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Biosorption of phenol by chicken feathers

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Abstract This work aimed at exploring the potential use of chicken feathers as a biosorbent for the removal of phenol from aqueous solutions. Batch kinetics and isotherm studies were performed to evaluate the effects of process parameters such as pH, temperature, initial phenol concentration, and sorbent concentration. Complete adsorption of phenol was noticed under certain process conditions. The adsorption of phenol increased with increasing initial phenol concentration, solution pH, temperature, and sorbent concentration. The adsorption equilibrium was well represented by the Freundlich and Langmuir adsorption isotherm models. The thermodynamic parameters obtained by means of the Langmuir model showed that the adsorption process was endothermic.

Introduction

The presence of phenol and its derivatives in water and wastewater are of major concern because of their toxicity and threat to human life and environment. Phenols are found naturally in fossil fuels but they are also produced by many industries. Although phenol has not been shown to be a carcinogen in humans there is some evidence from animal studies that phenol may be a reproductive toxin. Phenolic compounds with chlorine produce complexes with very objectionable taste and odor. Chlorine substitution on phenols not only increases taste and odor but also toxicity effects (Damis et al. 1998). Stringent US Environmental Protection Agency (EPA) regulations call for lowering phenol content in the wastewater to less than 1 mg/L (Dutta et al. 1992). The methods used to remove phenolic compounds from aqueous solutions were classified into destructive methods, such as oxidation with ozone, and recuperative methods, such as adsorption into porous solids (Dutta et al. 1998). Because of its strong affinity to most organic and inorganic pollutants and its high surface area per unit volume, activated carbon was the most widely studied adsorbent. However, because of the relatively high cost of activated carbon, many researchers have studied the feasibility of using low cost, naturally occurring materials as potential adsorbents.

Since the beginning of last decade, the use of biosorbents for the removal of heavy metals has been an area of active research, due to their potential to provide an effective and economic means for the treatment of heavy metal polluted wastewater (Tobin and Cooper 1990; Kapoor and Viraraghavan 1998). Chicken feathers were among the biosorbents that had been used for this purpose (Syama et al. 1996). Chicken feathers wasted in the process of food production are made of a fibrous protein known as keratin that has a complicated structure and contains a large surface area. Scientists at Auburn University estimated that there are 27,000 tons of cleaned and dried poultry feathers produced by the US poultry industry each week (Merka 1997). As chicken consumption in the world keeps growing, feather generation, as a by-product, will also grow. Figuring out what to do with all these feathers can be a real headache. Most farmers, at present, throw them away or grind them up and mix them into animal feed to add protein to animal diets. The success in using chicken feathers in decontamination of wastewater would add value to this by-product. Syama et al. (1996) used chicken feathers for the biosorption of precious metal ions such as gold and platinum. They found that chicken feathers were capable of adsorbing precious metal ions selectively from their dilute aqueous solutions with high yield in short contact time. The uptake of metal ions was found to be pH dependent. Nonetheless, little work has been done using biosorbents for the removal of organic pollutants such as phenol from aqueous and non-aqueous solutions (Payne et al. 1992; Tumbas et al. 1998).

The present study investigates the possible use of chicken feathers as an adsorbent for the removal of organic pollutants represented by phenol as a model component. Removal of phenol from aqueous solutions has often been employed as a test for adsorbability of organic compounds by activated carbon (Halhouli et al. 1995; Kilduff and King 1997). The effect of system conditions that might influence the adsorbability of phenol by chicken feathers, such as temperature and pH of solution, are also investigated.

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Materials and methods

Adsorbent

Raw chicken feathers directly obtained from a poultry-processing plant were washed with a detergent, rinsed

several times with distilled water, and then left to dry at room temperature. The dry feathers were ground to pass a 20-mesh screen and then used in the sorption tests.

Batch adsorption experiments

Sorbent was transferred into bottles containing 50 mL of phenol solution to give a final sorbent concentration of 4 mg/mL. The phenol concentrations were in the range of 10–100 ppm. Distilled water was used in preparing the solutions. A temperature-controlled shaker (Kottermann, Germany) was used to agitate the mixture at the desired temperature. Experiments were carried out at 20 °C, unless otherwise stated. Samples from the solutions were taken at predetermined time intervals, for the purpose of studying the kinetics of the sorption process. Otherwise, the mixture was allowed to attain equilibrium and then the bottles were removed from the shaker for analysis. The sorbent was separated from the samples by centrifugation (300 *g*, for 10 min) and the supernatant was then analyzed for residual concentration of phenol. The method of Gales and Booth (1976), which is based on spectophotometric analysis of the developed color resulting from the reaction of phenol with 4-aminoantipyrine, was followed.

Sorption experiments were carried out at 20 °C, 35 °C, and 45 °C to find out the effect of temperature. The effect of pH was determined by studying the adsorption of phenol over a pH range of 2–8. The pH was adjusted by addition of a diluted acid or base. Each experiment was carried out in triplicate and the average results are presented in this work. The results are expressed in terms of the amount of phenol adsorbed per unit weight of sorbent, i.e., the uptake.

