Equilibrium adsorption of chlorophenols on granular activated carbon

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ABSTRACT: The adsorption of chlorinated phenols from aqueous solution on granular activated carbon was studied in batch reactors. Single-component equilibrium adsorption data for the eight compounds in two concentration ranges at pH 7.0 and 30°C were fit well by both the Langmuir and the Freundlich equations. The adsorptive capacities at pH 7.0 increase from pentachlorophenol to trichlorophenols and are fairly constant from trichlorophenols to monochlorophenols. Equilibrium measurements were also conducted for 2,4,5-trichlorophenol, 2,4-dichlorophenol, and 4-chlorophenol over a wide pH range. A surface complexation model has been proposed to describe the effect of pH on adsorption equilibria of chlorophenols on activated carbon. Activated carbon surface functional sites are divided into acidic and basic groups with which molecular and ionized forms of chlorophenols interact, respectively, and form two neutral complexes. The simulations of the model are in excellent agreement with the experimental data. *Water Environ. Res.*, **67**, 892 (1995).

KEYWORDS: activated carbon, adsorption, isotherms, chlorophenols.

Chemical process and forest product industries discharge wastewater containing chlorophenolic compounds. These compounds are taste and odor producing and have been found to be toxic and carcinogenic. Activated carbon adsorption has been successfully implemented as a unit process in both potable and wastewater treatment. It has been found that chlorinated phenols can be strongly adsorbed by activated carbon (Montgomery, 1985). The recent concern with the removal of chlorinated phenols has focused attention on the biodegradation of these compounds on granular activated carbon (Speitel *et al.*, 1989). The highly chlorinated phenols, that is, tetra- and pentachlorophenol, can be biodegraded anaerobically, and various lower chlorinated phenols, that is, tri-, di-, and monochlorophenols, are formed as metabolites (Nicholson *et al.*, 1992). Biodegradation and adsorption of various chlorinated phenols will occur simultaneously in activated carbon treatment systems. Many investigators (Weber and Morris, 1964; Snoeyink *et al.*, 1969; Gretzen and Ward, 1969; Ward and Gretzen, 1970; and Jain and Snoeyink, 1973) have noted that pH plays an important role in adsorption of compounds with acidic functional groups on activated carbon.

In the past quarter century there has been increasing interest in the sorption properties and surface chemistry of hydrous metal oxides, and different surface complexation models have been proposed to describe the sorption reactions (Schindler and Kamber, 1968; Schindler and Gamsjager, 1972; Stumm *et al.*, 1970; Huang and Stumm, 1973; Davis *et al.*, 1978; and Dzombak and Morel, 1990). Surface complexation models have been widely applied to hydrous oxides/inorganic ion systems, whereas a few studies have applied surface complexation models to activated carbon/inorganic ion systems. To gain better insight into the mechanism of cadmium removal, Huang and Ostovic (1978) characterized the surface properties of activated carbon in terms of its surface acidity and hydroxo groups. The association between cadmium ions and activated carbon (GAC) was interpreted and described by a surface complexation model. No studies were found that applied surface complexation models to activated carbon/organic acid systems.

This present work concerns the adsorption of chlorinated phenols by granular activated carbon from aqueous solutions under varying pH conditions and presents a surface complexation model for describing the effect of pH on adsorption of chlorophenols on activated carbon.

Materials and methods

Chemicals. Eight chlorinated phenols were studied, pentachlorophenol (PCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,4,5-trichlorophenol (2,4,5-TCP), 2,4-dichlorophenol (2,4-DCP),3,4-dichlorophenol (3,4-DCP), 2-chlorophenol (2-CP) and 4-chlorophenol (4-CP). The pK_a values for these compounds are given in Table 1. Aqueous solutions of each chlorinated phenol were prepared by dissolution in glass-distilled deionized water, having varying concentrations of 0.35–2.3 mM. Preliminary studies indicated that in the neutral pH range (6.5–7.5), a 5-mM phosphate (NaH_2PO_4 and Na_2HPO_4) buffer could maintain the pH of solutions with adsorbate concentrations of less than 2.3 mM within 0.2 unit fluctuation during adsorption (Yang, 1993). A 5-mM phosphate buffer was included in all subsequent experiments, unless noted otherwise. The pH of solutions was adjusted with minimum amounts of HCl and NaOH solutions, as needed.

