The Use of Human Hair Waste as a Phenol Biosorbent

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ABSTRACT: Human hair waste was tested as an adsorbent for the removal of phenol from aqueous solutions. Batch experiments were carried out to determine the effects of contact time, adsorbent concentration, initial pH, temperature and salt addition on this adsorption process. It was found that the uptake of phenol was virtually complete after 1 h. Up to 92% phenol removal was achieved at an initial phenol concentration of 60 ppm. The initial pH of the solution had a strong effect on the uptake of phenol and increasing the measurement temperature also increased the uptake. The presence of NaCl salt in the adsorption system had only a marginal effect on phenol adsorption.

INTRODUCTION

Phenolic compounds are among the most frequent contaminants in wastewater disposed of by several industries. Because of their toxicity, the Environmental Protection Agency (EPA) (Bigley and Grob 1985; Caturla *et al.* 1988) has designated 11 phenolic compounds as priority pollutants. Different methods are currently used to remove these compounds from water and wastewater; however, of these, adsorption is the most popular (Srivastava *et al.* 1997). Activated carbons are extensively used as adsorbents to remove many phenolic compounds from wastewater (Kilduff and King 1997; Daifullah and Girgis 1998) because of their good characteristics such as high affinity and high surface area per unit volume. However, the relatively high capital and regeneration costs of activated carbons have encouraged many researchers to study the feasibility of using other low-cost adsorbents (Pollard *et al.* 1992).

Biosorbents have caught the attention of many researchers for the removal of heavy metals as environmental contaminants from aqueous solutions, with an abundant literature existing with respect to such processes. For example, Al-Asheh *et al.* (1999) used spent animal bones for the removal of copper and zinc, Christian *et al.* (1999) used lignite for the removal of mercury, cadmium and lead, Kappor and Viraraghavan (1998) used immobilized fungal biomass for the removal of different metal ions and Periasamy and Namasivayan (1994) used peanut hulls for the removal of cadmium. Human hair has also been used as a biosorbent for the removal of different metal ions (Tan *et al.* 1985). The uptake of metal ions by these materials was attributed to their constituents which contain such functional groups as carboxy, hydroxy, phosphate and amine that act as binders for these ions.

In contrast, literature on the use of biosorbents for the removal of phenolic compounds is very limited. Chen *et al.* (1998) studied the capability of the microbial biomass *Spirulina subsalsa* as a sorbent for phenolic compounds. Payne *et al.* (1992) explored the technical feasibility of an

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enzymatic approach for the selective removal of phenols from aqueous mixtures, using the enzyme tyrsinase (obtained from mushrooms) to convert the phenols to an *o*-quinone product that was then adsorbed on chitosan. The authors reported that the enzymatic approach was effective for the complete removal of phenols.

Human hair is made of a fibrous proteinaceous material known as keratin that has a complicated structure and contains a large surface area. As mentioned earlier, with and without chemical treatment, human hair has been shown to be a good biosorbent for metal ions (Tan *et al.* 1985). Recently, laboratory tests at NASA showed that human hair filters can mop up a gallon of oil in just 2 min (Business Week Magazine 1998). The use of such human hair waste as an adsorbent would help to reduce the cost of wastewater treatment and would make a contribution in cleaning the environment.

In the present work, the ability of human hair not subject to chemical treatment as a biosorbent for phenol has been examined. Phenol has been frequently used as a model component for testing the adsorbability of organic compounds by activated carbons (Halhouli *et al.* 1995; Saylikan and Cetinkaya 1991). The effect of process parameters that might influence the adsorption process, such as pH, temperature, salt addition and sorbent concentration, has also been considered.

MATERIALS AND METHODS

Human hair waste collected from hair salons was washed with a detergent, rinsed several times with distilled water and left to dry at room temperature before being used in the adsorption tests.

Batch sorption tests were conducted by placing a known quantity of the sorbent in bottles containing 10 ml of an aqueous solution of phenol with a predetermined concentration. The final sorbent concentration was 5 mg/ml unless otherwise stated while the initial phenol concentration was in the range of 10–80 ppm. The sample bottles were placed in a temperature-controlled water bath shaker (Kottermann, Germany) which was used to agitate the mixture at the desired temperature. Samples were withdrawn at known periods of time in order to study the kinetics of the sorption process. In other experiments the samples were allowed to come to equilibrium (24 h) and then filtered.

The residual phenol in the filtrate was analyzed spectrophotometrically using a Spectronic 21 UVD spectrophotometer (Milton Roy Company) following the method of Gales and Booth (1976). This is based on the spectrophotometric analysis of the colour developed as a result of the reaction of phenol with 4-aminoantipyrine Concentrated solutions were suitably diluted and the amount of phenol adsorbed was calculated from the difference between the concentrations before and after the adsorption process. Two replicates per sample were used with the average results being presented below.

