

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231542280>

Adsorption Isotherms of Phenolic Compounds from Aqueous Solution onto Activated Carbon Fibers

ARTICLE *in* JOURNAL OF CHEMICAL & ENGINEERING DATA · MAY 1996

Impact Factor: 2.04 · DOI: 10.1021/je950238g

CITATIONS

87

READS

57

3 AUTHORS, INCLUDING:



Ruey-Shin Juang

Chang Gung University

307 PUBLICATIONS 11,240 CITATIONS

SEE PROFILE



Feng-Chin Wu

National United University

55 PUBLICATIONS 3,984 CITATIONS

SEE PROFILE

Adsorption Isotherms of Phenolic Compounds from Aqueous Solutions onto Activated Carbon Fibers

Ruey-Shin Juang,^{*,†} Feng-Chin Wu,[‡] and Ru-Ling Tseng[‡]

Department of Chemical Engineering, Yuan-Ze Institute of Technology, Nei-Li, Taoyuan 320, Taiwan, and Department of Chemical and Environmental Engineering, Lien-Ho Junior College of Technology, Miaoli 360, Taiwan

Liquid-phase adsorption equilibria of eight phenolic compounds onto activated carbon fibers were measured in the concentration range 40–500 g·m⁻³ at 303 K. High adsorption capacities were observed for the chlorinated phenols compared to the methyl-substituted phenols. Several two- and three-parameter isotherm equations were tested. Among the equations tried, the three-parameter equation of Jossens *et al.* based on a heterogeneous surface adsorption theory was found to be the most satisfactory over the entire range of concentration. The widely used two-parameter equations of Langmuir and Freundlich were not applicable to the present adsorption systems.

Introduction

Phenolic compounds exist widely in the industrial effluents such as those from oil refineries and the coal tar, plastics, leather, paint, pharmaceutical, and steel industries (Singh and Rawat, 1994). Since they are highly toxic and are, in general, not amenable to biological degradation, methods of treatment are continuously being modified and developed. Possible methods include chemical oxidation, coagulation, solvent extraction, liquid membrane permeation, and adsorption.

Of all the methods, adsorption appears to offer the best prospects for overall treatment, especially for the effluents with moderate and low concentrations. Because granular or powder activated carbon has a good capacity for adsorption of organic matter, it is the most widely used adsorbent for this process (Caturla *et al.*, 1988; Dvorak *et al.*, 1993; Streat *et al.*, 1995). Although activated carbon has been widely used for this purpose, it requires a container and careful filling is generally necessary; replacement of the adsorbent is by no means a simple procedure. Also, the use of powder activated carbon for liquid solutions involves subsequent filtration.

The activated carbon fiber employed in the present study can obviate the above disadvantage (Cal *et al.*, 1994; Suzuki, 1994). It has been extensively used for the adsorption of gaseous pollutants such as acetone, benzene, water vapor, N₂, and CO₂, hexane, chloroform, carbon tetrachloride, dichloroethane, and ethanol, HCN, NH₃, NO, NO₂, and SO₂ and liquid pollutants such as fatty acids and benzene derivatives, phenol, benzoic acid, tri- and tetrachloroethylene, inorganic and organic phosphates, Cr(VI), Hg(II), and iodine (Suzuki, 1994).

Although the pioneer work of phenol adsorption using activated carbon fiber has been done since 1976 (Economy and Lin, 1976), to our knowledge, few systematic studies on the adsorption of phenolic compounds have been made. In this paper, the adsorption equilibria of eight phenolic compounds were measured over a wide range of concentration (40–500 g·m⁻³) onto activated carbon fiber at 303 K. A comparison was made on the applicability of various two-

Table 1. Physical Properties of the Activated Carbon Fiber (Charsob CP-1300)

property	value
material	poly(acrylonitrile)
thickness	0.61 mm
weight	80 g·m ⁻²
total micropore volume ^a	0.586 cm ³ ·g ⁻¹
mean micropore volume ^a	0.576 cm ³ ·g ⁻¹
micropore radius ^a	1.67 nm
BET specific surface area ^a	1380 m ² ·g ⁻¹

^a Measured in this work.

and three-parameter isotherm equations to find an equation which correlates the equilibrium data most satisfactorily.

Experimental Section

Reagents, Activated Carbon Fiber, and Solutions.

