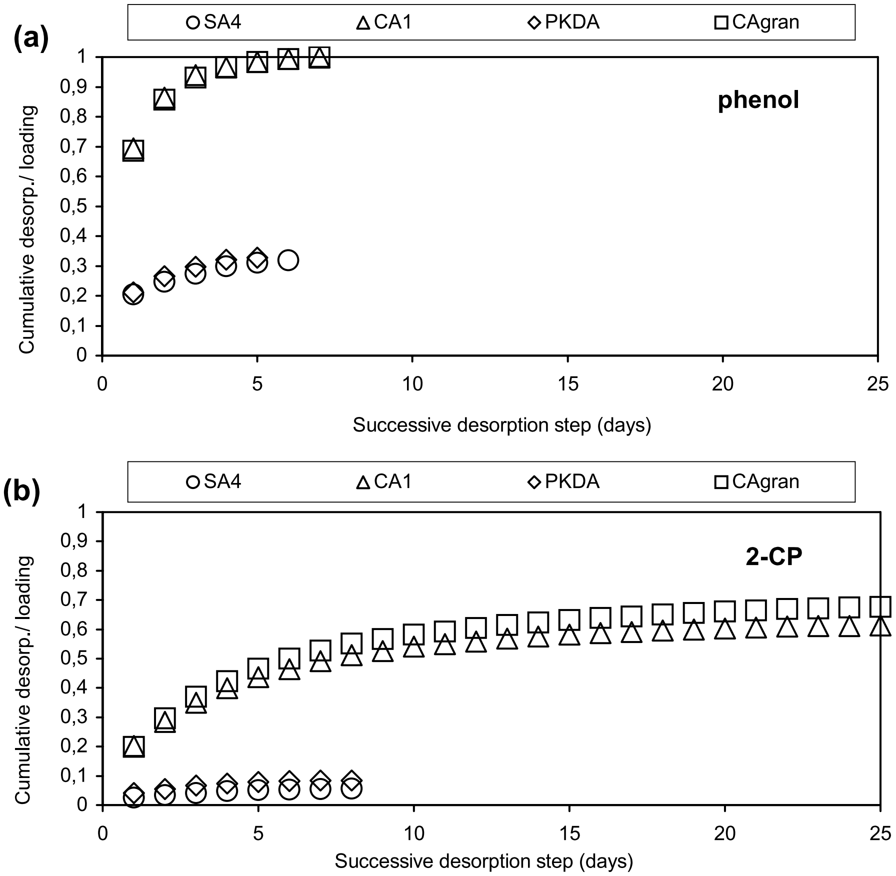
		Carbon type	Initial loading (mg/g carbon)	K [(mg/g) (L/mg)^n]	n	R^2
Bi-solute	phenol	SA4	67.13	45.36	0.0505	0.94
		CA1	38.31	0.30	1.0571	0.87
		PKDA	62.56	41.45	0.0501	0.91
		CAgran	39.88	0.25	1.1390	0.88
Bi-solute	2-CP	SA4	93.81	89.66	0.0110	0.92
		CA1	69.50	30.99	0.1459	0.91
		PKDA	86.73	80.62	0.0125	0.87
		CAgran	69.45	25.83	0.2127	0.97
Single-solute	phenol	SA4	149.35	120.46	0.0242	0.85
		CA1	74.60	8.31	0.307	0.81
		PKDA	120.35	89.29	0.0358	0.89
		CAgran	75.80	9.07	0.2158	0.87
Single-solute	2-CP	SA4	195.25	169.21	0.0348	0.97
		CA1	159.55	39.29	0.2575	0.99
		PKDA	181.30	155.36	0.0320	0.95
		CAgran	160.45	35.42	0.2861	0.99

shown in Fig. 2 and desorption Freundlich isotherm constants are shown in Table 4. High K values for thermally activated carbons SA4 and PKDA showed that both phenol and 2-CP loadings were still high after desorption. In the bi-solute case, desorption capacity of these compounds from thermally activated carbons was lower, as in the case of single-solute desorption (Aktaş and Çeçen 2006a, 2007). Also, lower n values in the case of thermally activated carbons indicated that desorption was more difficult from these carbons. Desorption capacities were higher for the chemically activated carbons CA1 and CAgran both for phenol and 2-CP (Fig. 3). The greater reversibility of adsorption on chemically activated carbons was due to more physical adsorption of phenol and 2-CP on these carbons. The absence of chemisorption for these carbons should be related to water adsorption on surface functional groups most of which contain oxygen. Hydrogen bonding of water with these functional groups prevents chemisorption of phenol and 2-CP on chemically activated carbons. However, functional groups on the surface of thermally activated carbons do not contain oxygen, because thermal treatment results in a decrease in the number of acidic surface functional groups (Julien et al. 1998). Hence, thermally activated carbons possess more chemisorption which resulted in more irreversible adsorption.