Sorption experiments were carried out at 20°C, 35°C and 45°C for the purpose of investigating the effect of temperature on the sorption process. The effect of pH was determined by studying the adsorption of phenol over a pH range of 2–8. Adjustments to the pH value were made by the addition of appropriate amounts of 0.1 M HCl or 0.1 M NaOH solutions.

RESULTS AND DISCUSSION

Effect of contact time

The variation of phenol uptake by human hair with respect to time is shown in Figure 1 at various initial phenol concentrations. From the isotherms depicted, it will be seen that the rate of phenol

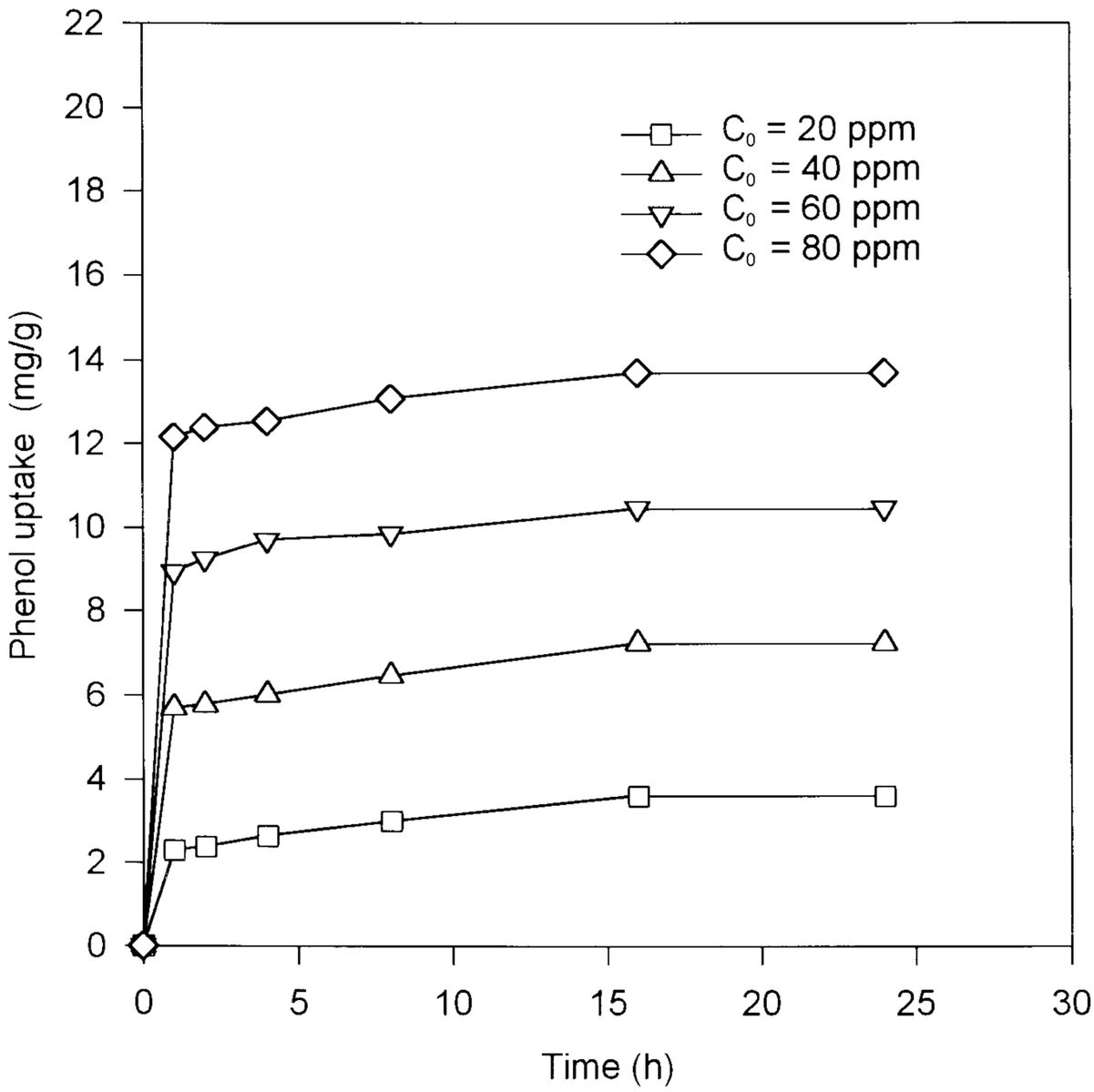

Figure 1. Kinetics of phenol adsorption by human hair as a sorbent at 5 mg/ml concentration.

uptake was high during the first hour of contact, with additional removal after that time being small. The high initial rates of phenol uptake suggest that adsorption takes place on the external surface of the hair. The data depicted in Figure 1 also show that an increase in the initial phenol concentration resulted in an increase in the phenol uptake. As the initial phenol concentration increased, the concentration gradient between the bulk solution and adsorbent surfaces also increased and this led to an increase in the migration rate and in the final adsorption capacity.