All phenolic compounds used in this study, including phenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, *o*-cresol, *m*-cresol, and *p*-cresol, were from Merck Co., as analytical grade. They were used without further purification. The activated carbon fiber (Charsob CP-1300) was supplied by Yih Hsin Chemical Co., Taipei, Taiwan, and was used as received. It was manufactured by carbonizing poly(acrylonitrile) at 200–300 °C in air and activating at 800–1200 °C. The BET surface area, micropore volume, and mean micropore size of activated carbon fiber measured from N₂ adsorption using Micromeritics Model ASAP 2000, together with other physical properties provided by the manufacturer, are listed in Table 1. The aqueous solutions were prepared by diluting phenolic compounds in deionized water to the required concentrations (40–500 g·m⁻³). Deionized water employed in this work was produced by a Millipore Milli-Q Water System.

Procedure. In adsorption experiments, a fixed amount of activated carbon fiber (0.1–0.2 g) and 100 cm³ of an aqueous solution were placed in a 250 cm³ glass-stoppered flask and shaken at 130 rpm for 3 days using a thermostated shaker bath (Firstek Model B603, Taiwan). Preliminary experiments had shown the adsorption processes studied to attain equilibrium only after 1 day. The initial and equilibrium concentrations of phenolic compounds in the aqueous solutions were analyzed using a UV/visible

* Author to whom all correspondence should be addressed. Fax: +886-3-4559373. E-mail: cejuang@ce.yzit.edu.tw.

[†] Yuan-Ze Institute of Technology.

[‡] Lien-Ho Junior College of Technology.

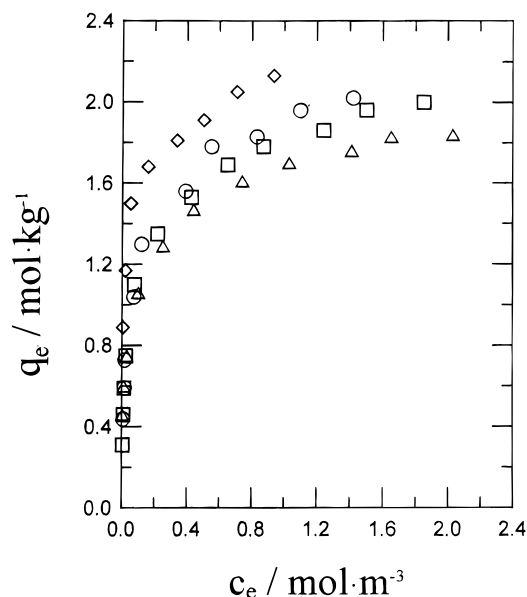


Figure 1. Equilibrium adsorption on activated carbon fiber: (Δ) 2-chlorophenol; (□) 3-chlorophenol; (○) 4-chlorophenol; (◇) 2,4-dichlorophenol.

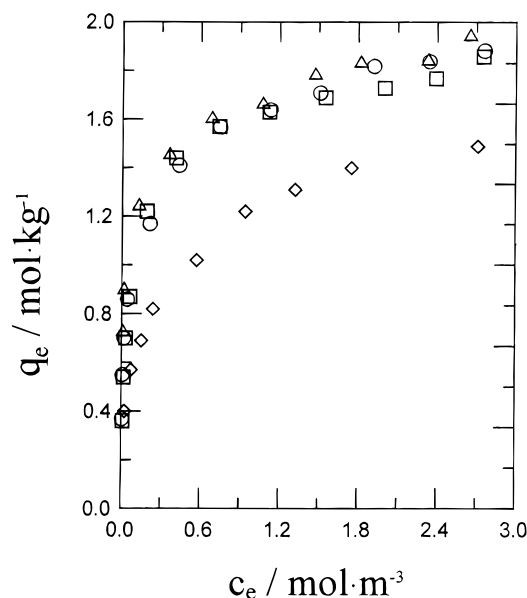


Figure 2. Equilibrium adsorption on activated carbon fiber: (◇) phenol; (□) *p*-cresol; (○) *m*-cresol; (Δ) *o*-cresol.

spectrophotometer (Hitachi Model U-2000) at appropriate wavelengths. Each experiment was duplicated under identical conditions.

Results and Discussion

Equilibrium Adsorption. Figures 1 and 2 show adsorption isotherms, i.e., the relations between the amount of phenolic compounds adsorbed per unit mass of activated carbon fiber (q_e) and their remaining concentrations in the aqueous solutions (c_e). The adsorption capacity, defined as the amount at the plateau of the isotherm, has the following order: 2,4-dichlorophenol > 4-chlorophenol > 3-chlorophenol > *o*-cresol > *m*-cresol > 2-chlorophenol > *p*-cresol > phenol. In general, high capacities are obtained for the chlorinated phenols. Streat et al. (1995) have also found that 4-chlorophenol shows a higher adsorption than that for phenol on all granular activated carbon, wood, shell, rubber, and coal adsorbents. Also, a larger adsorption capacity of 4-chlorophenol on granular activated

carbon was reported by comparison with *p*-cresol (Radke and Prausnitz, 1972).

