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Effects of pH and Inorganic Salts on the Adsorption of Phenol from Aqueous Systems on Activated Decolorizing Charcoal

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ABSTRACT

An experimental investigation of the effects of pH and three inorganic salts (KCl, KI, and NaCl) on the adsorption isotherms of phenol (from a dilute aqueous solution) on activated charcoal was conducted. Each salt was studied at three different concentrations, i.e., 0.1, 0.01, and 0.005 M. The effect of pH (in the pH range 3 to 11) in the presence of KI, KCl, and NaCl was also investigated. The concentration of phenol in the aqueous systems studied ranged from 10 to 200 ppm. The temperature effect was also studied, and the resulting experimental equilibrium isotherms at 30, 40, and 55°C are well represented by Freundlich, Langmuir, and Redlich–Paterson isotherms. The relevant parameters for these isotherms are presented.

Key Words. Adsorption; Phenol; Salts; NaCl; KCl; KI; pH; Charcoal

INTRODUCTION AND LITERATURE REVIEW

Activated carbon has long been recognized as one of the most versatile adsorbents for the effective removal of low concentrations of organic substances from solution. The properties of activated carbon are attributed mainly to its highly porous structure and relatively large surface area, which is between 450 and 1500 m^2/g (1).

Removal of phenolic pollutants, of which phenol is typical, is necessary because of its toxicity and slightly pungent odor. There are many methods to remove phenolic materials from aqueous solution, e.g., steam distillation (2) and oxidation using a strong oxidizing agent such as hydrogen peroxide (3). In water treatment, however, the most widely used method is adsorption on the surface of active materials (4–8).

It is known (9) that the adsorbability of organic pollutants on activated carbon is influenced by their degree of ionization as established by the pH of the solution. The presence of inorganic salts can also have significant effects on the adsorbability of organic species on activated carbon (10). Literature on the adsorption of phenol is abundant. In a recent study Payne et al. (11) explored the feasibility of an enzymatic approach for the selective removal of phenol from solutions. They used the enzyme mushroom tyrosinase to convert phenol to *o*-quinone which, in turn, was adsorbed on chitosan. It was found by those authors that the enzymatic approach was effective for the complete removal of phenol. Li et al. (12) showed that the mono- to pentachlorophenols in synthetic solutions were successfully degraded in the presence of visible light radiation, methylene blue, and air aeration. Nishijima et al. (13) studied the biodegradation of organic substances, including phenol, by biologically activated carbon. Those authors attached bacteria on the activated carbon to clarify the advantages of granular activated carbon as a support medium over conventional media without adsorption capacity. They found that the biodegrability of phenol on biologically activated carbon is approximately three times as high as that by conventional bacterial supports. Graveiro and Malina (14) investigated the removal (desorption) of phenol adsorbed onto granular activated carbon under anaerobic methanogenic conditions. Those authors found that granular activated carbon was regenerated biologically and that the phenol concentration gradient affected this regeneration process. Groszekl et al. (15) investigated the effect of carbon porosity and surface chemistry on the adsorption of phenol from aqueous solution. In particular, those authors studied the heats of adsorption of phenol on two types of carbon; one porous and the other nonporous. This study was conducted in a flow microcalorimeter. They used the results for the identification of surface sites responsible for adsorption. Choma and Jaroniec (16) used a three-parameter isotherm equation corresponding to the gamma distribution function that characterizes structural heterogeneity of the micropore. The three-parameter isotherm equation was applied to describe the adsorption of organic compounds from dilute aqueous solutions on microporous activated carbons. Abuzeid and Harrazin (17) showed that the presence of CO_2 significantly reduces the adsorptive capacity of activated carbon for phenol and *o*-cresol. Costa et al. (18) studied the kinetics and equilibria of adsorption of phenol and *p*-nitrophenol on activated carbon in a stirred tank system. Experimental data, including equilibrium isotherms and concentration decay curves, were presented for each adsorbate for three temperature values in the 1 to 40°C range. Mckay (19) investigated the ability of fluidized beds of activated carbon to remove pollutants, including phenol, from aqueous solution. The effects of flow rate and pollutant concentration, together with equilibrium isotherms, have been studied. Koganovskii et al. (20) studied the effect of surface ionized functional groups of active carbons on the adsorption of phenol from aqueous dilute solution. Those investigators developed a criterion for the selection of an active carbon to treat natural water. Cooney and Wijaya (9) studied the adsorption of aromatic compounds with different numbers of acidic and/or basic ionizable groups onto activated carbon as a function of pH. Higher pH values were found to decrease the equilibrium capacity for adsorption. Coughlin and Tan (21) studied the effect of adding 0.002 and 0.004 M $CaCl_2$ to solutions of sodium benzenesulfonate in contact with activated carbon. The adsorption of sodium benzenesulfonate was increased by the addition of $CaCl_2$. Jawaid and Weber (10) investigated the effects on sodium benzenesulfonate adsorption by a pelleted activated carbon caused by adding zinc chloride, calcium chloride, or potassium carbonate in the amount of 1 part salt per 100 parts charcoal. Randtke and Jepsen (22) reviewed the literature on salts effects, particularly their effects on activated carbon adsorption of humic and fulvic acids.

