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Effects of Temperature and Inorganic Salts on the Adsorption of Phenol from Multicomponent Systems onto a Decolorizing Carbon

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ABSTRACT

Experimental investigation of the effect of temperature and two inorganic salts (KCl and NaCl) on the adsorption of phenol from dilute (10–200 mg/dm^3) multicomponent systems onto activated carbon was studied. Focusing on the adsorption of phenol, all combinations of phenol with two other aromatic organic components, (1,4-dihydroxybenzene and 4-amino,1-naphthalene sulfonic acid-sodium salt) in aqueous solutions were considered. Equilibrium isotherms at three different temperatures (30, 40, and 55°C) were generated. The adsorption of phenol from binary and ternary as well as from single aqueous systems increases with decreasing temperature, as expected of physical adsorption. Effects of KCl and NaCl salts at a concentration of 0.05 M at 30°C were also investigated. The adsorption of phenol from bisolute and trisolute systems slightly decreases by adding either of the salts.

Key Words. Adsorption; Phenol; Salts; NaCl; KCl; Multicomponent; Carbon

INTRODUCTION AND LITERATURE REVIEW

Activated carbon is one of the most important adsorbents for removing organic substances from aqueous solutions. Therefore, it is widely used for water treatment applications. Its efficiency in removing organic compounds is mainly attributed to its high affinity to many organic compounds and to its large internal surface area, which ranges between 450 and 1500 m^2/g (1).

Because of its toxicity and slightly pungent odor, the removal of phenol from aqueous solutions by adsorption onto activated carbon is the concern of many researchers. Most studies in this area, however, have dealt primarily with the equilibrium and kinetics of phenol adsorption from single component systems (2–6). Studies of the effects of pH, dissolved gases, and inorganic salts on the adsorption of phenol from single component systems are also abundant (7–10). Similar studies of adsorption from binary and ternary aqueous systems are fewer in number (11–15).

Multicomponent adsorption studies of organic components from aqueous solutions (e.g., quaternary adsorption studies) are scarce. This is a direct consequence of the difficulty of experimentation and analyses involved in such studies. These studies, however, are indispensable in developing, testing, and validating theories and mathematical models of the equilibrium and kinetics of multicomponent adsorption processes. Seidel and Gelbin (16) measured the adsorption equilibria of organic components from aqueous multicomponent solutions onto activated carbon. The applicability of the ideal adsorbed solution (IAS) theory was tested, and a systematic deviation between experiments and theory was reported. This deviation was attributed to the adsorbed phase activity coefficients. Ceresi and Tien (17) studied experimentally the adsorption of phenol from aqueous solution onto activated carbon in the presence of three other adsorbates. The purposes of the study were to validate the multicomponent adsorption algorithm of Wang and Tien and to explore the application of the method developed by Tien and coworkers in characterizing the adsorption affinity of background organics in fixed-bed calculations. The experimental results were found to give good agreement with predictions based on the Wang–Tien algorithm, while they were marginally accurate with the use of the characterization results.

In this work the adsorption of phenol from multicomponent aqueous systems containing 1,4-dihydroxybenzene and 4-amino,1-naphthalene sulfonic acid-sodium salt onto activated decolorizing carbon was studied at 30, 40, and 55°C. A survey of the open literature indicated no studies of these industrially important aromatic contaminants typically existent in industrial wastewater. The effect of adding 0.05 M NaCl and KCl on the adsorption of phenol was also investigated. The adsorption of 1,4-dihydroxybenzene and the adsorption of 4-amino,1-naphthalene sulfonic acid-sodium salt from multicomponent systems onto activated carbon, which has been recently accomplished (18), will be the subject of forthcoming papers.

EXPERIMENTAL

All chemicals used in this study were of research grade quality and were used without further treatment. The carbon used was "decolorizing" powder supplied by BDH Chemicals.