Competitive adsorption of phenol and 2-CP in the initial phase of loading of carbons with these compounds resulted in lower phenol and 2-CP loadings (Table 4) compared with the single-solute loadings (Aktaş and Çeçen 2006a, 2007). The reduction in the initial loading resulted in lower K values in the case of bi-solute desorption (Table 4). The previously obtained single-solute K values (Aktaş and Çeçen 2006a, 2007) were higher compared with bi-solute desorption (Table 4). The decrease in K in the bi-solute desorption of both compounds was more notable in the case of thermally activated carbons, which are prone to higher irreversible adsorption. This indicated that competition between phenol and 2-CP was severe for adsorption to more energetically active chemisorption sites. Previously, chemisorption was suggested as the dominant adsorption mechanism for the thermally activated carbons SA4 and PKDA (Aktaş and Çeçen 2006a). On the other hand, oxidative polymerization reactions cannot be considered as a reason for irreversible adsorption in this study, since no oxygen was supplied continuously to the flasks.

On the other hand, n values in bi-solute phenol desorption (Table 4) were higher than single-solute n values for phenol (Aktaş and Çeçen 2006a). However, n values in bi-solute 2-CP desorption (Table 4) were lower than single-solute n values for 2-CP (Aktaş and Çeçen 2007). This showed that phenol was desorbed more easily in the bi-solute case, but desorption of 2-CP was more difficult in this case for each type of activated carbon. Therefore, it is suggested that 2-CP was preferentially adsorbed on adsorption

Fig. 3 Cumulative desorption of (**a**) phenol and (**b**) 2-CP from competitively loaded activated carbons at the end of each successive desorption step



sites with greater energy. On the other hand, phenol was adsorbed on less energetic sites with smaller adsorption energies, so that it was more readily desorbed from each carbon type.

This finding was also supported by much higher desorption efficiencies for phenol although adsorption efficiencies were lower for phenol compared with 2-CP (Table 5). Phenol adsorption efficiencies in Table 5 were also much lower than the previously obtained single-solute adsorption efficiencies (Aktaş and Çeçen 2006a). However, bi-solute 2-CP adsorption efficiencies (Table 5) were close to the single solute adsorption efficiencies (Aktaş and Çeçen 2007). These findings are in agreement with the adsorption studies, which showed that 2-CP adsorption was not negatively affected in the presence of phenol. On the other hand, phenol desorption efficiencies in Table 5 were much higher than the single-solute desorption efficiencies (Aktaş and Çeçen 2006a). Contrary to that, bi-solute 2-CP desorption efficiencies (Table 5) were lower than the single solute desorption efficiencies (Aktaş and Çeçen 2007).

The degree of hysteresis is an indicator for adsorption reversibility, which bases on the difference between adsorption and desorption intensities. The lower reversibility of 2-CP adsorption in the bi-solute case was also shown by the calculation of the degree of hysteresis (w) using (6).

$$w(\%) = (n_{\mathrm{ads}}/n_{\mathrm{des}} - 1) * 100 \tag{6}$$

where n_{des} and n_{ads} are the desorption and adsorption intensities in the Freundlich equation, respectively. Higher degrees of hysteresis were calculated for the thermally activated carbons (Table 5). These were also higher in bi-solute desorption of 2-CP compared with the single-solute values (Aktaş and Çeçen 2007). The degree of hysteresis could not be calculated for phenol, because phenol adsorption did not fit the Freundlich equation.