It is generally accepted that the capacity for activated carbon adsorption is higher when the adsorbate has a high molar mass or a smaller solubility in water (Caturla et al., 1988; Dvorak et al., 1993; Streat et al., 1995). However, this is not the case here. Mattson et al. (1969) indicated that the adsorption capacity of phenols on granular activated carbon is affected by hydrogen-bonding between adsorbates and adsorbents. On the activated carbon fiber surface, there are many conjugated π bonds, which are nonlocalized and highly active. After activation, a number of oxygen-containing functional groups exist in the crystal lattice of the surface, including electron acceptors (e.g., carbonyl and carboxyl) and electron donors (e.g., hydroxyl). It is hence probable to form hydrogen bonds between the electron-acceptor groups on the activated carbon fiber surface and the hydrogen atoms on phenolic compounds (Mattson et al., 1969). Judging from the electrophilic nature of the studied phenols, the present results are somewhat in agreement with this effect.

With regard to adsorption capacity, the present ordering is somewhat opposite to many of those observed using other adsorbents. For example, Caturla et al. (1988) found the ordering to be phenol > 4-chlorophenol > 2,4-dichlorophenol, as expected from the molecular volume of the adsorbate. A sequence of *p*-cresol > phenol > *m*-cresol > *o*-cresol has also been reported for their adsorption on either fly ash or Al(III)- and Fe(III)-impregnated fly ash (Singh and Rawat, 1994). Jossens et al. (1978) found the following ordering: 2,4-dichlorophenol > phenol > 4-chlorophenol for their adsorption on granular activated carbon. Furthermore, Itaya et al. (1984) observed that the ordering is 4-chlorophenol > phenol > *p*-cresol on Amberlite XAD-4 resin and the order changes to *p*-cresol > 4-chlorophenol > phenol on XAD-7 resins.

Such discrepancies are probably due to the differences in pore structure between activated carbon fiber and other adsorbents. Also, the possible oxidative coupling of phenolic compounds on carbon surfaces is a cause (Grant and King, 1990). Activated carbon is essentially characterized by a broad pore size distribution containing micro- (<2 nm), meso- (2–50 nm), and macropores (>250 nm). It is believed that the major adsorption sites on activated carbon are located in micropores rather than in mesopores where only weaker adsorption is observed (Yang et al., 1993). The adsorption on activated carbon must proceed through a sequence of diffusion steps from the bulk phase into the mesopores and then to micropores. Thus, the adsorption capacity would be lower for an adsorbate with a larger molecular volume (Caturla et al., 1988). However, for activated carbon fiber the micropores of depth less than the radius of a fiber (about 6 μm) are directly exposed on the external surface (Sakoda et al., 1987; Yang et al., 1993). It is thus deduced that the micropore size and its distribution play an important role in the activated carbon fiber adsorption of phenols (Foster et al., 1992). Perhaps, the effect of hydrophobic interaction between poly(acrylonitrile) fibers and adsorbates cannot be ignored (Itaya et al., 1984).

In general, adsorption isotherms are important to describe how adsorbates will interact with activated carbon fiber and are critical in optimizing the use of activated carbon fiber as an adsorbent. In this regard, the correlation of adsorption data using either a theoretical or empirical equation is essential to practical adsorption operation. Five two- and three-parameter isotherm equations are tried in the present study.

Table 2. Parameters and Normalized Deviations in the Langmuir Equation

solute	Langmuir I, eq 2				Langmuir II, eq 4			
	$q_{\text{mon}}/\text{mol}\cdot\text{kg}^{-1}$	$K_L/\text{m}^3\cdot\text{mol}^{-1}$	r	$\Delta q/\%$	$q_{\text{mon}}/\text{mol}\cdot\text{kg}^{-1}$	$K_L/\text{m}^3\cdot\text{mol}^{-1}$	r	$\Delta q/\%$
phenol	1.653	4.004	0.940	12.9	1.250	17.64	0.936	16.4
2-chlorophenol	1.860	14.52	0.946	18.6	1.482	140.5	0.922	20.6
3-chlorophenol	2.011	14.92	0.954	20.1	1.607	54.62	0.976	11.9
4-chlorophenol	2.046	16.73	0.956	16.4	1.644	50.54	0.956	11.8
2,4-dichlorophenol	2.136	33.92	0.946	16.3	1.807	204.4	0.933	9.63
<i>p</i> -cresol	1.841	11.69	0.967	13.3	1.623	27.64	0.980	7.75
<i>m</i> -cresol	1.888	11.79	0.936	23.2	1.628	89.67	0.927	16.9
<i>o</i> -cresol	1.939	11.93	0.946	17.7	1.637	106.0	0.935	11.0

