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Adsorption equilibrium and kinetics of copper ions and phenol onto modified adsorbents

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Abstract The adsorption equilibrium and kinetics of single and binary component copper ions and phenol onto powdered activated carbon (PAC), alginate beads and alginate-activated carbon beads (AAC) were studied. Adsorption equilibrium data for single component copper ions and phenol onto the adsorbents could be represented by the Langmuir equation. Multicomponent equilibrium data were correlated by the extended Langmuir and ideal adsorbed solution theory (IAST). The IAST gave the best fit to our data. The amount of copper ions adsorbed onto the AAC beads in the binary component was greater than that of phenol. The internal diffusion coefficients were determined by comparing the experimental concentration curves with those predicted from surface diffusion and pore diffusion model.

Keywords Activated carbon · Alginate · Copper ions · Equilibrium · Kinetic · Phenol

Abbreviations

A_S	surface area of adsorbent (m^2/g)
C_i	initial concentration of bulk fluid (mol/m^3)
C_e	saturation concentration of the adsorbate in the liquid phase (mol/m^3)
d_P	particle diameter (m)
D_P	pore diffusion coefficient (m^2/s)
D_S	surface diffusion coefficient (m^2/s)
k_f	film mass transfer coefficient (m/s)
k_F	isotherm parameter $(mol/kg)(mol/m^3)^{-1/n}$
k_L	isotherm parameter (m^3/mol)
k_S	isotherm parameter $(mol/m^3)^{-1/n}$
N_A	rate of mass transfer of adsobates to the external surface of the adsorbent (mol/s)
N	number of component
q	equilibrium amount adsorbed on the adsorbent (mol/kg)
q_m	maximum adsorption capacity of adsorbent (mol/kg)
R_P	particle radius (m)
V	volume of solution (m^3)
W	weight of adsorbent (kg)

1 Introduction

The presence of heavy metals contamination in aqueous streams arises from the discharge of untreated metal containing effluents into water bodies. These metals are nondegradable in the environment and can be harmful to a variety of living species. Besides their toxic and harmful effects to organisms living in water, heavy metals also accumulate throughout the food chain, and may eventually affect human beings (Martins et al. 2004). Therefore, the removal of heavy metals from waters and wastewaters is important in terms of protecting public health and the environment (Uluozlu et al. 2008).

Phenols are widely distributed as environmental pollutants, and the treatment of industrial wastewaters contaminated with phenolic compounds is a daunting problem. They exist at various concentrations in wastewater discharges from many industrial processes, including the petrochemical industry, coking, synthetic rubber, plastics, paper, and oil refineries, as well as phenolic resin industries (Bayramoglu

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and Arica 2008; Tepe and Dursun 2008). Wastewater containing heavy metals and phenolic compounds present serious discharge problems due to their poor biodegradability, high toxicity and long term ecological damage. Due to the high toxicity of heavy metals and phenols, they are strictly regulated, and their industrial use is increasingly avoided by their substitution with less harmful compounds.

Various methods have been suggested and applied for the removal of toxic metals and organics from aqueous solution, such as chemical precipitation, evaporation, ion-exchange, adsorption, cementation, electrolysis and reverse osmosis. Due to the specific nature of industrial effluents from various processes (pH, cations and anions, oil emulsions, suspended solids, etc.), the effective removal of metal ions has proven to be a very difficult and costly process (Crist et al. 1996). Although adsorption using resin is a very effective and widely used method for the removal of heavy metal ions (WanNgah et al. 2002), commercial chelating resins, some of the widely utilized sorbents, are expensive and mostly non-biodegradable. To overcome these problems, investigations have focused on the preparation of cheap and effective novel sorbents. A very promising material, with such advantages, is alginate, a natural anionic polymer. Alginic acid, a heteropolysaccharide composed of β-D-mannuronic acid and α-L-guluronic acid, is widely distributed in organisms as diverse as seaweeds and bacteria. Many biopolymers are known to have a strong affinity for metal ions, and the application of alginic acid as an adsorbent for the recovery of valuable metal ions as well as removal of toxic metal ions has been studied (Deans and Dixon 1992; Davis et al. 2003). Alginic acid is a biopolymer containing carboxyl groups that are capable of forming complexes with metal ions.

Activated carbon has typically been employed as an adsorbent for the control of various environmental pollutants, including organics, because of its high pore volume and large exposed surface area to volume ratio (Bressa et al. 1983; McKay et al. 1986; Jia et al. 1999).

One of the important properties of alginate is the ability to form hydrogels (Clark and Ross-Murphy 1987; Gilson and Thomas 1995). An aqueous solution of alginate is readily transformed into a hydrogel by the addition of metallic divalent cations, such as Ca^{2+}. Moreover, an important contribution of alginate to certain biological entities; the uptake of heavy metal ions by algae, has been reported (Stewart et al. 2009). Also, activated carbons immobilized with calcium alginate beads have been used for the removal of phenol.