The aim of the present study is to investigate, experimentally, the effect of pH and three inorganic salts (NaCl, KCl, and KI) on the adsorption of phenol from dilute aqueous solutions on activated decolorizing charcoal.

EXPERIMENTAL

All chemicals used in this study were research grade and were used without further purification. The charcoal used was a "decolorizing" powder supplied by B.D.H. Chemicals. Adjustment of pH was accomplished by using an 85% phosphoric acid solution or a 30% sodium hydroxide solution. A digital pH meter (Microprocessor HI 8520), calibrated with standard pH solutions, was used to adjust the pH values.

A set of seven glass tubes was used to generate the needed data for each adsorption isotherm. Each tube was charged with a 50-mL solution of the same initial concentration of phenol. The amount of solid adsorbent (charcoal) differed from one tube to another so that the final equilibrium data covered a range of concentrations from 10 to 200 ppm of phenol in the solution. The amount of charcoal introduced ranged from 0.005 to 1 g per 50 mL of solution. An analytical balance (Mettler AJ100) with an accuracy of 1×10^{-4} g was used to measure the different weights. This set of tubes, tightly closed, was shaken for sufficient time in a thermostated water bath shaker (Karl Kolb D-6072) where the temperature was maintained constant within ±0.1°C. When equilibrium was attained, as reflected by the constancy of the concentration of phenol in the solution, the solid adsorbent was removed by filtration. Then a 10-mL sample of the solution was withdrawn and analyzed to determine the equilibrium concentration of phenol. Reproducibility was ensured by repeating the experiment under the same conditions. The method of analysis used here is the standard method adopted by Gales and Booth (3), which is based on spectrophotometric analysis of the developed color resulting from the reaction of phenol with 4-aminoantipyrine.

A calibration curve relating the concentration of phenol in aqueous systems to the absorbence, using a Spectronic 21 UVD spectrophotometer, was used to find the concentration of phenol in the samples. The amount of phenol adsorbed at equilibrium per unit mass of solid adsorbent was found from a simple material balance:

$$q_e = V(C_0 - C_e)/m$$

where C_0 and C_e are the initial and the equilibrium mass concentrations of phenol in solution, respectively, V is the volume of the solution, and m is the mass of the activated charcoal.

RESULTS AND DISCUSSION

The equilibrium adsorption of phenol per gram of charcoal for different pH values is shown in Fig. 1. As expected, the adsorbed amount increases with increasing equilibrium concentration of phenol. It is clear from the figure that the pH of the solution affects the adsorbability of phenol. For low phenol concentrations (below 70 ppm), the effect of pH (up to pH 10) is negligible. The adsorption of phenol increases with decreasing pH value for phenol concentrations greater than 70 ppm. The effect is very slight for pH values up to 10. Figure 2 is deduced from Fig. 1 for the phenol equilibrium concentration at 100 ppm. It is clear from this figure that the adsorption of phenol on activated charcoal decreases slightly with increasing pH of the solution until the pH value reaches 10. As the pH rises above 10, and hence the degree of ionization of phenol increases, the adsorbabilities fall sharply to much lower values (from 40 to 20 mg/g). These results are in good agreement with Cooney and Wijaya's conclusion (9) regarding the effect of pH on adsorption. According to those authors, phenol, which is a weak acid, will be adsorbed to a lesser extent at higher pH values due to repulsive forces prevailing at higher pH values