Activated carbon. The adsorbent used throughout this study was Calgon Filtrasorb-400 activated carbon, the properties of which are described elsewhere (Montgomery, 1985). The carbon received from the manufacturer was ground in an analytical mill and sieved to yield a 30 × 40 mesh size. After sieving, the carbon was washed with glass-distilled deionized water to remove all fines, dried 48 h in an oven at 105°C, and stored in an air-tight desiccator until use.

Equilibrium studies. Batch studies were used to obtain the equilibrium data. Forty-milliliter portions of the solution with the desired pH and adsorbate concentration were placed in 50-ml polytetrafluorethylene tubes containing accurately weighed amounts of carbon. Then the tubes were continuously mixed in a constant-temperature (30°C) shaker-bath for 6 days. This equilibration time was determined from preliminary kinetic studies (Yang, 1993). After adsorption equilibrium was reached, the solutions were left standing for 20 min to allow the carbon to settle, the equilibrium concentration was measured, and the extent of adsorption was calculated. If the desired solution pH was outside the phosphate-buffering region (pH 6.5–7.5) and the acidic- and basic-buffering region (pH < 4 or pH > 10), occa-

Table 1—pK_a values for chlorophenols.

Compound	pK_a
PCP	5.25[a]
	4.74[b]
2,3,4,6-TeCP	5.40[a]
2,4,6-TCP	6.15[a]
	5.99[b]
2,4,5-TCP	6.94[a]
2,4-DCP	7.85[a]
4-CP	9.18[c]
2-CP	8.49[c]
	8.52[b]

[a] After Schellenberg *et al.* (1984).
[b] After Westall *et al.* (1985).
[c] After CRC Handbook of Chemistry and Physics (1990–1991).

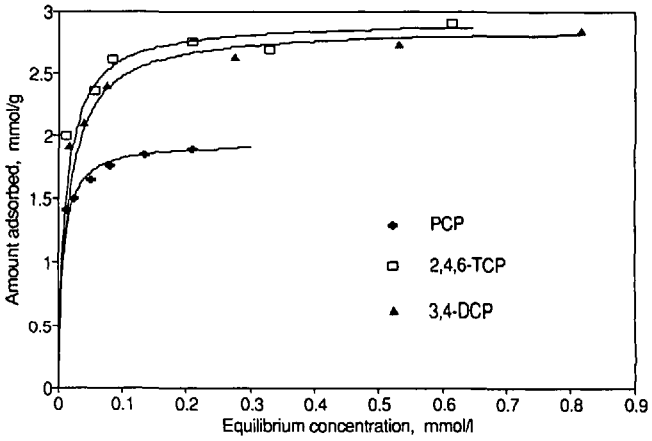

Figure 1—Langmuir isotherms for adsorption of PCP, 2,4,6-TCP, and 3,4-DCP (high concentration range).

sionally it was necessary to adjust pH during the equilibration period to maintain the desired pH. The final pH was measured and reported as the equilibrium value. Oxygen concentrations in the test solutions were controlled by headspace air and initial solution saturation and remained aerobic with final dissolved oxygen concentrations typically 4–5 mg/L.

Analytical techniques. Five-milliliter aliquots were used for analysis of chlorophenols. The samples were first acetylated and then extracted into hexane. Each sample was added to 45 mL of glass-distilled water in a 150-mL separatory funnel using a 5-mL volumetric pipette. Fifty microliters of internal standard (either 2,4,6-tribromophenol for 2,4,5-TCP or 2,6-dibromophenol for other chlorophenols) was added using a 50-μL syringe. After 1 mL of a 0.73-g/mL solution of potassium carbonate and 1 mL of acetic anhydride were added, the funnel was shaken for exactly 2 min. The complete acetylation reaction would take about 2 h, after which 5 mL of hexane was added using a dedicated 5-mL volumetric pipette, and again the funnel was shaken for another 2 min. After 30 min, the water layer was drained and the hexane layer was withdrawn using a new pasteur pipette and transferred to a 2-mL amber glass vial with polytetrafluorethylene-lined cap, which was stored in a refrigerator until gas chromatograph analysis was conducted.

Using an autosampler, 1 μL of hexane solution was injected into a Hewlett Packard model 5890A gas chromatograph equipped with an Ni-63 electron capture detector (ECD) and 30 m by 0.323 mm ID DB-5 fused-silica capillary column (J + W Scientific, Orangeville, CA). Helium (5 psi) was used as the carrier gas and a 95% argon/5% methane mixture was used as the ECD auxiliary gas. The detector temperature was set at 320°C and injector temperature was 250°C. The samples were run using a temperature program as follows: an initial oven temperature of 45°C was held for 2 min, increased by 15°C/min to 150°C, and then by 5°C/min to a final temperature of 215°C that was held for 5 min.