Two-Parameter Isotherm Equations. (1) Langmuir Equation. The most widely used two-parameter equation is the Langmuir equation, which is represented as

$$\theta = q_e/q_{\text{mon}} = K_L c_e / (1 + K_L c_e) \quad (1)$$

where θ is the fractional coverage and q_{mon} is the amount adsorbed per unit mass of adsorbent corresponding to complete coverage. K_L is the Langmuir constant. Rearranging eq 1, we have

$$c_e/q_e = (1/K_L q_{\text{mon}}) + (1/q_{\text{mon}}) c_e \quad (2)$$

A plot of (c_e/q_e) vs c_e would give K_L and q_{mon} from the slope and intercept. In order to compare the applicability of various isotherm equations more definitely, a normalized deviation, Δq , is calculated and defined as follows:

$$\Delta q = (1/N) \sum_{i=1}^N |(q_{e,i}^{\text{calc}} - q_{e,i}^{\text{expt}})/q_{e,i}^{\text{expt}}| \quad (3)$$

where the superscripts "calc" and "expt" are the calculated and experimental values, respectively; N is the number of measurements.

The parameters of the Langmuir equation (designated as Langmuir I) obtained for all systems, together with the normalized deviation, Δq , are listed in Table 2. It is evident that the value of Δq is considerably large (12.9–23.2%), although the linear fit is fairly good (correlation coefficient $r > 0.936$). The Langmuir equation I (eq 2) is essentially good only in higher concentration ranges (not shown). An alternative form of the Langmuir equation was suggested for relatively lower concentrations (McKay, 1982).

$$1/q_e = (1/q_{\text{mon}}) + (1/K_L q_{\text{mon}})(1/c_e) \quad (4)$$

This is called Langmuir equation II. Similarly, the values of K_L and q_{mon} are determined from the plot of $(1/q_e)$ vs $(1/c_e)$. The parameters and Δq are also listed in Table 2. In general, Δq are slightly reduced for most systems (7.75–20.6%) compared to the Langmuir equation I. As expected, the Langmuir equation II fits better at lower liquid concentrations (not shown).

(2) Freundlich Equation. The Freundlich equation is an empirical one used to describe the isotherm data:

$$q_e = K_F c_e^{1/n} \quad (5)$$

A linear form of this equation can be obtained as follows.

$$\ln q_e = \ln K_F + (1/n) \ln c_e \quad (6)$$

A plot of $\ln q_e$ vs $\ln c_e$ would give n and K_F from the slope and intercept. The results are listed in Table 3. It is found that the fit is better, especially for *o*-cresol ($\Delta q = 1.83\%$);

Table 3. Parameters and Normalized Deviations in the Freundlich Equation

solute	$K_F/\text{mol}^{n+1}\cdot\text{kg}^{-1}\cdot\text{m}^{-3n}$	n	r	$\Delta q/\%$
phenol	1.166	3.644	0.992	3.25
2-chlorophenol	1.672	4.495	0.992	3.63
3-chlorophenol	1.875	3.558	0.974	9.28
4-chlorophenol	1.999	3.666	0.978	6.08
2,4-dichlorophenol	2.186	6.374	0.980	2.85
<i>p</i> -cresol	1.570	3.868	0.970	10.5
<i>m</i> -cresol	1.600	4.385	0.980	5.93
<i>o</i> -cresol	1.678	6.283	0.996	1.83

however, the deviations between experimental and modeled results at lower concentrations are still significant (not shown).

The Freundlich equation, which is suitable for highly heterogeneous surfaces, frequently gives good representation of adsorption data over a restricted range of concentrations (e.g., the need of piecewise fitting) (Cal et al., 1994; Fritz and Schlunder, 1981). It does not reduce to Henry's law at concentrations approaching zero. It is often seen that when it is fit to data at high and moderate concentrations, it provides a poor fit for adsorption data at low concentrations (Jossens et al., 1978).

Since in all systems Langmuir and Freundlich equations give a relatively poor fit over the entire range of concentrations, the applicability of empirical equations containing three adjustable parameters was examined. Each of these can reduce to Henry's law at extremely low concentrations.