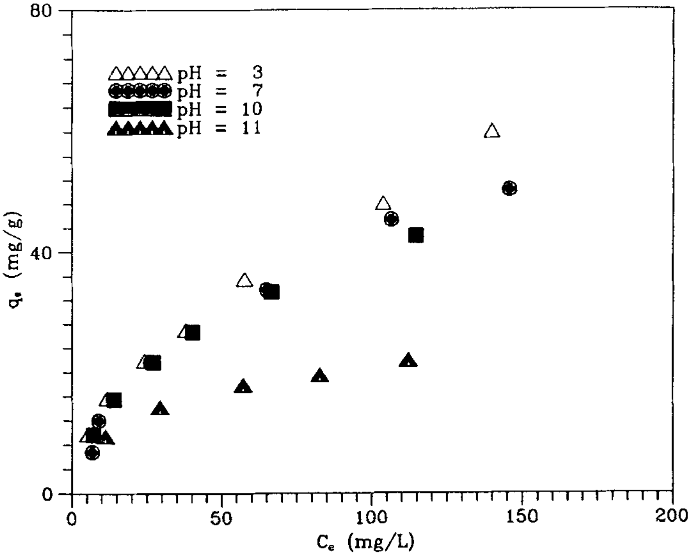

FIG. 1 Effect of pH on phenol adsorption on activated charcoal at 30°C.

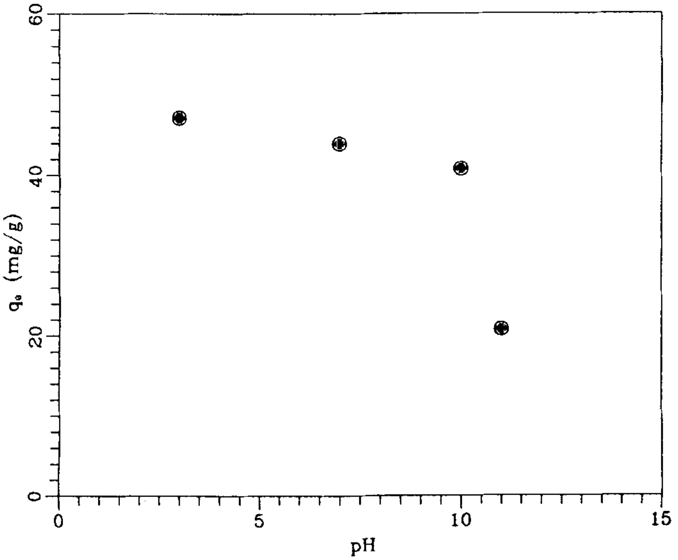

FIG. 2 Effect of pH on phenol adsorption on activated charcoal at 30°C and C_e = 100 ppm.

between the adsorbed ions. Moreover, according to the explanation they advanced, the pH of the solution will have a definite adverse effect on the adsorbability of the adsorbent at values greater than the pK_a of the adsorbate, which is around 10 in this case (23), and which clearly occurs in this case.

Figures 3–5 display the effect of potassium chloride (KCl), potassium iodide (KI), and sodium chloride (NaCl) on phenol adsorption on activated charcoal. As shown in Fig. 3, potassium chloride has no effect on the equilibrium adsorption of phenol on activated charcoal. The presence of ionized KI salt seems to decrease the adsorption of phenol at high KI concentration (0.10 M). At low KI concentrations the effect is negligible. This is shown in Fig. 4. However, sodium chloride increases the adsorption of phenol on activated charcoal. This increase in the adsorption of phenol increases with higher concentrations of NaCl; this is evident in Fig. 5. The results obtained here for the effect of NaCl is compatible with previous findings (9) for the effect of NaCl on the adsorbability of benzoic acid on activated carbon. This is attributed to partially nullifying the repulsive forces between adjacent adsorbed $C_6H_6O^-$ ions.