The uptake of sorbate species by sorbents is usually limited by intraparticle diffusion (Ajmal *et al.* 1998). To determine if intraparticle diffusion was the rate-determining step for adsorption, the data in Figure 1 were re-plotted against the square root of time (Figure 2) as suggested by Weber and Morris (1963). According to these authors, if intraparticle diffusion were involved in the sorption process, the uptake of sorbate would vary linearly with the square root of time and, furthermore, if intraparticle diffusion were the controlling step then this line would pass through the origin. As shown in Figure 2, the plots depicted are linear but do not pass through the origin. Hence, although intraparticle diffusion was involved in the adsorption process it was not the sole limiting factor (Poots *et al.* 1976).

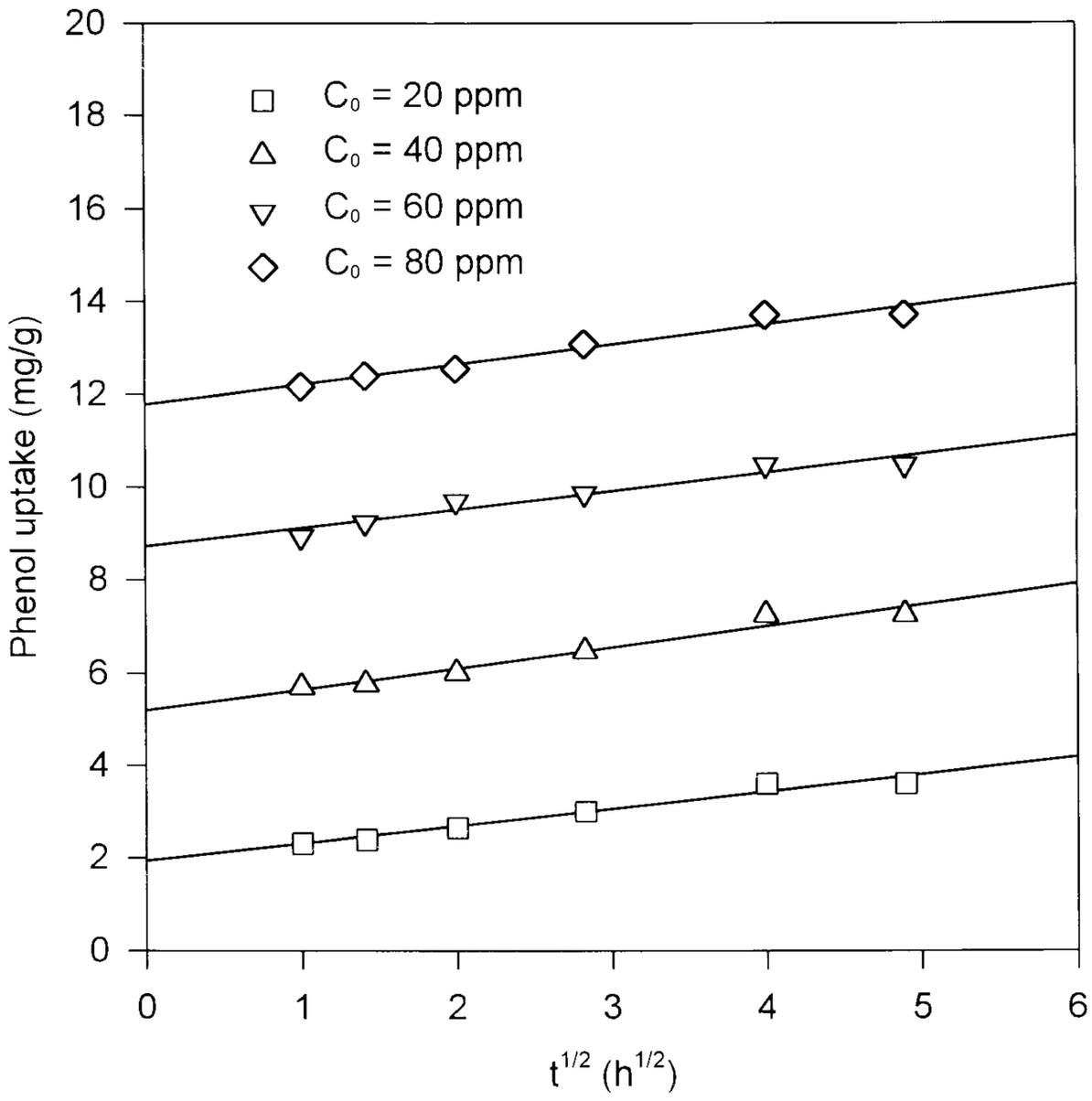

Figure 2. Plot of phenol uptake versus the square root of time.