In this study, alginate beads and alginate-activated carbon beads (AAC) were prepared by reaction with calcium chloride. The separation characteristics for single and binary component of copper ions and phenol onto powdered activated carbon (PAC), alginate beads and AAC beads were experimentally and theoretically studied.

2 Isotherm modeling

2.1 Single-species equilibrium

Adsorption mechanisms are extremely complicated; therefore, no simple theory can adequately explain adsorption characteristics. Many expressions have been reported that describe the equilibrium relationship between an adsorbate and an adsorbent. The isotherm models of the Langmuir (1918), Freundlich (1907) and Sips (1948) have been used to describe equilibrium adsorption. These isotherm equations are as follows:

Langmuir isotherm

$$q = \frac{q_m k_L C_i}{1 + k_L C_i}, \tag{1}$$

where C_i is the supernatant concentration in the equilibrium state of the system (mol/m^3), k_L is the Langmuir affinity constant (m^3/mol) and q_m is the maximum adsorption capacity of the material (mol/kg) assuming the uptake of a monolayer of adsorbate by the adsorbent.

Freundlich isotherm

$$q = k_F C_i^{1/n}, \tag{2}$$

where k_F is the Freundlich constant related with adsorption capacity (mol/kg)(mol/m^3)$^{-1/n}$ and n is the Freundlich exponent (dimensionless).

Sips isotherm,

$$q = \frac{q_m k_s C_i^{1/n}}{1 + k_s C_i^{1/n}}, \tag{3}$$

where k_S is the Sips constant related with the affinity constant (mol/m^3)$^{-1/n}$ and q_m is the Sips maximum adsorption capacity (mol/kg).

2.2 Multi-species equilibrium

When two or more components exist with the possibility of occupying the same adsorption sites, equilibrium relationships become more complex. The simplest is the extension of the Langmuir isotherm by assuming no interaction between adsorbing molecules (Ruthven 1984; Yang 1986). This equation enables quick estimation of equilibrium relations of multi-species adsorption from Langmuir parameters determined from the single-species isotherm of each component. Extended Langmuir equations are as follows:

$$q_i = \frac{q_m k_L C_i}{1 + \sum_{j=1}^{N} k_{Lj} C_i}. \tag{4}$$

One of the most widely used thermodynamic models is the ideal adsorbed solution theory (IAST) of Myers and

Prausnitz (1965). Assuming that adsorbates on the surface form an ideal solution, multicomponent adsorption equilibrium data can be estimated by the IAST. This assumption, together with the Langmuir equation as a single-species isotherm, provides a set of equation for multicomponent adsorption. According to the IAST, q_i and C_i are related by the following set of equations:

$$q_i = q_T z_i, \tag{5}$$

$$q_T = \left[\sum_{i=1}^{N} \frac{z_i}{q_i^o}\right]^{-1}, \tag{6}$$

$$C_i = C_i^o(\pi_i, T) z_i, \tag{7}$$

$$q_i = f(C_i^o \pi_i), \tag{8}$$

$$\sum_{i=1}^{N} z_i = 1, \tag{9}$$

where C_i^o and q_i^o are the liquid-phase concentration and the amount of adsorption in single-species adsorption which gives the spreading pressure, π for the adsorbed mixture (Myers and Prausnitz 1965). q_T is the total amount of adsorption and z_i is the mole fraction of species i in the adsorbed phased. According to the Gibbs isotherm (Ruthven 1984), the spreading pressure may be calculated by

$$\Pi_i = \frac{\pi A}{RT} = \int_0^{C_i^o} \frac{q_i^o}{C_i^o} dC_i^o. \tag{10}$$

If single-species isotherm is given by the Langmuir equation, Π_i and C_i^o are related by the expression

$$\Pi_i = q_{mi} \ln(1 + K_{Li} C_i^o). \tag{11}$$

Once the spreading pressure is evaluated at a given condition, it completes the adsorption calculation (Myers and Prausnitz 1965; Moon and Tien 1988).

3 Materials and methods

3.1 Materials

Alginate and PAC were obtained in powdered forms from Junsei and Yacuri chemical Co., Japan, and used without further purification. All reagents used, including $CuCl_2 \cdot 2H_2O$ (Junsei chemical Co., Japan), phenol (Sigma Co., USA), calcium chloride anhydrate (Duksan Pharm. Co., Korea) and phosphate buffered saline solution, were of reagent grade. In most cases the alginate was a nonporous powdered type. The low internal surface area of the nonporous powder limits the access to interior adsorption sites. Furthermore, the powdered form of alginate easily swells and crumbles; thus, does not behave ideally in a packed column. In order to improve these disadvantages, porous alginate and AAC beads were obtained using the sol-gel method. The powdered alginate was dissolved in a phosphate buffer saline solution to produce a viscous solution with approximately 3 wt% alginate. The biopolymer alginate solution was then cast into beads using the phase-inversion technique employing calcium chloride solution. After mixing 3 g of activated carbon with 100 ml of 3 wt% alginate solution, the solution was caste into the calcium chloride solution in the same manner as for the preparation of the AAC beads.