Figure 6 shows the effect of adding KCl, KI, or NaCl to solutions whose pH values are 3. The amount of salt added is enough to make the salt

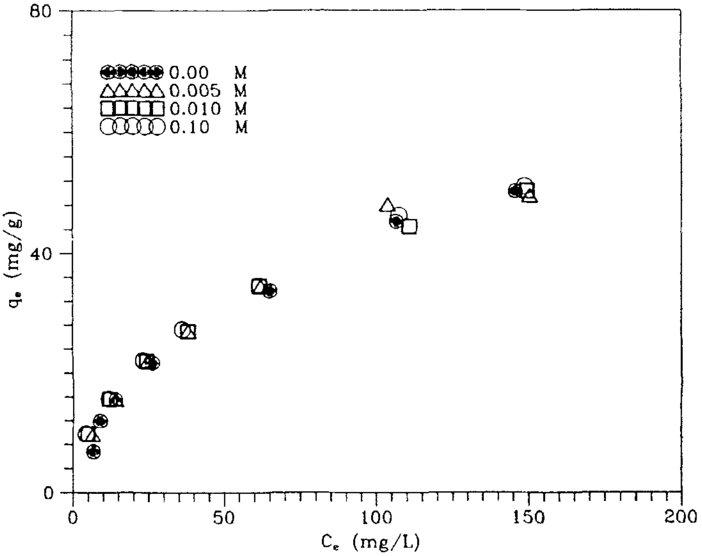

FIG. 3 Effect of potassium chloride (KCl) on phenol adsorption on activated charcoal at 30°C and pH 7.

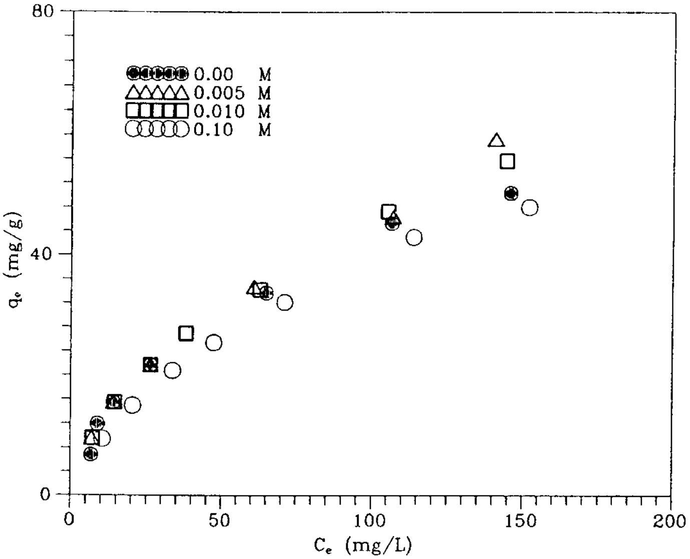

FIG. 4 Effect of potassium iodide (KI) on phenol adsorption on activated charcoal at 30°C and pH 7.

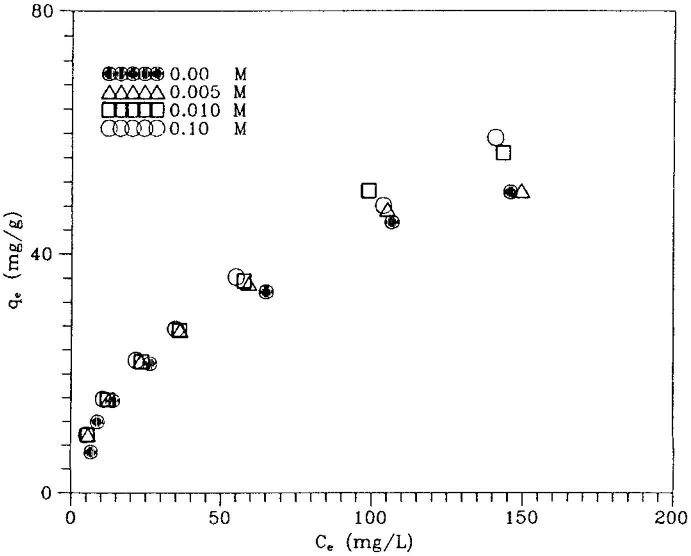

FIG. 5 Effect of sodium chloride (NaCl) on phenol adsorption on activated charcoal at 30°C and pH 7.