Effect of sorbent concentration

The effect of sorbent concentration on the removal of phenol was studied at a fixed initial phenol concentration of 40 ppm employing different adsorbent concentrations varying from 2 to 20 mg/ml. Adsorption was followed with shaking for 24 h to ensure equilibrium. It was noted that the equilibrium concentration of phenol decreased as the concentration of sorbent increased (see Figure 3). This trend was associated with an increase in the percentage of phenol removed from 74% to 92% as the sorbent concentration increased from 2 mg/ml to 20 mg/ml (Figure 3). Increasing the sorbent concentration at a fixed phenol concentration provided more available sorption sites for phenol and thus increased the extent of phenol removal.

Effect of initial pH

Numerous workers have studied the effect of pH on the adsorption of phenol by activated carbons (Halhouli *et al.* 1995; Kilduff and King 1997; Srivastava *et al.* 1997). Generally, they found that

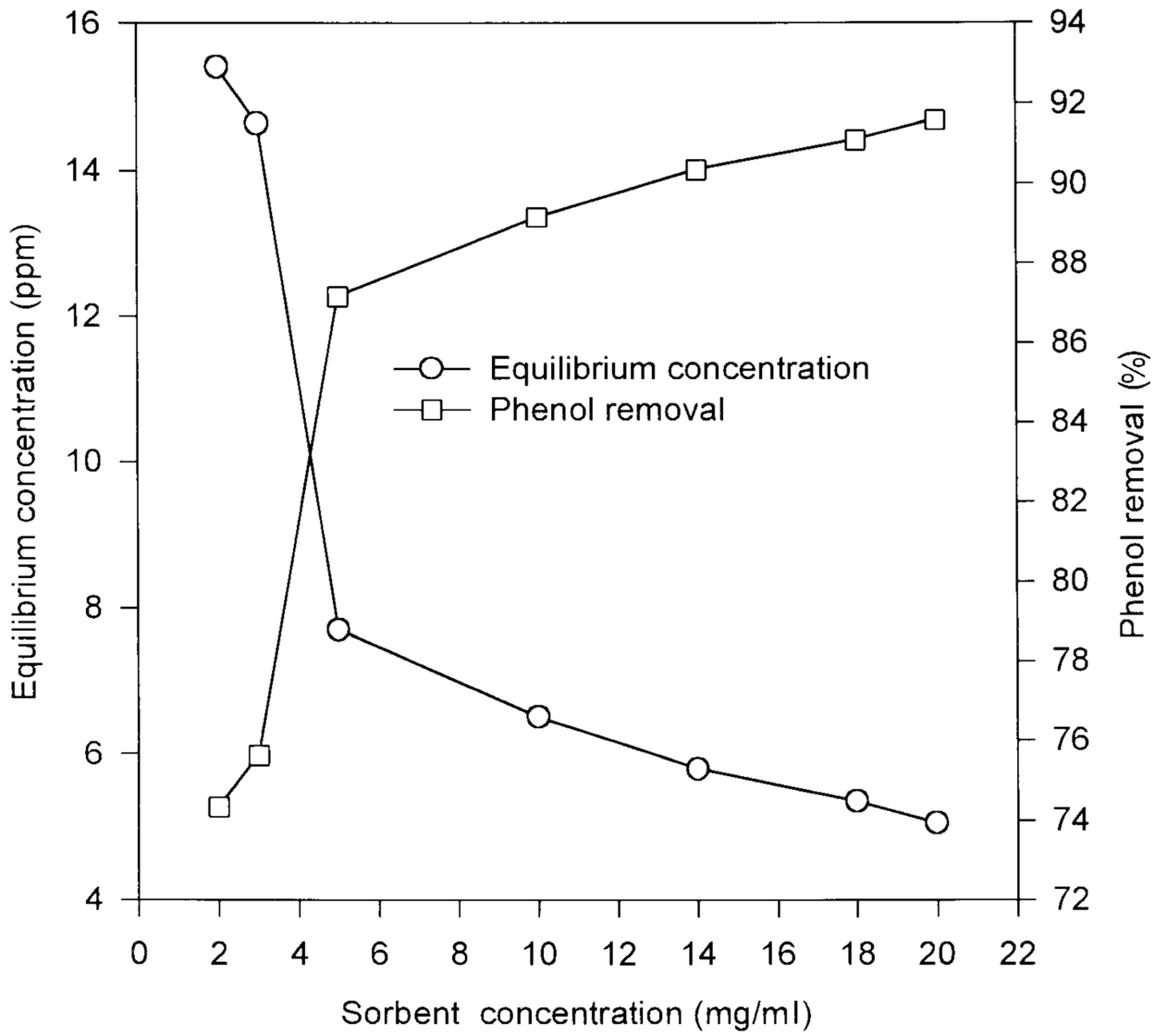

Figure 3. Effect of human hair concentration on the residual concentration of phenol and on the percentage phenol removal at an initial phenol concentration of 60 ppm.

as a weak acid phenol is adsorbed to a lesser extent at higher pH values due to the repulsive forces between the negative charge on the phenolate ion and the negatively charged surface of activated carbons.