Three-Parameter Isotherm Equations. (1) Redlich–Peterson Equation. The Redlich–Peterson equation (Redlich and Peterson, 1959) contains three parameters, a_R , b_R , and β .

$$q_e = a_R c_e / (1 + b_R c_e^\beta) \quad (7)$$

where β lies between 0 and 1. This equation gave a good representation for phenol adsorption from dilute aqueous solution on Amberlite XAD-8 (Farrier et al., 1979) and on XAD-4 and XAD-7 resins (Itaya et al., 1984). In a slightly different form, it was used also by Radke and Prausnitz (1972). Rewriting eq 7, we obtain

$$c_e/q_e = (1/a_R) + (b_R/a_R) c_e^\beta \quad (8)$$

For each system, the three parameters were obtained using a least-squares fitting procedure to minimize the deviation between calculated and experimental values. The calculated parameters are listed in Table 4. β ranges from 0.779 to 0.910. The values of Δq lie between 1.41 and 7.01%, which is a considerably better fit compared to the two-parameter equations.

(2) Toth Equation. The Toth equation (Toth, 1971), proposed for gas adsorption, has been applied for solute adsorption from dilute aqueous solutions (Jossens et al., 1978). It has three parameters: q^∞ , b_T , and M , in which is a semi-empirical parameter characteristic of the adsorbent

Table 4. Parameters and Normalized Deviations in the Redlich–Peterson Equation

solute	$a_R/\text{m}^3\cdot\text{kg}^{-1}$	$b_R/(\text{m}^3\cdot\text{mol}^{-1})^\beta$	β	r	$\Delta q/\%$
phenol	55.79	1.166	0.799	0.992	2.78
2-chlorophenol	112.9	1.672	0.865	0.989	7.01
3-chlorophenol	85.11	1.875	0.860	0.991	4.99
4-chlorophenol	115.2	1.999	0.843	0.990	3.53
2,4-dichlorophenol	1380	643.1	0.850	0.987	5.58
<i>p</i> -cresol	58.31	35.32	0.910	0.991	2.42
<i>m</i> -cresol	153.0	93.75	0.850	0.994	3.77
<i>o</i> -cresol	1133	673.2	0.860	0.992	1.41

Table 5. Parameters and Normalized Deviations in the Toth Equation

solute	$q^\infty/\text{mol}\cdot\text{kg}^{-1}$	$b_T/(\text{m}^3\cdot\text{mol}^{-1})^M$	M	$\Delta q/\%$
phenol	15.0	0.3416	0.1160	0.25
2-chlorophenol	16.7	0.2352	0.0919	2.70
3-chlorophenol	16.2	0.2819	0.1138	6.21
4-chlorophenol	3.34	0.1945	0.3837	9.60
2,4-dichlorophenol	4.34	0.1659	0.1659	2.14
<i>p</i> -cresol	2.86	0.2046	0.3446	5.81
<i>m</i> -cresol	3.87	0.2041	0.2253	5.52
<i>o</i> -cresol	9.26	0.1623	0.0886	0.94

only, irrespective of the temperature and the nature of the adsorbate.

$$q_e = q^\infty c_e / (b_T + c_e^M)^{1/M} \quad (9)$$

where q^∞ is an adjustable parameter, indicating a maximum adsorption when $c_e \rightarrow \infty$. The constants b_T and M are obtained as follows. First, Toth introduced a dimensionless quantity Ψ defined by

$$\Psi = (d \ln c_e / d \ln q_e) - 1 \quad (10)$$

where Ψ can be determined from the experimental results. The relation between Ψ and c_e is (Toth, 1971)

$$\Psi = a c_e^b \quad (11)$$

where a and b are constants. When we set $a = 1/b_T$ and $b = M$, integration of eq 10 gives the Toth equation, eq 9. In this integration, Toth uses the boundary condition $q_e \rightarrow q^\infty$ when $c_e \rightarrow \infty$.

For the Langmuir equation, $b = 1$, and for the Freundlich equation, $b = 0$. If Henry's law were to hold for all concentrations, a would have to be zero. Furthermore, at very low concentrations, $b_T \gg c_e^M$, the adsorption equation of eq 9 follows Henry's law. In this work, these parameters are determined as follows. Polynomial fitting of experimental data of $\ln c_e$ vs $\ln q_e$ is first made and Ψ is obtained by differentiating according to eq 10. The values of a and b , hence b_T and M , are obtained from eq 11, and then q^∞ is obtained from eq 9. Table 5 lists the results. Generally, the Toth equation shows no improvement of the overall fit compared to the Redlich–Peterson equation.