A set of seven glass tubes, each charged with a 100-mL solution containing the organic components, was used in each isothermal experiment. All solutions were prepared with the same initial concentrations of organic compounds (200 mg/dm^3). Different amounts of carbon, ranging between 0.05 to 1 g, were added to the tubes. The amount of carbon added differed from one tube to another, such that the final equilibrium concentration covered a range from 10 to 200 mg/dm^3 of each organic component in the solution. An analytical balance (Mettler AJ100) with a precision of ±0.1 mg was used for measuring the needed amounts of carbon. The tubes were tightly closed and rocked for a sufficient time in a thermostated water bath whose temperature was maintained constant within ±0.1°C. Rocking the tubes continued until equilibrium was achieved as verified by the constancy of the organic compounds' concentration in the solution. The solid adsorbent was removed by filtration, and 10 mL of the filtrate sample was diluted to 100 mL. The diluted sample was analyzed to determine the equilibrium concentration of each organic component in the solution. Reproducibility was ensured by repeating the experiment under the same conditions, and the experimental uncertainty was found to be better than 1 ppm.

Concentration analyses were performed using a "Spectronic 21 UVD" spectrophotometer. Wavelengths of 272, 290, and 310 nm for phenol, 1,4-dihydroxybenzene, and 4-amino,1-naphthalene sulfonic acid-sodium salt, respectively, were employed. Standard calibration, relating the absorbance and the concentration of organic component, indicated a linear relationship. These curves were used to calculate the concentration of each component in the samples by the McKay and Al Duri method (19).

RESULTS AND DISCUSSION

The adsorption of phenol from two different bisolute systems at three temperatures (30, 40, and 55°C) is shown in Figs. 1 and 2. The first bisolute system contains 4-amino,1-naphthalene sulfonic acid-sodium salt (ANSA) and phenol, while the second system contains 1,4-dihydroxybenzene (DHB) and phenol. The initial concentration of each component in the solution was 200 mg/dm^3. It is clear from these figures that the equilibrium adsorption of phenol in both systems decreases with increasing tempera-

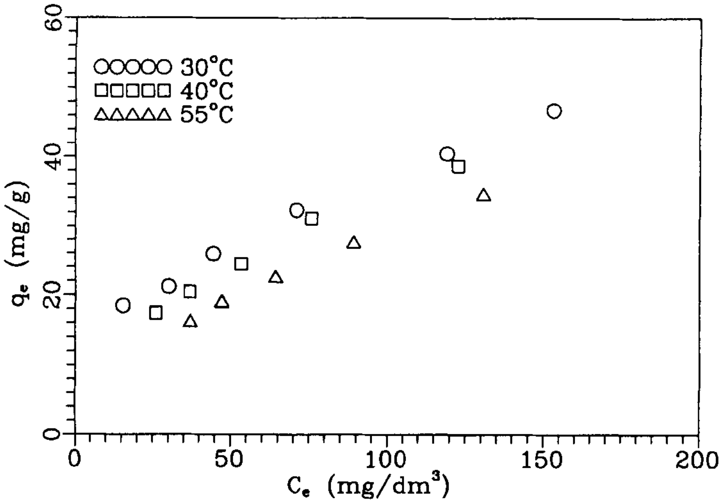

FIG. 1 Effect of temperature on the adsorption of phenol from a binary system containing 4-amino,1-naphthalene sulfonic acid-sodium salt (ANSA) onto activated carbon.

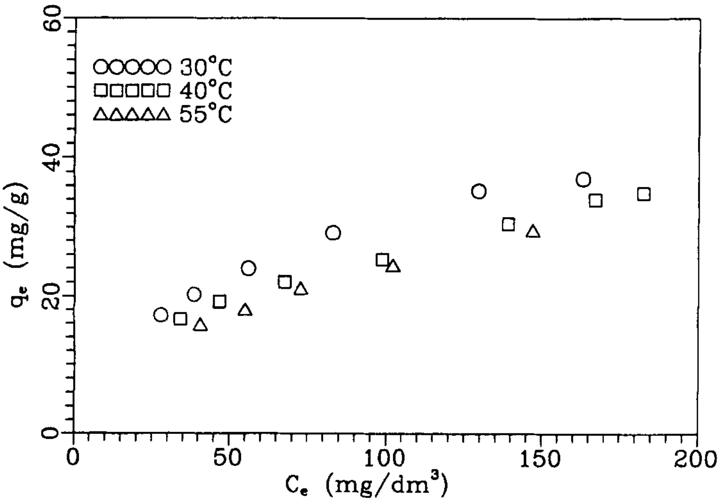

FIG. 2 Effect of temperature on the adsorption of phenol from a binary system containing 1,4-dihydroxybenzene (DHB) onto activated carbon.

ture. This effect of temperature on the adsorption of phenol is expected for physical adsorption that is exothermic in nature in most cases.