The effect of the initial pH value on the adsorption of phenol by human hair was studied by adjusting the initial pH value of the system by the addition of either an aqueous 0.1 M HCl solution or an aqueous 0.1 M NaOH solution. The initial pH values thus studied were 2, 4, 6 and 8 employing different initial phenol concentrations. It was found that the phenol uptake increased significantly when the pH value of the system increased from 2 to 6 but only to a slightly higher value when the pH was raised from 6 to 8 (Figure 4). This behaviour contradicts the findings of other workers who have studied the adsorption of phenol by activated carbons (Halhouli *et al.* 1995; Kilduff and King 1997; Srivastava *et al.* 1997). Indeed, in our case, increasing the pH value not only affected the ionization of phenol but also the balance between the positive and negative charges on the hair. As far as phenol is concerned, the ionic fraction of the phenolate ion in the system (ϕ_{ions}) can be calculated from the equation (Watts 1997):

$$\phi_{ions} = \left[\frac{1}{1 + 10^{(pK_a - pH)}}\right] \quad (1)$$

The pK_a value for phenol is ca. 10 and obviously the value of ϕ_{ions} increases as the pH value is increased. The ionic fraction of negatively charged phenolate ion present in the system at a pH value of 2 is ca. 10^{-8} whereas at a pH value of 8 this quantity is equal to 10^{-2}. Hence, the degree of ionization of phenol was minimal over the pH range studied in the present work with mainly phenol in its neutral form being present in the solution.