From Table 5 M is not constant and shows considerable scatter among adsorbates ranging from 0.0886 (for *o*-cresol) to 0.3837 (for 4-chlorophenol). This is opposite to the original meaning (Toth, 1971) and the results of Itaya et al. (1984). Also, the value of q^∞ calculated here are opposite to experimental observations, which is probably due to the unfixed M in the model calculation. Thus, there remains a problem as to whether this equation is applicable or not. An attempt was made to determine a constant M value using a least-squares fitting procedure for all the systems. The resulting isotherm equation gives a comparatively poorer fit to the adsorption data. It is hence deduced that the Toth equation is not suitable for describing adsorption of phenolic compounds on activated carbon fiber, as also

indicated for phenol adsorption on Amberlite XAD-4 and XAD-7 macroreticular resins (Itaya et al., 1984).

(3) Equation of Jossens et al. For a highly heterogeneous surface, the highest energy sites are filled first so that the enthalpy of adsorption declines rapidly with increased surface coverage. Assuming that an energy distribution function of adsorption sites, $f(E)$, obeys eq 12,

$$f(E) = A(E - E_0)^\alpha \quad (12)$$

the following relation between the isosteric enthalpy of adsorption, E , and the amount of adsorbate adsorbed per unit mass of adsorbent is derived (Jossens et al., 1978).

$$E - E_0 = Dq_e^p \quad (13)$$

where E_0 is the maximum enthalpy of adsorption (at zero coverage) and p is a constant related to the distribution of energy sites on the surface by the equation $\alpha = (1 - p)/p$, $0 < p < 1$, $A = 1/pE_0^{1/p}$, and $D = E_0/N_s^p$ (N_s : number of total adsorption sites). Then, the following isotherm equation is obtained.

$$c_e = (q_e/H) \exp(K_J q_e^p) \quad (14)$$

where H corresponds to Henry's law constant and is related to E_0 as follows.

$$E_0 = -RT^2(d \ln H/dT) \quad (15)$$

where R is the universal gas constant. K_J is a function of temperature T only:

$$D = -RT^2(dK_J/dT) \quad (16)$$

These equations have two desirable characteristics. At low coverage, eq 14 reduces to Henry's law, that is

$$\lim_{c_e \rightarrow 0} q_e = Hc_e \quad (17)$$

and at the highest coverage, an ultimate adsorption amount q^∞ can be obtained from eq 13, irrespective of temperature.

$$q^\infty = (E_0/D)^{1/p} \quad (18)$$

Thus, p is characteristic of the adsorbent only, irrespective of both temperature and the nature of adsorbates. For example, $p = 0$ corresponds to a uniform surface for which all sites have the same energy. A good representation of equilibrium data using this equation was reported for adsorption of phenolic compounds from aqueous solutions onto activated carbon (Jossens et al., 1978) and on Amberlite XAD-4 and XAD-7 macroreticular resins (Itaya et al., 1984).

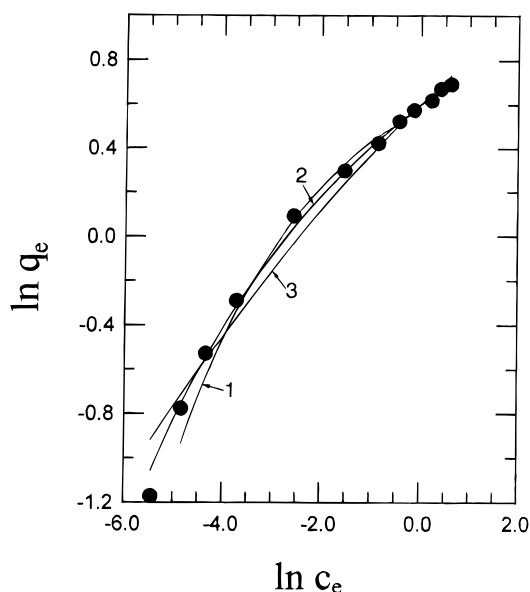
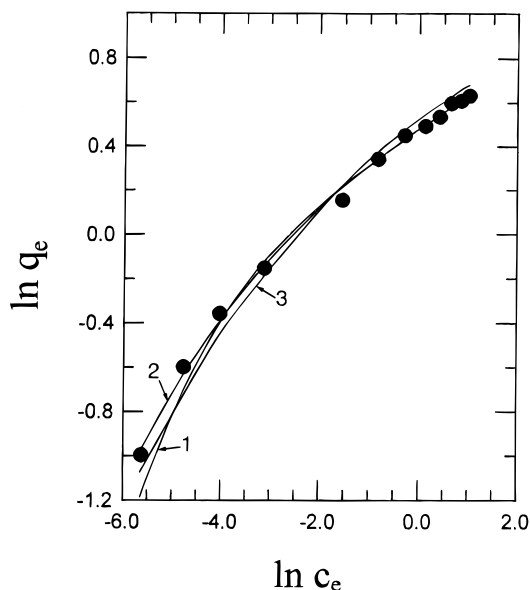
Rearranging eq 14, we have