Figure 3 showed that desorption of all reversibly adsorbed fraction of phenol from all carbon types and that of 2-CP from the thermally activated carbons occurred within 6–8 desorption steps. However, desorption of 2-CP from the chemically activated carbons occurred within 25 desorption steps although cumulative desorption was higher from these carbons. In the case of thermally activated carbons, 2-CP was mainly adsorbed chemically, so those chemically adsorbed 2-CP molecules did not desorb and physically adsorbed 2-CP, which contributes to a very small part in total, was readily desorbed (Fig. 3). On the other hand, most of the adsorbed 2-CP was physically adsorbed on chemically activated carbons. The van der Waals forces, which resulted in

Table 5 Adsorption and desorption efficiencies (carbon dose of 2 g/L) for bi-solute mixtures of phenol and 2-CP and for phenol and 2-CP as a single solute

		Carbon type	Adsorption efficiency (%)	Desorption efficiency (%)	Irreversible adsorption (%)	Degree of hysteresis w (%)
Bi-solute	phenol	SA4	33.4	31.9	68.1	n.a.
		CA1	19.1	99.9	0.1	n.a.
		PKDA	31.2	32.8	67.2	n.a.
		CAgran	19.9	99.9	0.1	n.a.
Bi-solute	2-CP	SA4	86.2	5.7	94.3	2070
		CA1	63.9	61.3	38.7	319
		PKDA	79.7	8.4	91.6	1848
		CAgran	63.8	67.7	32.3	207
Single-solute	phenol	SA4	63.1	20.3	79.7	656
		CA1	31.5	86.6	13.4	57
		PKDA	50.9	25.8	74.2	421
		CAgran	32	87.5	12.5	6
Single-solute	2-CP	SA4	80.3	12.9	87.1	459
		CA1	65.6	66.0	34.0	58
		PKDA	74.5	14.4	85.6	858
		CAgran	66.0	67.7	32.3	93

n.a.: not applicable because bi-solute phenol adsorption did not fit the Freundlich equation

physical adsorption, could be broken down. But, it probably required more desorption steps, particularly for 2-CP molecules adsorbed on narrow micropores rather than those adsorbed on larger pores. Desorption of phenol occurred faster, obviously because phenol was adsorbed with a weaker energy than 2-CP as discussed earlier.

4 Conclusions

In bi-solute adsorption, the thermally activated carbons (SA4 and PKDA) adsorbed both phenol and 2-chlorophenol better than chemically activated carbons (CA1 and CAgran), as also observed in single-solute adsorption in previous studies (Aktaş and Çeçen, 2006a, 2007). The bi-solute adsorption of 2-CP was not negatively affected by the presence of phenol, although phenol adsorption was suppressed to a great extent. This showed that 2-CP was adsorbed preferentially by each type of activated carbon, but phenol was adsorbed competitively. In bisolute adsorption, cumulative adsorption of phenol and 2-CP was higher than single-solute adsorption of 2-CP since some phenol was also adsorbed on sites which were not occupied by 2-CP.

The SIAS model underestimated the 2-CP loadings on each type of activated carbon and overestimated phenol loadings, particularly those on the thermally activated carbons SA4 and PKDA. Competition between phenol and 2-CP was non-ideal and in favor of 2-CP. Irreversible adsorption and unequal competition for adsorption sites were the main reasons for the failure of the SIAS model. On the other hand, the ISIAS model accounting for non-ideal competition for adsorption sites provided a reasonable fit for bi-solute data. A modified ISIAS model was also used considering solubilities of competing phenol and 2-CP. But this model was not successful in describing the bi-solute data for the chemically activated carbons, although it could reasonably predict data for thermally activated ones. The conditional applicability of several models was not tested before in literature in the case of carbons subjected to different types of activation. In the present study, the type of the carbon was found to be very important and decisive for the choice of either the improved and modified forms of the ideal adsorbed solution model and in the application of competition factors.

Competitively loaded phenol and 2-CP desorbed less from thermally activated carbons compared with the chemically activated ones, as in the cases of single-solute desorption (Aktaş and Çeçen 2006a, 2007). More phenol was desorbed in the bi-solute case, but desorption of 2-CP was less compared with single-solute desorption for each type of activated carbon. Therefore, it was suggested that 2-CP was preferentially adsorbed on adsorption sites with greater energy, and phenol was adsorbed on less energetic sites so that phenol was more readily desorbed.

The main novelty in this study was investigating the effect of activated carbon type on competitive adsorption and desorption of a bi-solute mixture and also on the use of models to predict competitive adsorption. In wastewater treatment applications with activated carbon adsorption only, use of thermally activated carbons is recommended due to higher adsorption capacity and lower desorption capacity of phenolic compounds. However, in activated carbon applications in combination with biological treatment systems, chemically activated carbons might be a better choice. Higher desorption capacities of mixtures of phenolic compounds from these carbons will facilitate the bioregeneration resulting in an increased service life. In continuation to the present study, the influence of competitive adsorption on bioregeneration of activated carbons loaded with a bi-solute mixture of phenol and 2-CP will be investigated.

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