Results and discussion

Isotherms of chlorophenols at pH 7. Equilibrium adsorption data at pH 7.0 for all compounds were fit by the Langmuir equation, $q = QbC/(1 + bC)$, and the Freundlich equation, $q = kC^n$. The constants in the Langmuir and Freundlich equations were determined by nonlinear least-squares (NLLS) regression. Because it was not possible to describe well all of the data with one set of isotherm constants, the data were divided into two concentration ranges and values of Q, b, k, and n were determined for each range. Representative Langmuir plots of PCP, 2,4,6-TCP, and 3,4-DCP for high and low concentration ranges are shown in Figures 1 and 2, respectively. The values of Q, b, k, and n are given in Table 2, together with the regression coefficients (R^2). The values of R^2 indicate that both isotherm equations fit the equilibrium data well. The goodness of the Langmuir fit suggests that a fixed number of sites is accessible on the surface of the carbon over a given range of solute concentration. The adsorption constants are concentration dependent as evidenced by the significant differences in the magnitudes of the constants between the two concentration ranges. The higher concentration range caused a larger Q and smaller b, k, and n.

The Langmuir adsorptive capacities (Q) increase from pentachlorophenol to trichlorophenols and remain nearly constant from trichlorophenols to monochlorophenols. For molecular (neutral) species, the more chlorinated a chlorophenol, the less soluble in water or the more hydrophobic, and hence the more adsorptive is the compound. A comparison of the pK_a values of the compounds reveals that at pH 7 the percentage of neutral molecules in all species increases from pentachlorophenol to

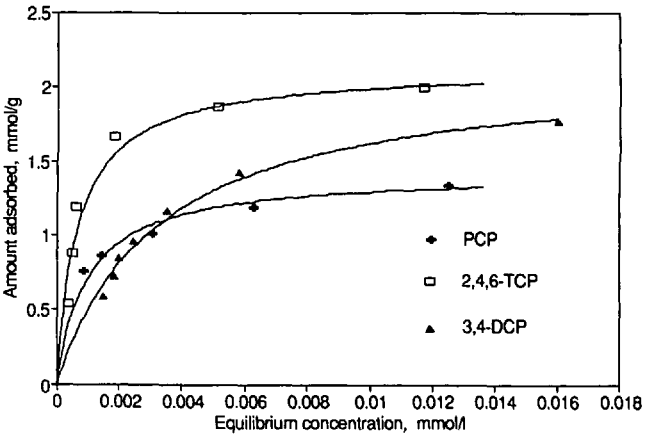

Figure 2—Langmuir isotherms for adsorption of PCP, 2,4,6-TCP, and 3,4-DCP (low concentration range).

Table 2—Adsorption constants for chlorophenols at pH 7 (T = 30°C).

Adsorbate	Concentration range, 10^{-3} mmol/L	Langmuir Q, mmol/g	Langmuir b, L/mmol	Langmuir R^2	Freundlich k	Freundlich n	Freundlich R^2
PCP	0.843–12.53	1.419	1012	0.985	3.324	0.206	0.999
	13.2–208.4	1.898	185.3	0.995	2.298	0.112	0.999
2,3,4,6-TeCP	0.317–5.55	1.478	2875	0.989	3.734	0.186	0.994
	5.55–492.9	2.059	302.5	0.974	2.352	0.096	0.997
2,4,6-TCP	0.39–11.70	2.181	1351	0.971	6.819	0.257	0.904
	11.70–614.4	2.781	195.8	0.989	3.066	0.088	0.993
2,4,5-TCP	0.157–10.33	1.927	1981	0.988	8.358	0.252	0.946
	2.60–171.2	2.378	628.2	0.970	3.184	0.115	1.000
2,4-DCP	0.712–15.52	1.962	1199	0.976	5.004	0.222	0.962
	15.83–960.7	2.713	133.6	0.982	2.893	0.090	0.998
3,4-DCP	1.47–16.01	2.187	299.4	0.992	8.967	0.380	0.959
	17.3–816.4	2.760	108.3	0.911	2.935	0.097	0.998
4-CP	2.06–23.42	1.756	333.9	0.992	4.818	0.288	0.997
	20.15–781.9	2.791	30.93	0.949	3.098	0.210	0.996
2-CP	1.90–21.86	1.808	754.5	0.983	3.762	0.193	0.997
	21.86–791.3	2.954	58.84	0.979	3.200	0.143	0.998