By comparing the respective adsorption isotherms in Figs. 1 and 2, one finds that the amount of phenol adsorbed in the presence of DHB is less than that adsorbed in the presence of ANSA. This may be attributed to the higher affinity of DHB.

Figure 3 shows the equilibrium adsorption isotherms of phenol from a ternary system containing DHB, ANSA, and phenol, with an initial concentration of 200 mg/dm^3 of each component. The same temperature effect appears on the adsorption of phenol as shown by the two binary systems.

Figure 4 shows the adsorption of phenol from different systems at 30°C. It is clear from this figure that the amount of phenol adsorbed from the ternary system is less than that adsorbed from both binary systems, which is, in turn, less than that adsorbed from the single system. The same observation is seen in similar figures for the isotherms at 40 and 55°C. As an example, when the equilibrium concentration of phenol equals 100 mg/dm^3, the adsorbed amounts of phenol from single, binary, and ternary systems at different temperatures are as shown in Table 1.

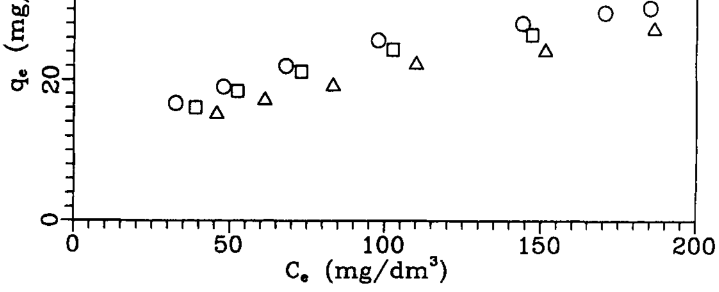

FIG. 3 Effect of temperature on the adsorption of phenol from a ternary system containing both 4-amino,1-naphthalene sulfonic acid-sodium salt (ANSA) and 1,4-dihydroxybenzene (DHB) onto activated carbon.

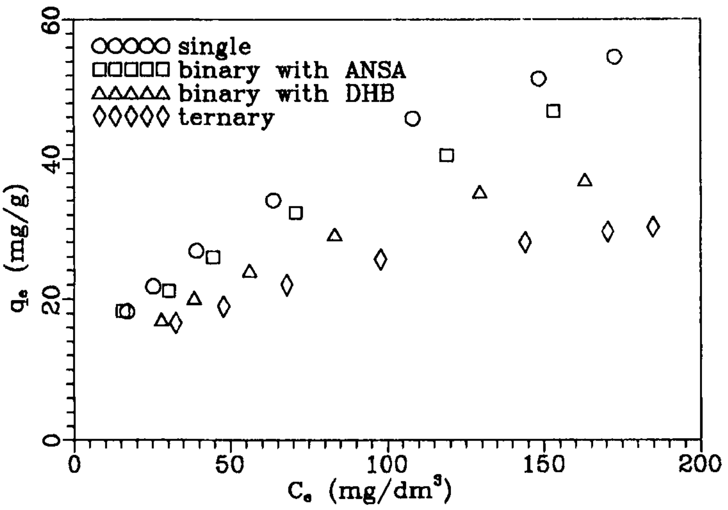

FIG. 4 Adsorption isotherms of phenol from single, binary with 4-amino,1-naphthalene sulfonic acid-sodium salt (ANSA), binary with 1,4-dihydroxybenzene (DHB), and ternary containing both ANSA and DHB at 30°C.