$$\ln(c_e/q_e) = -\ln H + K_J q_e^p \quad (19)$$

If p is known, the values of H and K_J can be obtained either from the plot of $\ln(c_e/q_e)$ against q_e or using a least-squares fitting procedure. Here, an optimal value of p is taken to be 0.9773 ± 0.0624 for all the systems using the trial and error method. The parameters and Δq in the equation of Jossens et al. are listed in Table 6. The value of Δq is always less than 3.26%. As a whole, this equation gives the best fit of adsorption data for most systems, although Δq is slightly smaller for phenol and *o*-cresol using the Toth equation. Figures 3 and 4 compare the measured data for

Table 6. Parameters and Normalized Deviations in the Equation of Jossens et al.

solute	$H/\text{m}^3\cdot\text{kg}^{-1}$	$K_J/(\text{kg}\cdot\text{mol}^{-1})^p$	p	r	$\Delta q/\%$
phenol	39.06	2.846	0.9773	0.984	2.96
2-chlorophenol	455.6	3.409	0.9773	0.985	2.50
3-chlorophenol	209.2	2.637	0.9773	0.996	2.48
4-chlorophenol	214.3	2.486	0.9773	0.990	3.26
2,4-dichlorophenol	5892	3.800	0.9773	0.989	1.82
<i>p</i> -cresol	215.4	3.114	0.9773	0.986	3.06
<i>m</i> -cresol	395.1	3.431	0.9773	0.996	1.59
<i>o</i> -cresol	2232	4.287	0.9773	0.994	1.56

**Figure 3.** Experimental and calculated results for 3-chlorophenol adsorption on activated carbon fiber using three-parameter isotherm equations: (1) Redlich–Peterson; (2) Jossens; (3) Toth.**Figure 4.** Experimental and calculated results for *m*-cresol adsorption on activated carbon fiber using three-parameter isotherm equations: (1) Redlich–Peterson; (2) Jossens; (3) Toth.

3-chlorophenol and *m*-cresol to the fit following various three-parameter equations. The Redlich–Peterson equation is rather valid in the higher concentration ranges and the equation of Jossens et al. gives the best fit over the entire ranges.

From the theory of Jossens et al., the value of H should give some indication of the order of adsorption of different solutes on a single adsorbent. However, this is not the case

here. From Table 6 H increases in the order phenol < 3-chlorophenol < 4-chlorophenol < *p*-cresol < *m*-cresol < 2-chlorophenol < *o*-cresol < 2,4-dichlorophenol. This is probably due to the “constant” nature of the p value. In the original work of Jossens et al. (1978), actually, the values of p obtained for a given activated carbon were not constant but ranged from 0.25 (for phenol) to 0.80 (for 4-chlorophenol). In addition, they found the following order of H : 4-chlorophenol < phenol < 4-nitrophenol < 2,4-dichlorophenol < 2-phenylphenol. Furthermore, the following order for H , phenol < *p*-cresol < 4-chlorophenol, was reported for their adsorption on Amberlite XAD-4 and XAD-7 resins (Itaya et al., 1984), which is opposite to the findings of Jossens et al. as well as the solubility of the adsorbates in water. Their explanation is that hydrophobic interaction between the resins and adsorbates plays an important role in the adsorption process.

Conclusions

Equilibrium studies for the adsorption of eight phenolic compounds from aqueous solutions onto activated carbon fiber have been carried out in the concentration range 40–500 g·m⁻³ at 303 K. The following results are obtained.

(1) High adsorption capacities (about 2.0 mol·kg⁻¹) are generally obtained for the chlorinated phenols compared to the methyl-substituted ones (about 1.8 mol·kg⁻¹).

(2) For two-parameter equations, the Langmuir equation gives the poorest overall fit. The Freundlich equation yields a somewhat better fit but still deviates considerably from experimental data at lower liquid concentrations.

(3) For three-parameter isotherm equations, the normalized percent deviation obtained using the Redlich–Peterson equation (1.4–7.0%) is nearly the same as that obtained using the Toth equation (0.3–9.6%). Of the equations tried, the equation of Jossens et al. gives the most satisfactory fit over the entire range of concentrations and yields a normalized percent deviation less than 3.3%.