The water contents of the wet alginate and AAC beads were determined from the weights of the beads before and after drying in an oven at 100°C for 24 h, and were about 95 and 89%, respectively.

3.2 Experimental

The adsorption equilibrium isotherms were determined by bringing carefully weighted amounts of PAC, alginate beads and AAC beads into contact a volume of solution in a conical flask. The amounts of the adsorbents were varied from 0.001 to 0.25 g, with 200 ml of 1.06 mol/m^3 copper ions or phenol in both the single and binary component tests. HCl and NaOH solutions were used to adjust the pH of the solution. The flasks were shaken for 2 days to provide sufficient time and contact to establish equilibrium between the solid and liquid phases. Prior to the analyses, samples were removed from the flask and filtered to remove suspended PAC particles. The phenol and copper ion concentrations in the solution were determined with an UV spectrophotometer (Shimadzu 1601) at $\lambda = 270$ nm and ICP (Shimadzu), respectively.

The amounts of copper ions and phenol adsorbed at equilibrium were calculated from the following mass balance equation:

$$q = (C_0 - C_i)\frac{V}{W}, \tag{12}$$

where q is the amount adsorbed onto the adsorbent (mol/kg) at equilibrium, C_0 is the initial concentration in the bulk fluid (mol/m^3), V is the volume of solution (m^3) and W is the weight of adsorbent (kg).

Batch adsorption experiments were conducted in a Carberry-type batch adsorber. All the experiments were carried out at approximately 400 rpm, since the film mass transfer coefficient, k_f, is practically constant under this condition. The samples were withdrawn from the batch reactor and analyzed for phenols and copper ions using a UV spectrophotometer and ICP.

4 Results and discussion

4.1 Adsorbent characterization

The surface area of the adsorbent is important factor affecting adsorption in some case. The specific surface area and pore size distribution of the PAC, alginate beads and AAC beads was measured by a nitrogen adsorption analyzer (Quantachrome, USA) and their values are listed in Table 1. The specific surface area of AAC beads was determined to be 321.5 m^2/g, which is comparable to that of alginate beads (25.32 m^2/g). Figure 1 shows pore size distributions of three sorbents measured by desorption isotherms. The average pore diameter of alginate beads is 40.49 Å while those of PAC and AAC beads are 17.90 and 26.50 Å, respectively. The pore size distribution of alginate beads has a broad distribution compared with those for PAC and AAC beads. According to the International Union of Pure and Applied Chemistry (IUPAC) classifications, the pores can be divided in broad terms according to diameter (d) into macropores ($d > 50$ nm), mesopores ($2 < d < 50$ nm) and micropores ($d < 2$ nm). Based on results, it can be concluded that alginate beads and AAC beads fall into the category of macropores.

Table 1 Structural characteristics of the adsorbents used in this study

Property	Alginate bead	PAC	AAC bead
Mean diameter [mm]	1.70	0.04	2.30
BET surface area [m^2/g]	25.32	364.70	321.50
Average pore diameter [Å]	40.49	17.90	26.50

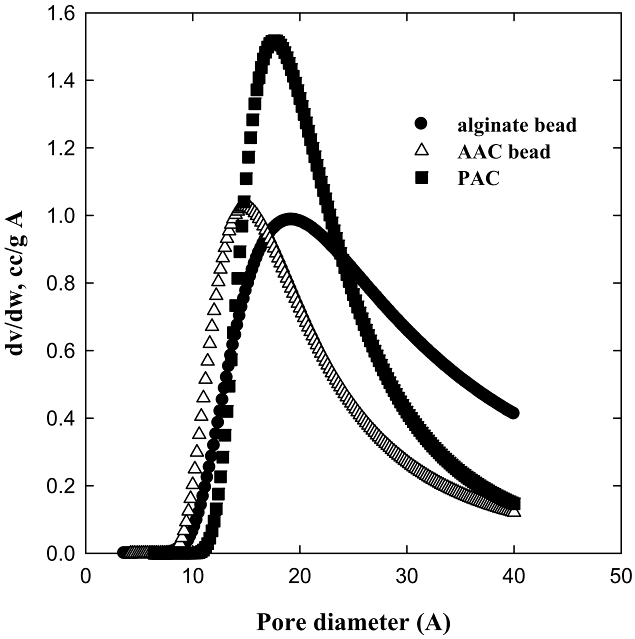

Fig. 1 Pore size distribution of the adsorbents calculated from desorption experiments of N_2