monochlorophenols. The dominant species is the ionized form for pentachlorophenol and the molecular form for monochlorophenols, respectively. The adsorptive capacity for the neutral molecules is higher than that for the ionized forms. It is the combination of two factors, chlorination level and dissociation extent, that results in the observed adsorptive capacities for chlorophenols. In addition, from the comparisons of adsorption constants between 2,4,5-TCP and 2,4,6-TCP, 2,4-DCP and 3,4-DCP, and 4-CP and 2-CP, it can be deduced that the position of chlorine on the phenyl ring has little or no influence on the adsorption of chlorophenols.

Isotherms of 2,4,5-TCP at various pH values. Isotherms for adsorption of 2,4,5-TCP at pH values of 4.15 ± 0.2, 5.22 ± 0.1, 6.58 ± 0.01, 8.17 ± 0.2, 9.3 ± 0.2, and 10.25 ± 0.1 were determined. Representative isotherms are presented in Figure 3. The solid lines shown in Figure 3 represent the Langmuir plots of best fit. There are only slight differences between the isotherms for pH 4.15 ± 0.2 and pH 5.22 ± 0.1, but significant differences exist for other pH values. Similar results have been observed by Snoeyink *et al.* (1969).

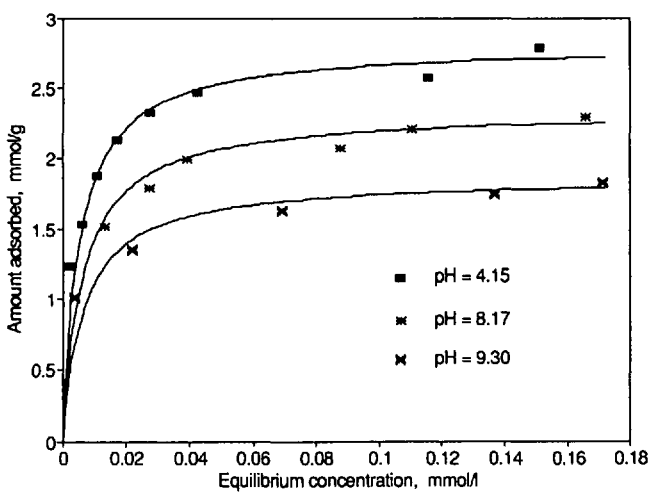

Figure 3—Langmuir isotherms for adsorption of 2,4,5-TCP at different pH values.

Langmuir constants Q and b for 2,4,5-TCP at different pH values were determined by NLLS regression. To minimize the effect of concentration range on the magnitude of the constants, only data within close concentration range for various pH values (except pH 10.25 ± 0.1) were used. Several observations are evident from the data (Table 3). The magnitude of b remains fairly constant among the various pH values within the same solute concentration ranges. It decreases significantly for pH 10.25 ± 0.1, which can be attributed to the much higher solute concentration range (see also Table 2). Decreasing pH value below the compound's pK_a (6.94) appears to have little influence on the adsorptive capacity of 2,4,5-TCP, but a linear decrease with pH in the adsorptive capacity of the compound occurs at pH values greater than its pK_a (Figure 4).

Surface complexation model. It is well known that the Langmuir equation can be derived from the representation of adsorption as a surface complexation reaction (for example, Nelson *et al.*, 1981). A logical extension of the above Langmuir analysis is to describe the chlorophenol adsorption data in terms of a surface complexation model. To simplify analysis, activated carbon surface functional groups can be divided into two generalized types (Jankowska *et al.*, 1991, and Muller *et al.*, 1980): acidic groups that may undergo neutralization by bases and basic

Table 3—Effect of pH on Langmuir constants for 2,4,5-TCP (T = 30°C).

pH	Q, mmol/g	b, L/mmol	Concentration range, mmol/L
4.15	2.719	230.9	0.00293–0.151
5.22	2.675	354.8	0.00227–0.141
6.58	2.540	351.0	0.00200–0.128
8.17	2.090	566.0	0.00185–0.166
9.30	1.750	295.3	0.00387–0.171
10.25	1.637	51.37	0.0295–0.249