Literature Cited

- Cal, M. P.; Larson, S. M.; Rood, M. J. Experimental and Modeled Results Describing the Adsorption of Acetone and Benzene onto Activated Carbon Fibers. *Environ. Prog.* **1994**, *13*, 26–30.
- Caturla, F.; Martin-Martinez, J. M.; Molina-Sabio, M.; Rodriguez-Reinoso, F.; Torregrosa, R. Adsorption of Substituted Phenols on Activated Carbon. *J. Colloid Interface Sci.* **1988**, *124*, 528–534.
- Dvorak, B. I.; Lawler, D. F.; Speitel, G. E.; Jones, D. L.; Badway, D. A. Selecting Among Physical/Chemical Processes for Removing Synthetic Organics from Water. *Water Environ. Res.* **1993**, *65*, 827–839.
- Economy, J.; Lin, R. Y. Adsorption Characteristics of Activated Carbon Fibers. *Appl. Polym. Symp.* **1976**, *29*, 199–211.
- Farrier, D. S.; Hines, A. L.; Wang, S. W. Adsorption of Phenol and Benzoic Acid from Dilute Aqueous Solution onto a Macroporous Resin. *J. Colloid Interface Sci.* **1979**, *69*, 233–237.
- Foster, K. L.; Fuerman, R. G.; Economy, J.; Larson, S. M.; Rood, M. J. Adsorption Characteristics of Trace Volatile Organic Compounds in Gas Streams onto Activated Carbon Fibers. *Chem. Mater.* **1992**, *4*, 1068–1073.
- Fritz, W.; Schlunder, E. U. Competitive Adsorption of Two Dissolved Organics onto Activated Carbon. I. Adsorption Equilibria. *Chem. Eng. Sci.* **1981**, *36*, 721–730.
- Grant, T. M.; King, C. J. Mechanism of Irreversible Adsorption of Phenolic Compounds by Activated Carbons. *Ind. Eng. Chem. Res.* **1990**, *29*, 264–271.
- Itaya, A.; Kato, N.; Yamamoto, J. Liquid Phase Adsorption Equilibrium of Phenol and its Derivatives on Macroporous Adsorbents. *J. Chem. Eng. Jpn.* **1984**, *17*, 389–395.
- Jossens, L.; Prausnitz, J. M.; Fritz, W.; Schlunder, E. U.; Myers, A. L. Thermodynamics of Multi-Solutes Adsorption from Dilute Aqueous Solutions. *Chem. Eng. Sci.* **1978**, *33*, 1097–1106.
- Mattson, J. S.; Mark, H. B., Jr.; Malbin, M. D.; Weber, W. J., Jr.; Crittenden, J. C. Surface Chemistry of Active Carbon: Specific Adsorption of Phenols. *J. Colloid Interface Sci.* **1969**, *31*, 116–123.
- McKay, G. Adsorption of Dyes from Aqueous Solutions with Activated Carbon. I: Equilibrium and Batch Contact-Time Studies. *J. Chem. Technol. Biotechnol.* **1982**, *32*, 759–772.

- Radke, C. J.; Prausnitz, J. M. Adsorption of Organic Solutes from Dilute Aqueous Solutions on Activated Carbon. *Ind. Eng. Chem. Fundam.* **1972**, *11*, 445-451.
- Redlich, O.; Peterson, D. L. A Useful Adsorption Isotherm. *J. Phys. Chem.* **1959**, *63*, 1024.
- Sakoda, K.; Kawazoe, K.; Suzuki, M. Adsorption of Tri- and Tetra-chloroethylene from Aqueous Solutions on Activated Carbon Fibers. *Water Res.* **1987**, *21*, 712-722.
- Singh, B. N.; Rawat, N. S. Comparative Sorption Equilibrium Studies of Toxic Phenols on Flyash and Impregnated Flyash. *J. Chem. Technol. Biotechnol.* **1994**, *61*, 307-317.
- Streat, M.; Patrick, J. W.; Camporro Perez, M. J. Sorption of Phenol and *para*-Chlorophenol from Water Using Conventional and Novel Activated Carbon. *Water Res.* **1995**, *29*, 467-472.
- Suzuki, M. Activated Carbon Fibers: Fundamentals and Applications. *Carbon* **1994**, *32*, 577-586.
- Toth, J. State Equations of the Solid-Gas Interphase Layers. *Acta Chim. Acad. Sci. Hung.* **1971**, *69*, 311-328.
- Yang, O. B.; Kim, J. C.; Lee, J. S.; Kim, Y. G. Use of Activated Carbon Fiber for Direct Removal of Iodine from Acetic Acid Solution. *Ind. Eng. Chem. Res.* **1993**, *32*, 1692-1697.

Received for review September 23, 1995. Accepted January 21, 1996.*

JE950238G

* Abstract published in *Advance ACS Abstracts*, March 1, 1996.