4.2 Adsorption isotherm

Adsorption isotherms are essential for describing how solutes interact with adsorbents, and critical in optimizing the use of adsorbents. Figure 2 shows the amounts of copper ions adsorbed onto the three different adsorbents, which were in the following order: alginate beads > AAC beads > PAC. The alginate beads have many negative charges due to the dissociation of the carboxyl groups; whereas, the copper ions are mostly cationic; therefore, the attraction force between the beads surface and the cationic copper ions results in increased adsorption. In this study, three isotherm models; the Langmuir, Freundlich and Sips, were used to correlate our experimental equilibrium data. The Langmuir and Freundlich equations have two parameters, and the Sips equation has three. To find the parameters for each adsorption isotherm, the linear least square method and the pattern search algorithm were used. The value of the mean percentage error was used as a test criterion for the fit of the correlations. The mean percent deviation between the experimental and predicted values was obtained using (13)

$$\text{error}(\%) = \frac{100}{N}\sum_{k=1}^{N}\left[\frac{|q_{\exp,k} - q_{\text{mod},k}|}{q_{\exp,k}}\right], \tag{13}$$

where $q_{\text{mod},k}$ is each value of q predicted by the fitted model and $q_{\exp,k}$ is each value of q measured experimentally, and n is the number of experiments performed. The parameters

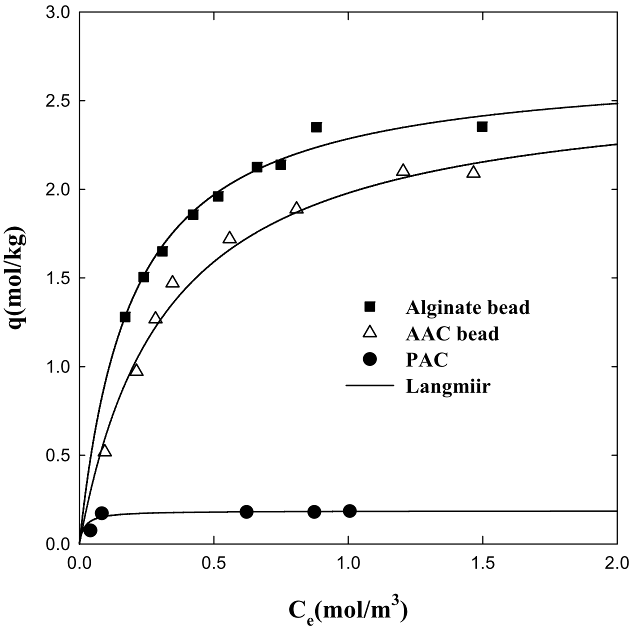

Fig. 2 Adsorption isotherms of Cu^{2+} onto the different adsorbents (T: 298 K, pH: 3.0, $C_0 = 1.06$ mol/m^3)

Table 2 Adsorption equilibrium constants of copper ions onto the different adsorbents (T: 298 K, pH: 3.0, C_0: 1.06 mol/m^3)

Isotherm type	Parameters	Adsorbents		
		PAC	AAC beads	Alginate beads
Langmuir	q_m	0.19	2.26	2.73
	b	29.72	3.55	5.23
	error(%)	4.83	6.04	5.86
Freundlich	k	0.20	1.77	2.31
	n	4.69	2.75	3.76
	error(%)	8.52	8.73	7.57
Sips	q_m	0.19	2.26	2.72
	b	34.18	3.72	5.64
	n	1.07	0.94	0.90
	error(%)	8.29	6.64	6.37

Table 3 Adsorption equilibrium constants of phenol onto the different adsorbents (T: 298 K, pH: 3.0, C_0: 1.06 mol/m^3)

Isotherm type	Parameters	Adsorbents		
		PAC	AAC beads	Alginate beads
Langmuir	q_m	1.19	1.02	0.07
	b	22.0	5.30	3.64
	error(%)	2.86	1.77	0.12
Freundlich	k	1.48	0.88	0.05
	n	2.97	3.80	4.45
	error(%)	8.63	1.19	0.12
Sips	q_m	1.26	1.24	0.07
	b	16.5	1.95	3.64
	n	1.04	1.01	0.99
	error(%)	2.93	1.75	0.12

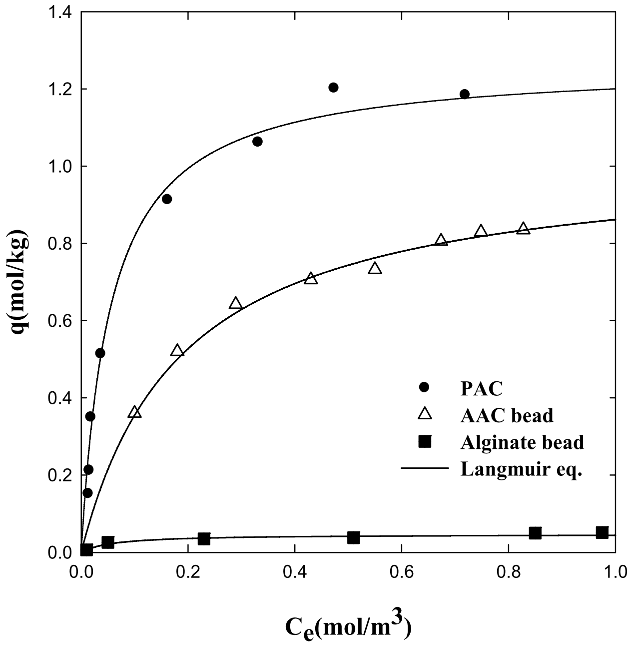

Fig. 3 Adsorption isotherms of phenol onto the different adsorbents (T: 298 K, pH: 3.0, C_0: 1.06 mol/m^3)

and average percentage differences between the measured and calculated values for the copper ions onto the different adsorbents are given in Table 2. As shown in the Table 2, the maximum adsorption capacities of copper ions onto PAC, AAC beads and alginate beads were 0.19, 2.26 and 2.73 mol/m^3, respectively. Of the three models, the Langmuir equation gave the best fit of our data. From this result, the Langmuir equation was deemed the most suitable for predicting the single-component adsorption of copper ions onto the adsorbents.