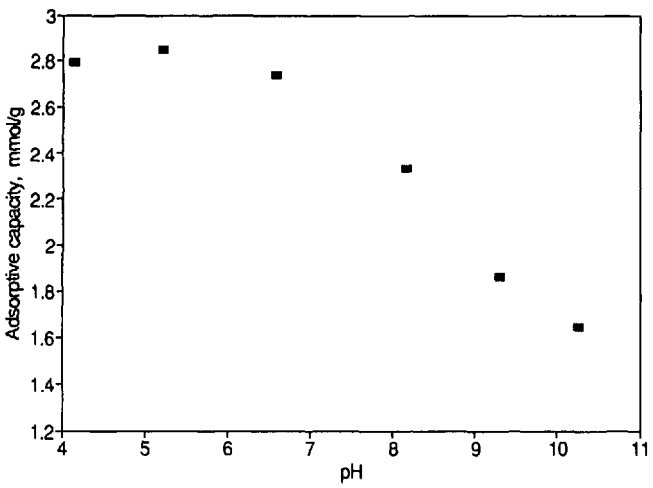

Figure 4—Adsorptive capacity of 2,4,5-TCP as a function of pH.

groups that may be neutralized by acids. Carboxyl, phenolic, quinonoid, and normal lactone are the principal types of acidic groups, whereas usually chromene or pyrone-like structures are attributed to the basic groups. The surface ionization reactions are therefore expressed by

$$\equiv AH \rightleftharpoons \equiv A^- + H_S^+ \quad K_a^{intr}, \tag{1}$$

$$\equiv BH^+ \rightleftharpoons \equiv B + H_S^+ \quad K_b^{intr}, \tag{2}$$

where $\equiv AH$ and $\equiv A$ represent neutral and negatively charged surface acidic groups, $\equiv BH^+$ and $\equiv B$ represent positively charged and neutral basic surface groups, K_a^{intr} and K_b^{intr} are intrinsic equilibrium constants, and H_S^+ denotes a proton at the carbon surface. The mass law equations corresponding to reactions 1 and 2 are

$$K_a^{intr} = \frac{[\equiv A^-]\,[H^+]_s}{[\equiv AH]}, \tag{3}$$

$$K_b^{intr} = \frac{[\equiv B]\,[H^+]_s}{[\equiv BH^+]}. \tag{4}$$

The concentration of protons at some location, i, in the electrical double layer is related to the bulk concentration by the Boltzmann distribution (Davis *et al.*, 1978, and Muller *et al.*, 1980), for example,

$$[H^+]_i = [H^+] \exp\left(\frac{-F\Psi}{RT}\right), \tag{5}$$

where Ψ is the surface potential, F is the Faraday's constant, R is the gas constant, and T is the absolute temperature.
Hence,

$$K_a^{intr} = \frac{[\equiv A^-][H^+] \exp(-F\Psi/RT)}{[\equiv AH]}, \tag{6}$$

and

$$K_b^{intr} = \frac{[\equiv B][H^+] \exp(-F\Psi/RT)}{[\equiv BH^+]}. \tag{7}$$

In the presence of chlorophenols, the following surface complexation reactions can be proposed:

$$\equiv AH + H^+ + ClP^- \rightleftharpoons \equiv AH - HClP \quad K_A^{intr}, \tag{8}$$

$$\equiv BH^+ + ClP^- \rightleftharpoons \equiv BH - ClP \quad K_B^{intr}, \tag{9}$$

where $HClP$ and ClP^- represent molecular and ionized forms of chlorophenol, K_A^{intr} and K_B^{intr} represent intrinsic equilibrium surface complexation constants, and $\equiv AH - HClP$ and $\equiv BH - ClP$ are neutral surface complexes.

The concentrations of ClP^- in the electrical double layer are expressed in terms of the Boltzmann distribution, for example,

$$[ClP^-]_i = [ClP^-] \exp(F\Psi/RT) \tag{10}$$

Thus, the mass law equations corresponding to reactions 8 and 9 are

$$K_A^{intr} = \frac{[\equiv AH - HClP]}{[\equiv AH]\,[H^+]\,[ClP^-]}, \tag{11}$$

$$K_B^{intr} = \frac{[\equiv BH - ClP]}{[\equiv BH^+]\,[ClP^-] \exp(F\Psi/RT)}. \tag{12}$$

The formation of the surface complexes, $\equiv AH - HClP$ and $\equiv BH - ClP$ readjusts the acid-base equilibrium and affects the surface charge. The formation of $\equiv BH - ClP$ serves to directly decrease (make more negative) the surface charge and hence the surface potential. The net surface charge density, in coulombs per square meter, is given by

$$\sigma = \frac{F}{AS}([\equiv BH^+] - [\equiv A^-]), \tag{13}$$

where A is the specific surface area (m^2/g) and S the solid (carbon) concentration (g/L).