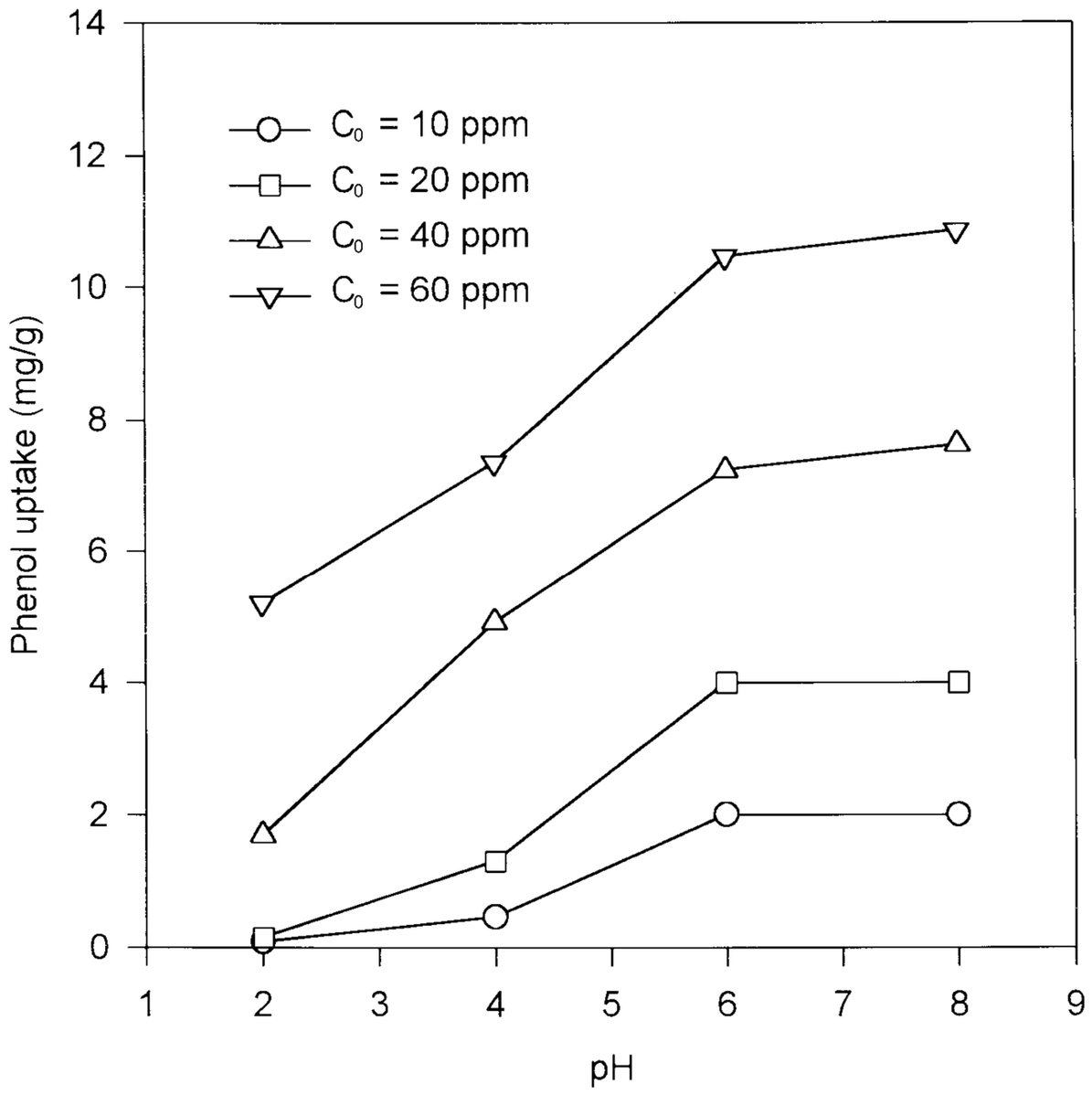

Figure 4. Effect of initial pH value on the adsorption of phenol at various initial phenol concentrations using human hair as a sorbent at 5 mg/ml concentration.

On the sorbent side, as a proteinaceous material, human hair possesses a large number of side chains. Some of these side chains contain basic groups $-NH_2$ and some side chains contain acidic groups –COOH. The existence of such acidic and basic side chains leads to positively and negatively charged groups being positioned along the protein chain, the behaviour of the protein being determined by the relative number of these positive and negative charges which in turn are affected by the acidity of the solution (Morrison and Boyd 1983). At low pH, the amino groups become positively charged ($-NH_3^+$), whereas at high pH the carboxylic acids become negatively charged (COO^-).

In its neutral form, phenol is sorbed on to negatively charged surfaces through hydrogen bonding and/or the formation of charge-transfer complexes (Hamaker and Thompson 1972). At the isoelectric point, the number of positive and negative charges on the protein are balanced. However, on the acidic side of the isoelectric point the number of positive charges exceeds those of the negative charges, whilst on the basic side of the isoelectric point the number of negative charges exceeds the number of positive charges. Hence, it appears likely that increasing the pH value of the solution would increase the number of negative charges on hair having a tendency to form hydrogen bonds with the neutral form of phenol and consequently increasing the phenol uptake. In conformity with Figure 1, the data depicted in Figure 4 also show that the uptake of phenol increased when the initial phenol concentration was increased.

Effect of temperature

To investigate the effect of temperature on the adsorption of phenol by human hair, experiments were conducted at 20°C, 35°C and 45°C using various initial phenol concentrations in the range between 10 ppm and 80 ppm. The samples were shaken for 24 h in the temperature-controlled water bath to ensure that equilibrium had been attained.

The Freundlich equation in its linearized form was fitted to the experimental adsorption data as shown in Figure 5. The linearized form of the Freundlich equation may be written as:

$$\log q = \log K + \frac{1}{n} \log C \tag{2}$$

where q is the equilibrium solid-phase concentration (mg/g), C is the equilibrium liquid-phase concentration (mg/l), K is the Freundlich capacity parameter and l/n is the Freundlich intensity parameter. The values of K and l/n may be calculated from the linear plots of log q versus log C. The values of these constants as obtained at the three temperatures studied are listed in Table 1. The values of R^2, which are a measure of the goodness-of-fit, indicate that the Freundlich model is adequate for the description of the experimental data obtained in this study.

The results depicted in Figure 5 indicate that phenol adsorption increased with increasing temperature. However, the variation in the phenol uptake over the temperature range 20–45°C was small, the increase in K with temperature listed in Table 1 emphasizing the effect of temperature on the sorption capacity of human hair.

The maximum adsorption capacity of phenol by human hair at 20°C, as calculated from the Langmuir equation, was 35 mg/g. This value is less than the maximum adsorption capacities for phenol on various types of activated carbons which extend from 135–200 mg/g as reported by Seidel *et al.* (1985). However, the adsorption capacity of human hair for phenol is better than that of other tested adsorbents such as spent oil shale (5 mg/g) (Darwish *et al.* 1996) and bentonite (1.7 mg/g) (Banat *et al.* 2000).