The decrease in adsorbed amount of phenol in the ternary system as compared to that in the single system (44.5 − 25.5 = 19 mg/g carbon) is equal to the sum of the decreased amounts in both binary systems as compared to the single system [(44.5 − 38) + (44.5 − 31.5) = 19.5]. This observation was checked for different temperatures and at different equilibrium concentrations, and found to be valid. The respective adsorbed amounts of coexisting species are shown in Tables 2 and 3.

TABLE 1
Amounts of Phenol Adsorbed from the Different Systems at Different Temperature Values at Equilibrium Concentration = 100 mg/dm^3

	Temperature (°C)		
Systems	30	40	55
Single system (18), mg/g	44.5	39.0	31.5
Binary with ANSA, mg/g	38.0	35.0	30.0
Binary with DHB, mg/g	31.5	27.5	25.5
Ternary system, mg/g	25.5	24.0	22.0

TABLE 2
Amounts of ANSA Adsorbed from the Different Systems at Different Temperature Values at Equilibrium Concentration = 100 mg/dm^3

	Temperature (°C)		
Systems	30	40	55
Single system (18), mg/g	92	80	72
Binary with phenol, mg/g	53	57	52
Ternary system, mg/g	55	77	88

The effects of adding NaCl and KCl on the adsorption of phenol from different systems are presented in Figs. 5 and 6, respectively. These figures show that neither NaCl nor KCl has a significant effect on the adsorption of phenol from single systems. This observation is in good agreement with that advanced by Halhouli et al. (10). The behavior of phenol (pK_a $\cong$ 10) in a neutral solution (pH $\cong$ 7) could be explained according to the findings of Cooney and Wijaya (9) as follows: At pH values below 10, the phenol ion is more and more protonated. Therefore, more and more undissociated phenol particles will be generated. The addition of charged ions from the salts will have a small repulsive effect on the adsorbed phenol molecules. Hence, there will be no observed effect on the adsorption.

Adding NaCl or KCl to a binary system which included ANSA decreased the adsorption of phenol significantly, as shown in Figs. 5 and 6. For example, at 30°C and C_e = 100 mg/dm^3, it decreased from 38.5 to about 28 mg/g in the presence of either NaCl or KCl. A plausible explanation for this decrease could include more adsorption of ANSA onto the

TABLE 3
Amounts of DHB Adsorbed from the Different Systems at Different Temperature Values at Equilibrium Concentration = 100 mg/dm^3

	Temperature (°C)		
Systems	30	40	55
Single system (18), mg/g	57	56	80
Binary with phenol, mg/g	38	45	57
Ternary system, mg/g	30	30	35

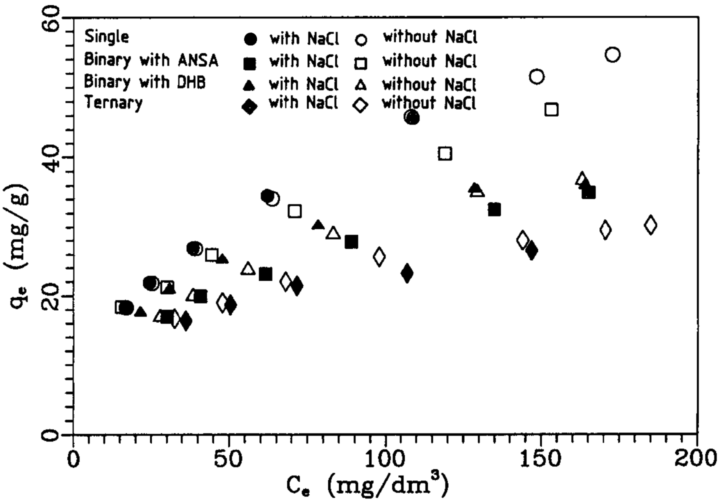

FIG. 5 Effect of NaCl on the adsorption isotherms of phenol from single, binary with 4-amino,1-naphthalene sulfonic acid-sodium salt (ANSA), binary with 1,4-dihydroxybenzene (DHB), and ternary containing both ANSA and DHB at 30°C.