To specify the influence of the excess surface charge density on the formation of surface complexes, we require an estimate of the surface potential. According to the Gouy-Chapman theory (for a symmetrical electrolyte with valence Z), the surface charge density σ is related to the surface potential Ψ (in volts) by

$$\sigma = \sqrt{8\epsilon RTI}\,\sinh\frac{ZF\Psi}{2RT}, \tag{14}$$

Table 4 summarizes the surface complexation and aqueous reactions and corresponding equilibrium constants for activated carbon/2,4,5-TCP system. The two surface complexation constants, K_A^{intr} and K_B^{intr} and total concentrations of acidic and basic groups can be extracted from adsorption data via the nonlinear regression program FITEQL (Westall, 1982). These constants and concentrations can in turn be used to simulate the adsorption data. The two properties of the electrical double layer,

Table 4—Surface complexation and aqueous reactions in activated carbon/2,4,5-TCP system.

Surface complexation reactions	log K^{intr}
$\equiv A^- + H^+ = \equiv AH$	7.78[a]
$\equiv B + H^+ = \equiv BH^+$	5.70[a]
$\equiv AH + H^+ + ClP^- = \equiv AH - HClP$	log K_A^{intr}
$\equiv BH^+ + ClP^- = \equiv BH - ClP$	log K_B^{intr}
Aqueous reactions	log K
$HClP = H^+ + ClP^-$	−6.94
$H_2O = H^+ + OH^-$	−14.0

[a] After Huang and Ostovic (1978).

specific surface area, and interface capacitance are assigned, respectively, 941 m^2/g (Huang and Ostovic, 1978) and 1.2 F/m^2 (Davis *et al.*, 1978, and Westall, 1982).

The optimal surface complexation constants for 2,4,5-TCP, 2,4-DCP, and 4-CP, together with overall variances that are the main indicator of the goodness of fit, were determined by analysis of the data using FITEQL (Table 5). Values of variance between 0.1 and 20 indicate a reasonably good fit (Westall, 1982, and Dzombak and Morel, 1990). The three values of variances are all in close proximity to 1, indicating that the proposed surface complexation model is very successful in fitting the adsorption data.

Equilibrium measurements were made for adsorption of 2,4,5-TCP from solutions at a pH range of 4–10 with phosphate buffer (Na_2HPO_4 and NaH_2PO_4) concentrations of zero and 5 mM. The solutions with or without phosphate contained the same initial 2,4,5-TCP concentrations of 1.525 mmol/L and the same carbon dosages were used. No phosphate effect can be observed in the whole pH range studied for these systems (Figure 5). This implies that for the two systems with and without phosphate, the equilibrium concentrations are essentially identical if the pH is the same, and therefore the influence of phosphate competition on adsorption can be neglected. Other investigators have reported similar results for systems with salts of low concentration. Zogorski *et al.* (1976) noted that 0.05 M phosphate buffer exhibited no discernible influence on the rate of adsorption of 2,4-DCP and 2,4-dinitrophenol, whether in an undissociated or dissociated form. Snoeyink *et al.* (1969) studied the effect of NaCl on the adsorption of phenol and *p*-nitrophenol (PNP) and found no distinguishable differences in capacity for NaCl concentrations of zero and 0.01 M at pH 2.0 and pH 10.0. However, they have observed a significant increase in capacity at lower surface coverage for the PNP system with 1.0 M NaCl at pH 10.0. This has been explained by the formation of ion pairing of the cation with the PNP anion, which would have the effect of increasing adsorptive capacity because the ion pair would behave more like the acid form of the PNP or by the reduction of repulsive forces between the adsorbed anions, which allows more molecules on the surface at lower solution concentrations. Westall *et al.* (1985) discussed the importance of organic-inorganic ion pairs in aqueous-nonaqueous phase-distributions of hydrophobic ionizable organic compounds (HIOC), but the strong complexation reactions of HIOCs on GAC probably masked this ion-pairing influence in this study.

Optimum fit of the surface complexation model for 2,4,5-TCP adsorption (Figure 5, both with and without phosphate buffer) and for 2,4-DCP and 4-CP adsorption data (Figure 6, without phosphate) as a function of pH demonstrate that the proposed surface complexation model can describe very well the adsorption behavior of chlorophenols on activated carbon. Similar to the relationship between adsorptive capacity and equilibrium pH for 2,4,5-TCP (Figure 4), little influence on adsorption is observed for decreasing pH values below the compounds' pK_a values, whereas marked decrease in amounts adsorbed occurs as pH increases above the pK_a values.