The adsorption capacities of the different adsorbents for phenol are presented in Fig. 3, which shows the amount of phenol adsorbed onto PAC was greater than those onto the AAC beads and alginate beads. The high adsorption capacity of the PAC was due to its high specific surface area as shown in Table 1. Phenol is considered as a weak acid; thus, its adsorption onto activated carbon should be enhanced by basic surface functional groups. Several studies have shown that phenol adsorption is dependent on both the porosity and the presence of surface groups (Vidic et al. 1997; Terzyk 2004). Oxidation may affect the adsorption of phenol since it affects the surface functional groups. The introduction of acidic functional groups may cause the π-electrons to be removed from the carbon matrix, leading to a decrease in the strength of the interactions between the aromatic ring of the phenol molecule and the carbon basal planes (Villacanas et al. 2006), resulting in an overall decrease in the average energy of the phenol adsorption sites (Salame and Bandozs 2003). Each isotherm parameters and the average percentage differences between the measured and calculated values for the adsorption of phenol onto the different adsorbents are given in Table 3. From the Table 3, the Langmuir equation was the most suitable for predicting the single-component adsorption of phenol onto the adsorbents.

The pH of the solution is a major factor influencing the adsorption capacity of compounds that can be ionized. Acid or alkali species may change the surface chemistry of the adsorbent by reacting with the surface groups, which may lead to significant pH dependent alterations in the adsorption equilibrium. The adsorption capacity of the AAC beads for phenol was evaluated by measuring the adsorption equilibrium data in terms of the initial pH of the solution. As shown in Fig. 4, adsorption capacity of the AAC beads for phenol increased with decreasing initial pH of the solution. This phenomenon can be attributed to the lower pH increasing the positively charged groups on the surface of the AAC beads, and the surface charges on the adsorbate at a value higher

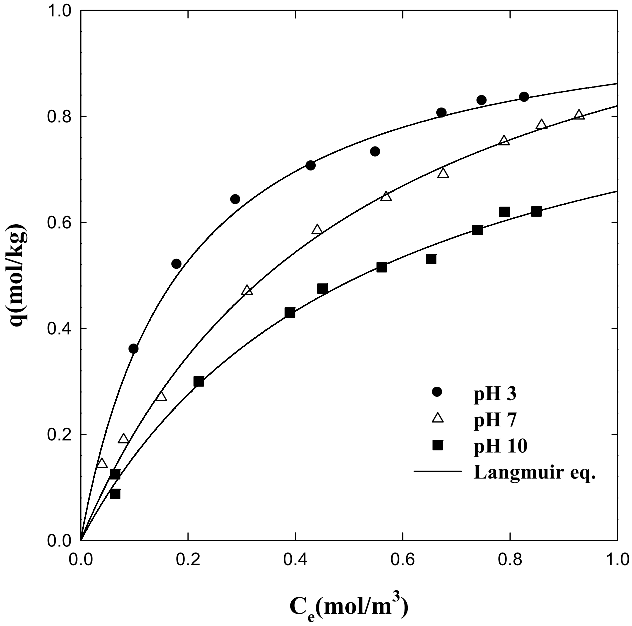

Fig. 4 Adsorption isotherms of phenol onto AAC beads at different pHs (T: 298 K, C_0: 1.06 mol/m^3)

Table 4 Adsorption equilibrium constants of phenol onto AAC beads at different pHs (T: 298 K, C_0: 1.06 mol/m^3)

Isotherm type	Parameters	pH		
		3	7	10
Langmuir	q_m	1.02	0.91	0.74
	b	5.30	5.85	5.05
	error(%)	1.77	1.00	1.80
Freundlich	k	0.88	0.83	0.67
	n	3.80	2.30	2.23
	error(%)	1.19	0.65	1.51
Sips	q_m	1.24	1.02	1.01
	b	1.95	5.24	1.86
	n	1.01	1.03	1.02
	error(%)	1.75	1.02	1.80