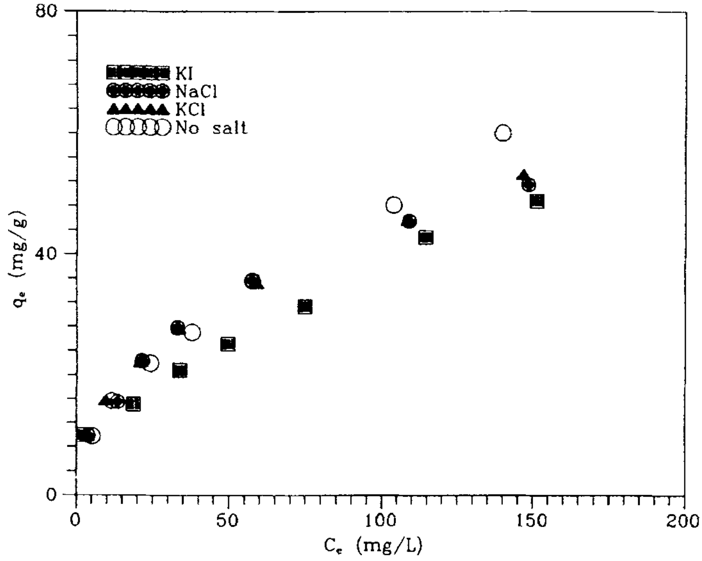

FIG. 6 Effect of salt addition to a solution of pH 3 on the adsorption of phenol on activated charcoal.

concentration 0.1 M. This addition of salt decreases the adsorption of phenol in the following order. KI, NaCl, and then KCl. KCl decreases the adsorption more than the other two salts when the solution is acidic (pH 3). When the same amount of salt is added to neutral solutions (pH 7), there is no serious effect for KI and KCl addition but there is a slight increase when NaCl is added. This is shown in Fig. 7. Figure 8 shows the effect of adding the same amount of the previous salts to basic solutions (pH 11). It is clear from the figure that no change occurs on the adsorptivity of phenol.

The effect of temperature on the adsorption of phenol on activated charcoal is presented in Fig. 9. Three different isotherms, at 30, 40 and 55°C, were generated experimentally to show this effect. The extent of equilibrium adsorption capacity of the adsorbent increases by decreasing the equilibrium temperature. When the equilibrium concentration of phenol is equal to 100 ppm, for example, the amounts of phenol adsorbed on activated charcoal were 43, 37, and 31 mg/g at 30, 40, and 55°C, respectively. This is expected for physical adsorption which is exothermic in nature in most cases. The heat of adsorption at zero coverage is 8.4 kJ/mol as extracted from the data shown in Fig. 9.

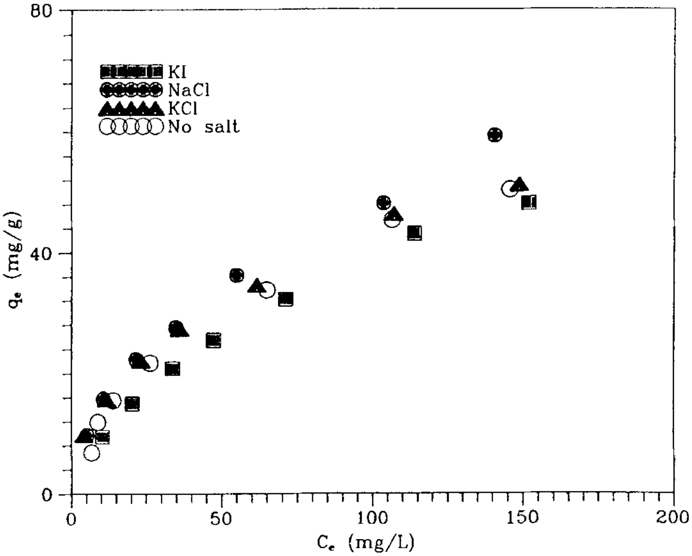

FIG. 7 Effect of salt addition to a solution of pH 7 on the adsorption of phenol on activated charcoal.