Surface speciation of activated carbon in 2,4,5-TCP solution is calculated as a function of pH with the surface complexation model (Figure 7). Total concentrations of basic ($\equiv BH^+$) and acidic ($\equiv AH$) groups derived from adsorption data with the optimization procedure are, respectively, 0.926 and 0.443 mmol/L (equivalent to 1.853 and 0.886 mmol/g), indicating that there are about twice as many basic sites as acidic sites. The surface complex of basic groups ($\equiv BH - ClP$) is relatively stable as pH increases, and site saturation is essentially attained below pH 9 for basic groups. However, the surface complex of acidic groups

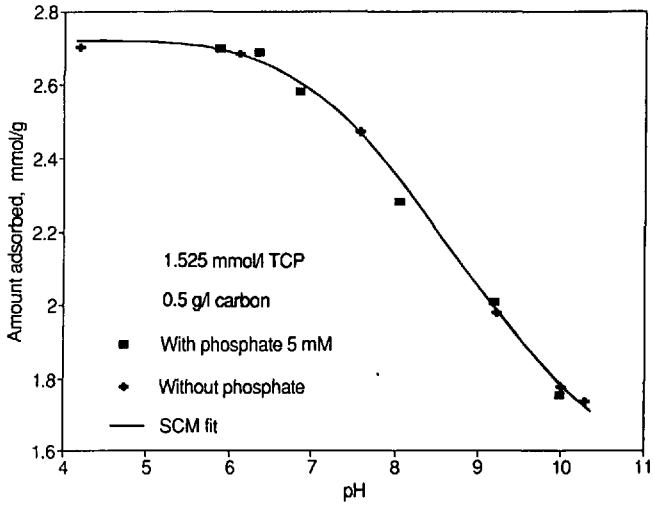

Figure 5—Effect of phosphate on adsorption of 2,4,5-TCP as a function of pH and optimum surface complexation model fit.

Table 5—Best estimates for chlorophenol/carbon surface complexation constants.

Adsorbate	$\log K_A^{intr}$	$\log K_B^{intr}$	Variance (SOS/df)[a]
2,4,5-TCP	21.48	16.65	2.28
2,4-DCP	25.19	13.05	0.38
4-CP	27.41	16.68	1.41

[a] SOS/df, sum of squares/degrees of freedom. Values of variance between 0.1 and 20 indicate good fit to data (Westall, 1982).

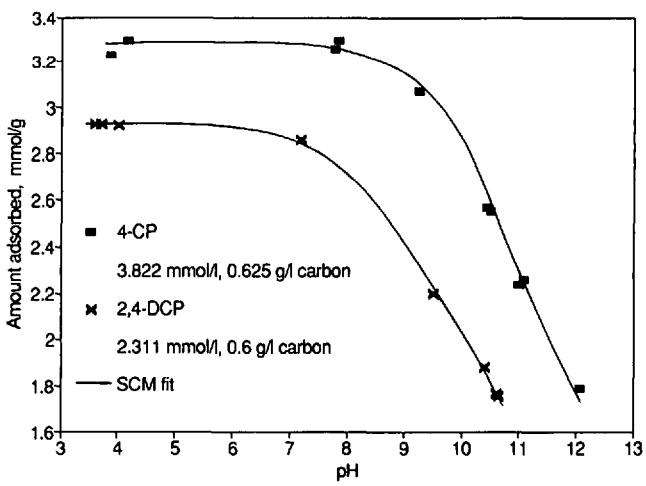

Figure 6—Amounts adsorbed of 4-CP and 2,4-DCP as a function of pH and optimum surface complexation model fits.