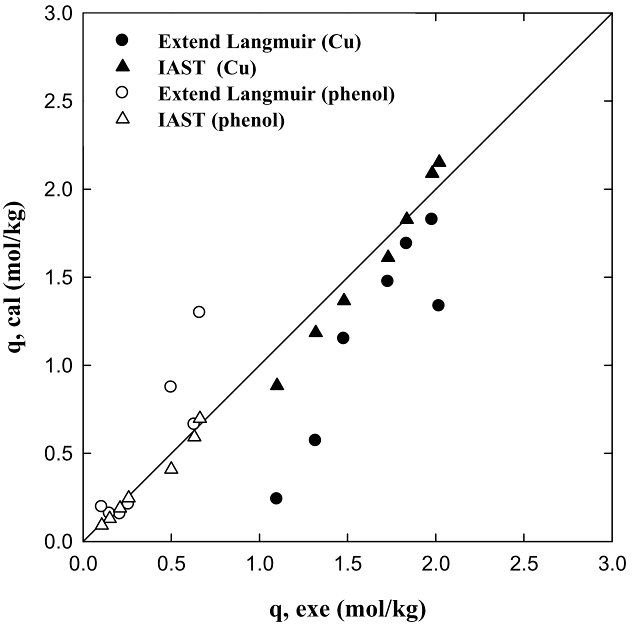

Fig. 5 Measured and predicted adsorption uptakes of copper ions and phenol onto AAC beads in binary components (T: 298 K, pH: 5.0, C_0: 1.06 mol/m^3)

than the pKa (9.89 for phenol) being mostly anionic. Conversely, the surface functional groups on the AAC beads, such as carboxyl and hydroxyl groups, are very weak under basic conditions. Therefore, the repulsion between the surface layer and the anionic phenol results in reduced adsorption. The estimated values of the adsorption equilibrium parameters of phenol in terms of pH onto the AAC beads are summarized in Table 4. The maximum amounts of phenol adsorbed onto the AAC beads at pH 3, 7 and 10 were 1.02, 0.94 and 0.74 mol/kg.

The adsorption competition between copper ions and phenol onto AAC beads was studied. Multispecies adsorption isotherms such as the extended Langmuir and IAST were used to predict those binary data. As shown in Fig. 5, the binary experiment for copper ions and phenol systems were performed under the conditions that $C_0 =$ 0.106 mol/m^3, contact time = 48 h, and temperature = 298 K. For multicomponent systems, adsorbent and adsorbate affinity will change due to competition for available adsorption sites. It can be seen from Fig. 5, the maximum adsorbed amount of copper ions and phenol in binary solutions was 2.37 and 0.74 mol/kg, respectively. The amount of copper ions adsorbed onto AAC beads was higher than that of phenol. The molecular weights of phenol are greater than copper ions hence, when in competition, the smaller molecule will occupy the pores in the AAC beads first. Basically, if most of the data are distributed around the 45° line (see Fig. 5), this indicates that the models suitably represent the experimental data of the system. However the extended Langmuir model gave considerable deviation between calculated and predicted amounts in the copper ions and phenol systems. But the IAST gave the best fit to all data in the binary systems. The IAST may be a favorable theory adaptable to remove of copper ions and phenol of binary systems using AAC beads.

4.3 Batch adsorption

For the modeling of the adsorption kinetics, two problems have to be considered: (i) the pore structure of adsorbents and (ii) the mass transfer resistance involved in the adsorption process. The adsorption onto a solid surface takes place

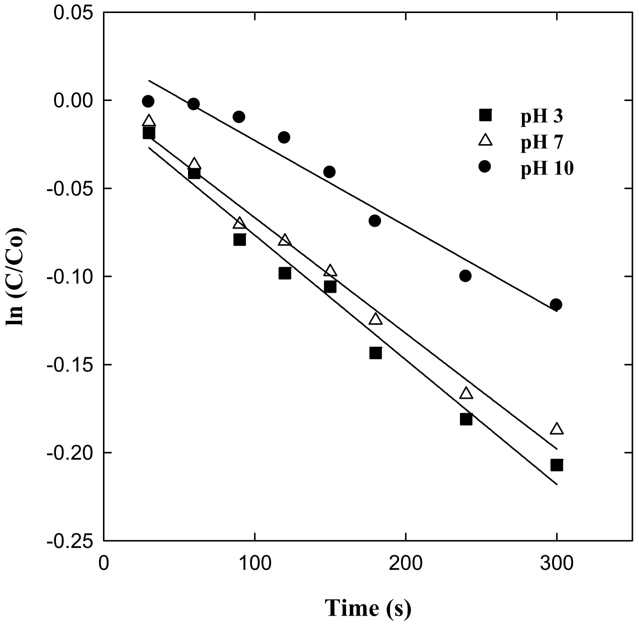

Fig. 6 Determination of k_f from an initial concentration decay plot for phenol onto AAC beads (298 K)