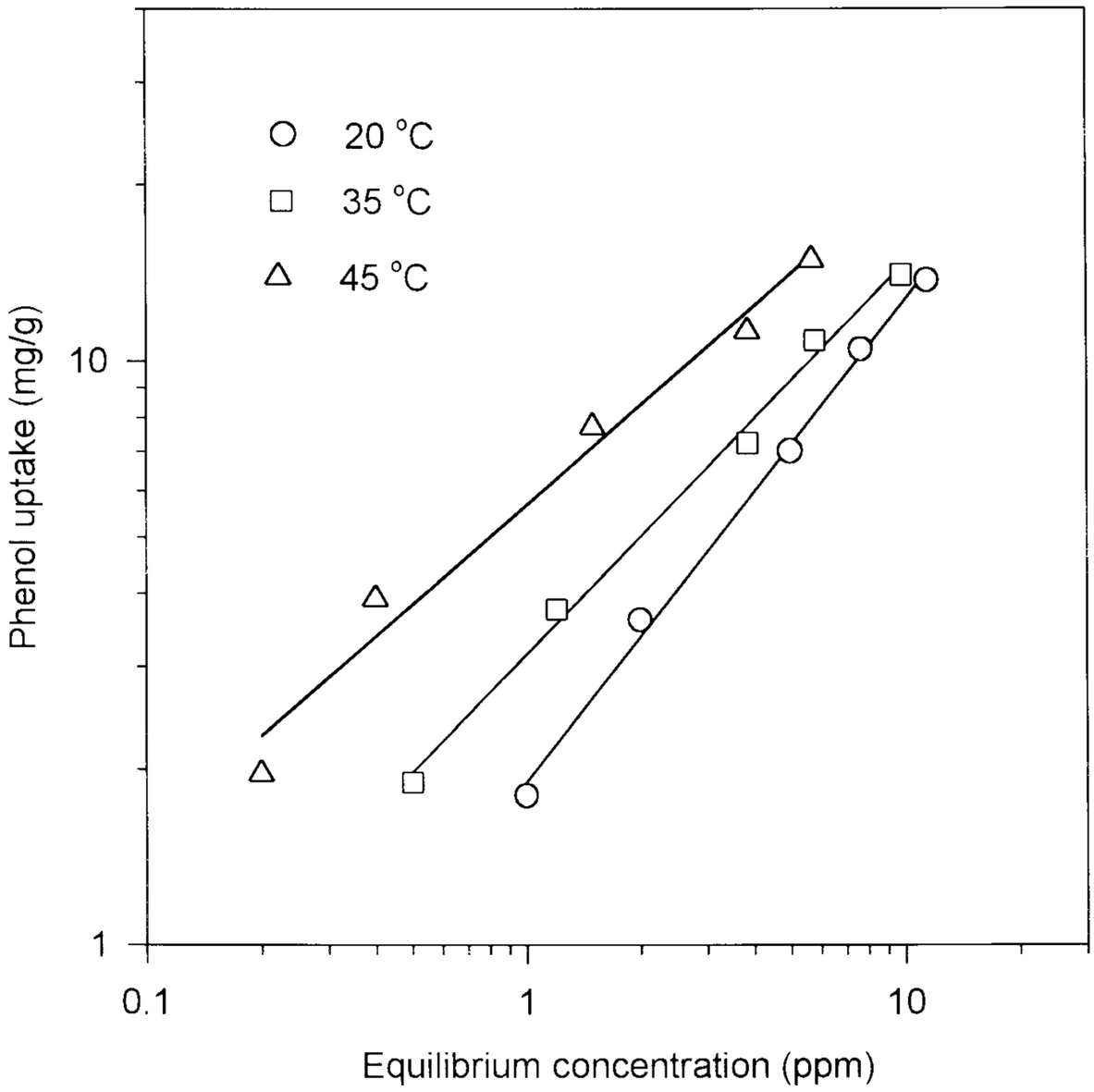

Figure 5. Freundlich adsorption isotherms for the adsorption of phenol by human hair at different temperatures.

TABLE 1. Freundlich Constants for the Adsorption of Phenol by Hair at Various Temperatures

Temperature (°C)	K	l/n	R^2
20	1.892	0.824	0.996
35	3.130	0.671	0.995
45	5.641	0.566	0.979

Effect of salt addition

Many researchers have studied the effect of the presence of inorganic salts on the adsorbability of organic species on activated carbons since most wastewaters contain dissolved salts. Thus, Halhouli *et al.* (1995) investigated the effects of three inorganic salts, i.e. KCl, KI and NaCl, on the adsorption of phenol by activated carbon. They found that the presence of these salts had only a minor effect on phenol adsorbability. Srivastava *et al.* (1997) studied the effect of different inorganic salts, viz. NaCl, $BaCl_2$ and $AlCl_3$, at various salt concentrations on the uptake of 2,4-dinitrophenol (DNP) by activated carbon developed from fertilizer waste slurry. They found that the presence of NaCl affected the uptake of DNP only at a pH value of 10, with no effect being observed at pH values of 2 and 4. The influence of the other two salts was marginal. The enhancement in uptake was attributed to ion-pair formation.