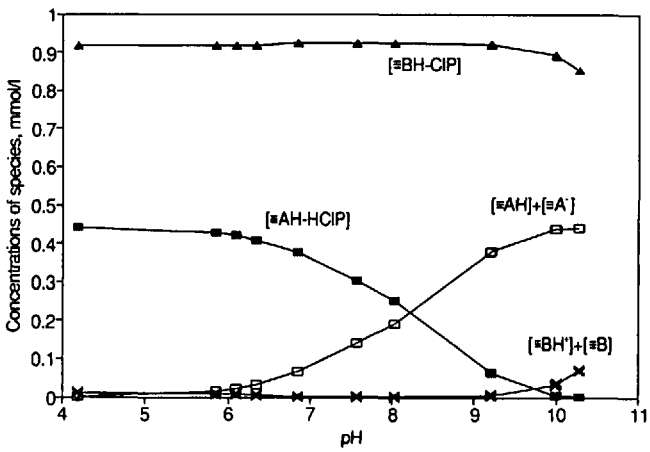

Figure 7—Calculated surface speciation of activated carbon (0.5 g/L) in the presence of 1.525 mmol/L 2,4,5-TCP ($\equiv BH - ClP$] + [$\equiv BH^+$] + [$\equiv B$] = 0.926 mmol/L, [$\equiv AH - HClP$] + [$\equiv AH$] + [$\equiv A^-$] = 0.443 mmol/L).

($\equiv AH - HClP$) is very susceptible to the change of pH and site saturation occurs only at pH values less than about 6.

Some investigators have given an insight into the mechanisms of adsorption of phenolic compounds on various substrates. Schellenberg *et al.* (1984) demonstrated the importance of the anionic phenolate ion in the sorption of chlorophenols by aquifer materials. On activated carbon, it has been suggested that chlorophenols are adsorbed with the phenyl ring parallel to the surface of the adsorbent and interaction is between the π-electron system of the phenyl ring and the aromatic surface structure (Coughlin and Ezra, 1968) of the carbon. Furthermore, under oxic conditions, an oxidative coupling occurs of phenolic compounds to the carbon surface (Grant and King, 1990) that is more pronounced for the phenolate anionic forms than for the parent neutral molecules (Vidic *et al.*, 1993). This could possibly account for the apparent importance of the basic surface site, especially at basic pH values where the phenolate anions predominate.

Mattson *et al.* (1970) substantiate the presence of significant numbers of carbonyl and carboxyl functional groups on the surfaces of activated carbon using infrared internal reflectance spectrophotometric techniques. Chlorophenols may be adsorbed at the carbonyl oxygens on the activated carbon surface according to a donor-acceptor complexation mechanism. The carbonyl oxygen acts as the electron donor and the aromatic ring of the solute acts as the electron acceptor. The functional groups containing oxygen, such as phenolic, carbonyl, carboxyl, lactone, and quinone (Boehm, 1964), may also offer adsorptive sites for hydrogen bonding of the phenolic protons, particularly at pH levels where the chlorophenols are predominantly in molecular form. These proposed mechanisms provide plausible explanations for the surface complexation reactions between chlorophenols (neutral or anionic forms) and the surface of activated carbon (acidic or basic sites). The magnitude and strength of the bonding of chlorophenols with basic sites explains the still substantial adsorption at pH values well above the pK_a values of the chlorophenols, whereas the reaction with protonated (neutral) acidic sites explains the change of adsorption with pH. Maximum adsorption on activated carbon is achieved when both reactions are operative at pH values below the pK_a values for the chlorophenolic compounds. In addition, because of the heterogeneous nature of the activated carbon surface, the surface complexation reactions and intrinsic adsorption constants reported here are likely to be concentration dependent, as are the Langmuir and Freundlich constants.

Summary and conclusions

Studies were undertaken of the adsorption of chlorinated phenols from aqueous solution on granular activated carbon. Single-component equilibrium adsorption data on the eight compounds in two concentration ranges at pH 7.0 and 30°C were well fit by both the Langmuir and Freundlich isotherms. The adsorptive capacities at pH 7.0 increase from pentachlorophenol to trichlorophenols and are fairly constant from trichlorophenols to monochlorophenols. The position of chlorine on the phenyl ring has minimal influence on the adsorption of chlorophenols.

Equilibrium measurements were also conducted for 2,4,5-TCP, 2,4-DCP, and 4-CP over a wide pH range. Little influence on adsorption is observed for decreasing pH values below the compounds' pK_a values, whereas marked decrease in amounts adsorbed occurs as pH increases above the pK_a values. A surface complexation model has been proposed to describe the effect of pH on adsorption equilibria of chlorophenols on activated carbon. Activated carbon surface functional sites are divided into acidic groups and basic groups that may be neutralized by bases or acids, respectively. Molecular and ionized forms of chlorophenols interact, respectively, with these two types of surface groups to form two neutral surface complexes, of which the complex of basic groups is more substantial and more stable than that of acidic groups. The simulations of the model are in excellent agreement with the experimental data.

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