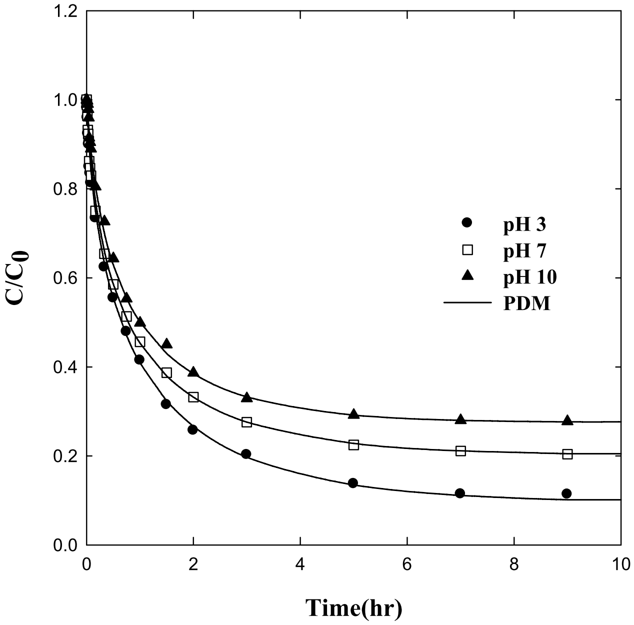

Fig. 7 Concentration decay curves of phenol onto AAC beads at different pH values (T: 298 K, C_0: 1.06 mol/m^3)

in several steps, including external diffusion, internal diffusion, and the actual adsorption. In general, the actual adsorption process is relatively fast compared to the previous two steps. The intraparticle diffusion has been usually considered as the rate-controlling step in the liquid-phase adsorption, but it is important to estimate the order of magnitude for the mass transfer coefficient. There are several correlations for estimating the film mass transfer coefficient, k_f, in a batch system. In this work, k_f was estimated from the initial concentration decay curve when the diffusion resistance does not prevail. The transfer rate of any species to the external surface of the adsorbent, N_A, can be expressed by:

$$N_A = K_f A_s (C - C_i). \tag{14}$$

For a batch system with an adsorption time of less than 300 seconds, the following approximation holds (Misic et al. 1982).

$$\ln(C/C_i) = -k_f A_s / V, \tag{15}$$

where V is the volume of solution. In this equation, the effective external surface area of adsorbent particles, A_S, can be expressed as:

$$A_s = 3W/\rho_p R_p, \tag{16}$$

where W is the total mass of adsorbent particles, ρ_p is the particle density, and R_P is the particle radius.

Figure 6 is a typical plot used to estimate the k_f values from initial concentration data in terms of pH for phenol onto the AAC beads at 298 K. The values of k_f for phenol obtained from the slopes in Fig. 6 were 4.14 × 10^{-5} (for pH 3), 3.80 × 10^{-5} (for pH 7) and 2.89 × 10^{-5} (for pH 10) m/s.

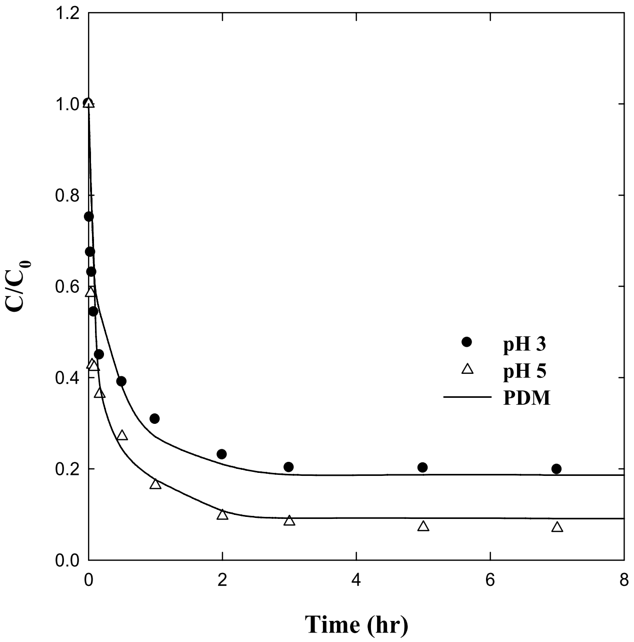

Fig. 8 Concentration decay curves of Cu^{2+} onto AAC beads at different pH values (T: 298 K, C_0: 1.06 mol/m^3)

Figures 7 and 8 show the experimental data and model predictions for single component copper ions and phenol onto the AAC beads in the batch adsorber. In this study, the pore diffusion coefficient, D_p, and surface diffusion coeffi-

Table 5 Kinetic parameters for phenol and Cu^{2+} onto AAC beads in the batch adsorber (T: 298 K, C_0: 1.06 mol/m^3)