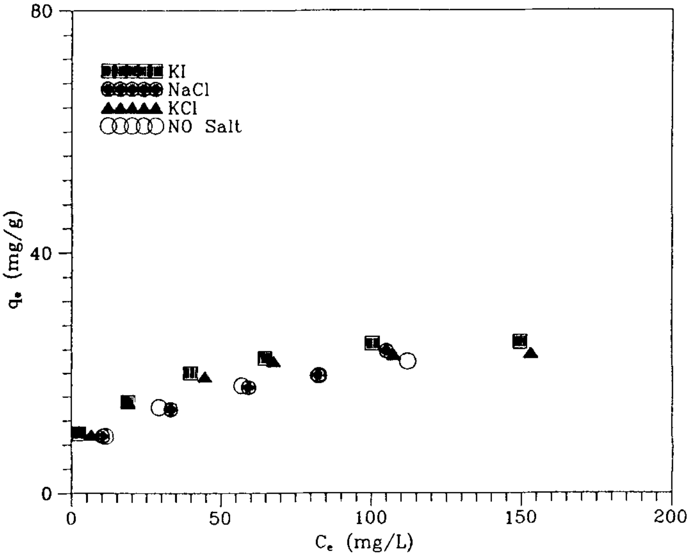

FIG. 8 Effect of salt addition to a solution of pH 11 on the adsorption of phenol on activated charcoal.

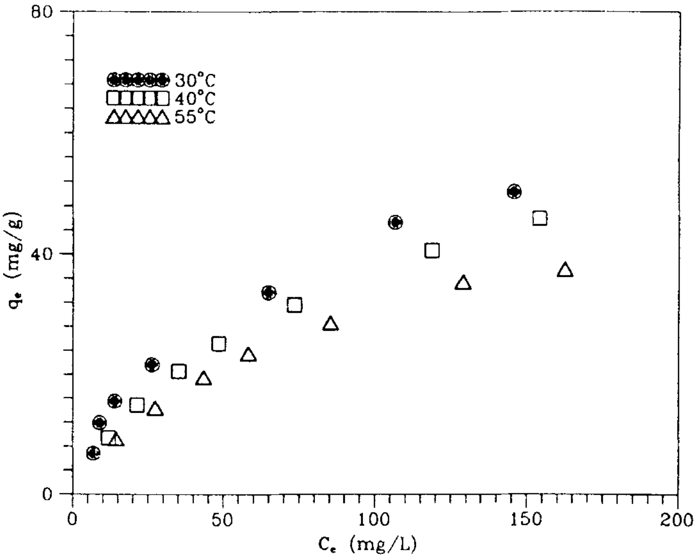

FIG. 9 Effect of temperature on the adsorption of phenol on activated charcoal at pH 7 and C_e = 200 ppm.

The equilibrium data are fitted by Langmuir, Freundlich, and Redlich–Paterson isotherms. The parameters of Langmuir, Freundlich, and Redlich–Paterson models obtained from regressing the experimental data are shown in Table 1.

CONCLUSIONS

The equilibrium isotherms of the adsorption of phenol on activated charcoals have been determined at 30, 40, and 55°C. The equilibrium experimental data have been fitted to Langmuir, Freundlich, and Redlich–Paterson equilibrium models, and the relevant parameters for these models have been determined. Effects of solution pH and three inorganic salts, i.e., KI, KCl, and NaCl, on the adsorption equilibria have also been investigated.

Experimental results show that acidic solution has no effect on the adsorption capacity of activated charcoal to phenol. Highly basic solution, on the other hand, reduces the adsorbability of charcoal. A minor effect was observed for the presence of inorganic salts on phenol adsorption on activated charcoal. The experimental results show that there is a certain degree of coupling between the solution pH and the presence of KI salt.

TABLE I
Constants for Langmuir, Freundlich, and Redlich–Paterson Isotherms

Temperature, °C	Langmuir, $q = (AC)/(1 + BC)$		Freundlich, $q = KC^N$		Redlich–Paterson, $q = (\lambda C)/(1 + \beta C^{\mu})$		
	A	B	K	N	λ	β	μ
30	1.17	0.02	4.14	0.51	3.40	0.43	0.65
40	1.13	0.02	2.95	0.55	1.18	0.08	0.73
55	0.69	0.01	2.87	0.51	0.71	0.01	0.98

The other two salts show no interaction with the solution pH. The experimental results are explained in terms of the degree of ionization of the adsorbate which is, in turn, controlled by the pH of the solution.

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