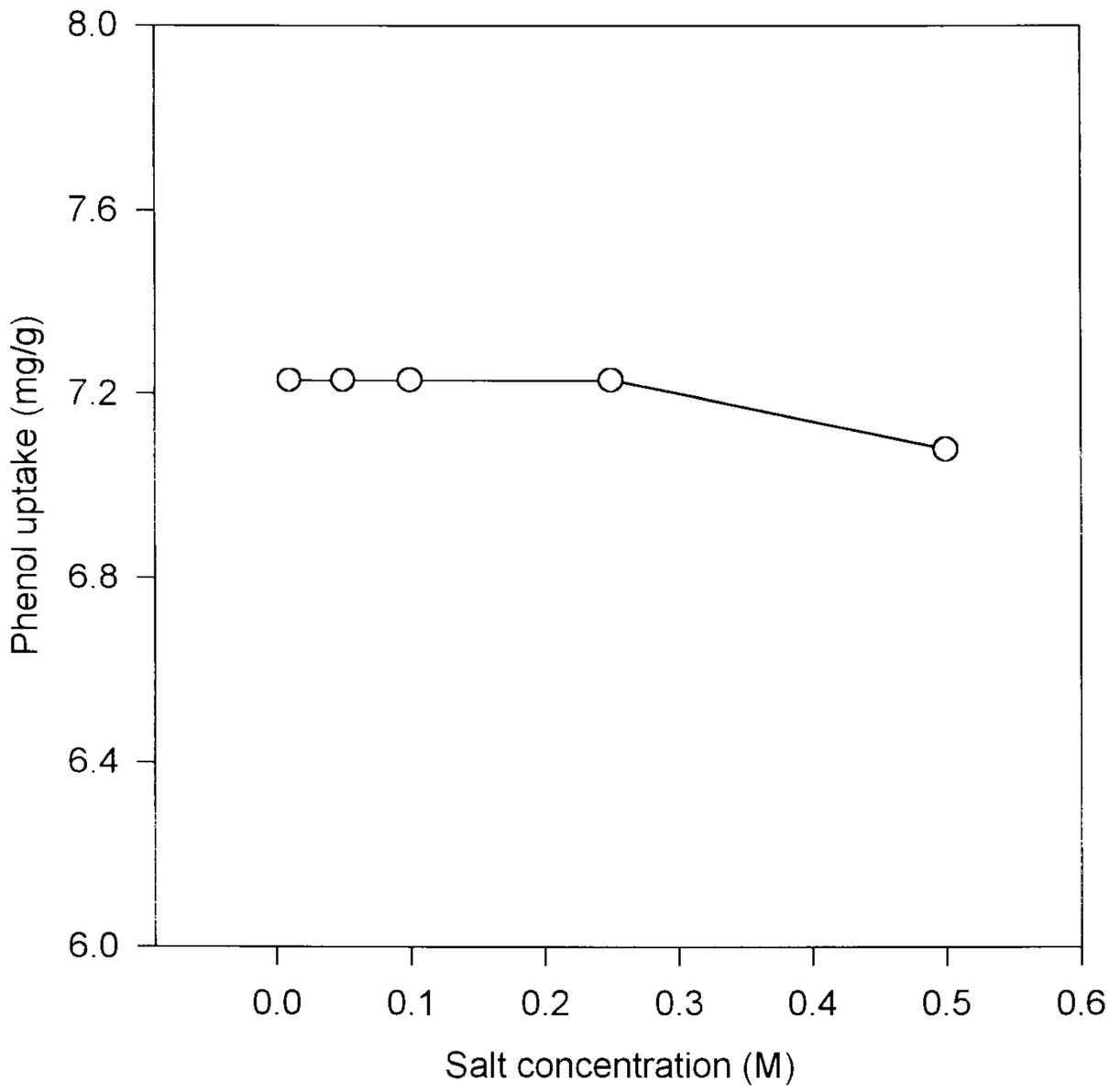

Figure 6. Effect of salt (NaCl) concentration on the adsorption of phenol at an initial concentration of 40 ppm by human hair as a sorbent at 5 mg/ml concentration.

In the present work the effect of different concentrations of NaCl on phenol adsorbability by human hair was evaluated. The results (see Figure 6) showed that the presence of ionized NaCl had hardly any influence on the adsorption of phenol by human hair, particularly at low salt concentrations. These observations are in agreement with the earlier findings of Hahouli *et al.* (1995).

CONCLUSIONS

The utilization of human hair waste for the removal of phenol from aqueous solutions was investigated experimentally. Although the samples were left to equilibrate for 24 h, the rate of phenol uptake was almost complete after 1 h. The percentage of phenol removed lay in the range 74–92% when the sorbent concentration was changed from 2 mg/ml to 20 mg/ml at an initial phenol concentration of 60 ppm. Increasing either the initial pH of the solution or the temperature resulted in an increase in the phenol uptake by human hair. The addition of NaCl to the sorbent/phenol suspension had only a limited influence on the uptake of phenol by human hair. The present study confirms the capability of human hair for the removal of micro-organic pollutants such as phenol from aqueous solutions and opens the door for further research designed to increase this capability.

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