Adsorbate	pH	$k_f \times 10^{-5}$ [m/s]	$D_p \times 10^{-9}$ [m^2/s]	$D_s \times 10^{-11}$ [m^2/s]	Bi [–]
Phenol	3	4.14	3.29	2.58	3.97
	7	3.80	3.01	0.93	11.33
	10	2.89	2.98	0.67	14.71
Cu^{2+}	3	8.34	7.39	8.71	1.07
	5	8.75	7.85	8.90	1.01

cient, D_s, were estimated using the pore diffusion and surface diffusion models, respectively (Masamune and Smith 1964; Ma and Lee 1976). The estimated values of k_f, D_p and D_s in terms of pH for copper ions and phenol onto AAC beads are listed in Table 5. In the case of phenol, the external fill mass transfer coefficient and effective diffusion coefficients increased with decreasing pH of the solution. The differences in the rates of adsorption onto the adsorbate were primarily attributable to the differences in the equilibrium adsorption capacities of the adsorbent (shown in Fig. 4). As shown in Figs. 7 and 8, the pore diffusion model satisfactorily simulated our data. On the other hand, the non-dimensional Biot number, Bi, in Table 5 was estimated by the following relationship (Traegner and Suidan 1989)

$$Bi = \frac{k_f d_p c_i}{2 D_s \rho_p q}. \tag{17}$$

The Biot number represents the ratio of the rate of transport across the liquid layer to the rate of diffusion within the AAC beads. For $Bi < 1$, the external mass transport resistance is the controlling mass transfer step; whereas, for $Bi > 100$, the surface diffusion is the controlling mass transfer mechanism. Bi numbers between 1 and 100 indicate that both mass transfer mechanisms are important in the mass transfer process.

It is well known that alginate beads are able to remove heavy metal ions and that activated carbon removes organics from aqueous solutions. AAC beads, which have the advantages of both alginate and PAC, were used as the adsorbent to remove binary component of the heavy metal ions and phenol from aqueous solution in the batch adsorber. Figure 9 shows the concentration decay curves of the binary component for copper ions and phenol onto AAC beads at different initial pHs. AAC beads possess higher adsorption activity against copper ions at the same initial pH (3 and 5). The heavy metal uptake capacity of alginate far exceeded that of the PAC, as shown in Figs. 2 and 3, and the mass transfer coefficient and effective diffusion coefficients of copper ions onto AAC beads were larger than those of phenol in the binary component, as shown in Table 6. However, activated carbon can also adsorb the heavy metal ions, and the activated carbon component within the AAC beads was found to especially contribute to the removal of phenol, but copper ions to a less extent. The adsorption efficiency of the AAC beads was found to be significantly improved by the addition of PAC, which mainly assisted in phenol adsorption.

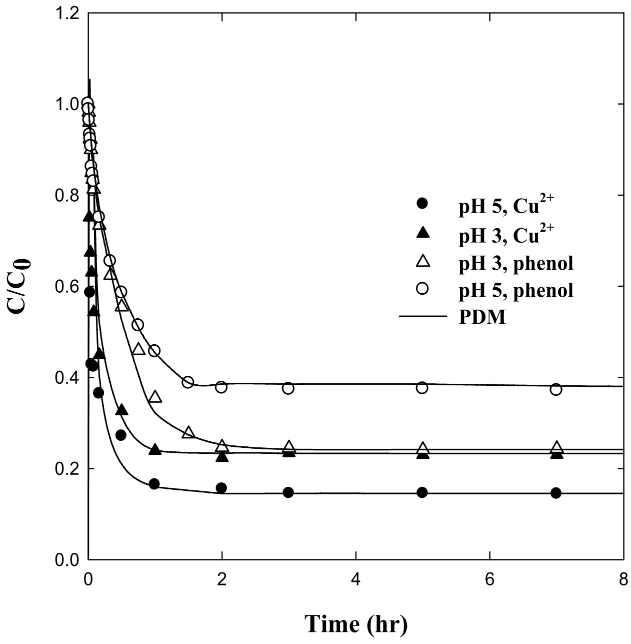

Fig. 9 Concentration decay curves of binary components onto AAC beads at different pHs (T: 298 K, C_0: 1.06 mol/m^3)

Table 6 Kinetic parameters for binary components onto AAC beads in the batch adsorber (T: 298 K, C_0: 1.06 mol/m^3)

Adsorbate	pH	$k_f \times 10^{-5}$ [m/s]	$D_p \times 10^{-9}$ [m^2/s]	$D_s \times 10^{-11}$ [m^2/s]	Bi [–]
Phenol	3	3.75	3.02	1.84	5.04
	5	3.05	2.83	1.07	3.08
Cu^{2+}	3	8.03	7.03	7.97	1.13
	5	8.37	7.29	8.65	0.99

5 Conclusions

Alginate—activated carbon beads were prepared in an attempt to improve the adsorption selectivity of the alginate beads. The adsorption capacities of copper ions onto the different adsorbents were in the following order: alginate beads > AAC beads > activated carbon. Conversely, those of phenol were: activated carbon > AAC beads > alginate beads. Multicomponent equilibrium data were correlated using extended Langmuir equation and ideal adsorbed solution theory (IAST). The IAST giving the best fit to our data. The amount of copper ions adsorbed onto the AAC beads was greater than that of phenol in the binary component. The kinetic parameters, such as the mass transfer coefficients and effective diffusion coefficients, for copper ions and phenol onto the adsorbents were evaluated. The differences in the adsorption rates of the adsorbates onto AAC beads were primarily attributable to the differences in the adsorption equilibria; the pore diffusion model satisfactorily simulated our data.

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