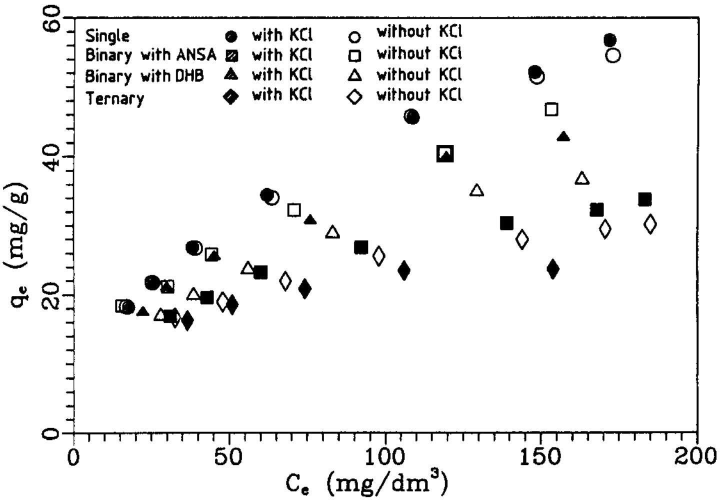

FIG. 6 Effect of KCl on the adsorption isotherms of phenol from different systems [single, binary with 4-amino,1-naphthalene sulfonic acid-sodium salt (ANSA), binary with 1,4-dihydroxybenzene (DHB), and ternary containing both ANSA and DHB] at 30°C.

carbon surface. For example, the adsorption of ANSA in the single system increased from 100 to 105 mg/g at C_e = 100 mg/dm^3 by the addition of either NaCl or KCl.* Since the available active sites on the surface of the solid carbon are limited, these sites will be occupied by either phenol or ANSA in a competitive manner. The addition of charged ions (from NaCl or KCl) enhances the adsorption of ANSA. Therefore, some of the adsorbed phenol will be desorbed. This decreases the adsorption of phenol. On the other hand, adding NaCl or KCl to a binary system containing DHB enhances the adsorption of phenol, as shown in the same figures. This increase in the adsorption of phenol could be attributed to a decrease in the adsorption of DHB because of the addition of the salts. NaCl or KCl ions inhibit the adsorption of DHB onto the carbon surface. For example, the adsorption of DHB in the single system decreased from 80 to 54 mg/g at C_e = 100 mg/dm^3 by the addition of either NaCl or KCl.† This gives a better chance for phenol to be adsorbed.

The effect of adding NaCl or KCl to a ternary system that contains ANSA, DHB, and phenol is also presented in Figs. 5 and 6. It is clear from these figures that adding these salts slightly decreased the adsorption of phenol. In this system ANSA enhances the adsorption of phenol in the presence of NaCl or KCl, while DHB inhibits that adsorption. Therefore, the net change is slight.

CONCLUSIONS

The equilibrium adsorption isotherms (at 30, 40, and 55°C) of aqueous systems of phenol from binary and ternary aqueous systems onto carbon have been determined. All combinations of phenol, 1,4-dihydroxybenzene (DHB), and 4-amino,1-naphthalene sulfonic acid-sodium salt (ANSA) have been considered. Analyses of the results have focused mainly on the adsorption of phenol from these systems. It is found that increasing the temperature decreases the adsorption of phenol in all systems. The presence of DHB or ANSA in binary systems decreases the adsorption of phenol. However, DHB has a greater effect on phenol adsorption. The presence of both ANSA and DHB in the ternary system decreases the adsorption of phenol more than in any of the binary systems.

Experimental results show that the presence of KCl or NaCl (in a concentration of 0.05 M in the aqueous solution) has a slight effect on phenol

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* The adsorption of ANSA from multicomponent systems will be the subject of a forthcoming paper by the authors. An increase in the adsorption of ANSA is observed.

† The adsorption of DHB from multicomponent systems will be the subject of a forthcoming paper by the authors. A decrease in the adsorption of DHB is observed.

adsorption from all single and multicomponent systems investigated in this study.

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