Results and discussion

Effect of sorbent concentration

The effect of sorbent concentration on the percentage of phenol removal from solution is presented in Fig. 1. It can be seen that the increase in the sorbent concentration from 1.0 mg/mL to 20 mg/mL, at a fixed initial phenol concentration of 50 mg/L, results in an increase of the removal of phenol, from 30% to 100%, respectively. When the sorbent concentration was 15 mg/mL or more, no residual phenol was detected in the solution at the end of the sorption process. Experiments were repeated three times and similar results were obtained. The increase in the sorbent concentration at a fixed phenol concentration grants more available sorption sites for phenol and thus more phenol removal.

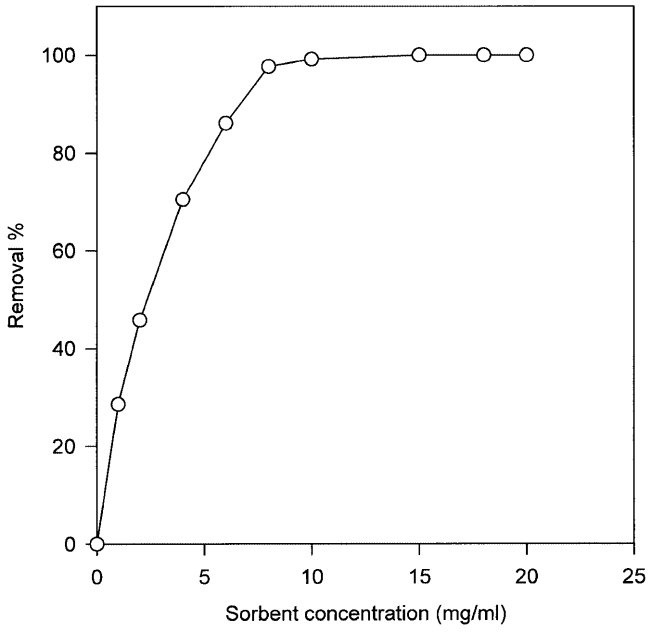

Fig. 1. Effect of sorbent concentration on the removal percentage of phenol

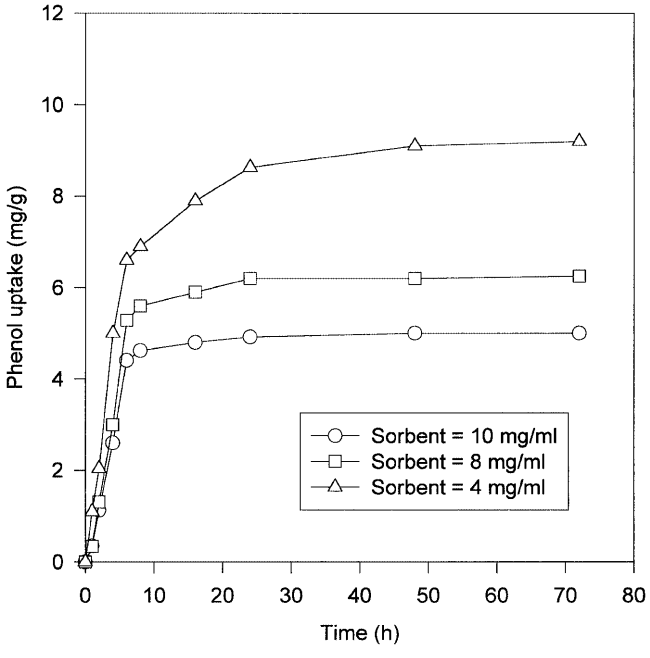

Fig. 2. Dependence of phenol uptake on contact time at different sorbent concentrations, with an initial phenol concentration of 50 mg/mL

Adsorption kinetics

The kinetics of adsorption of phenol on chicken feathers was studied by taking samples at different time intervals. The plot of phenol uptake versus time (Fig. 2) showed that the equilibrium time for phenol adsorption was about 25 h for the three studied sorbent concentrations, as after this time no significant sorption of phenol was noticed. According to Fig. 2, the kinetics of phenol adsorption can be divided into three stages. In the first stage, which lasts for about 10 h, sharp adsorption of phenol is seen, indicating, as expected, that adsorption takes place at the external surface of the feathers. In the second stage, a gradual increase of phenol adsorption is seen, indicating that intrapore diffusion becomes the controlling factor. In the last stage, the equilibrium stage, which occurs after 25 h, the uptake of phenol becomes asymptotic to the time axis, because of extremely low solute concentration in the solution and/or the solid

becoming saturated with the solute. The results (Fig. 2) also indicated that the uptake of phenol decreased as the sorbent concentration was increased. Actually, the amount of adsorbed phenol increases as the concentration of sorbent is increased. This trend is attributed to the increase in the number of solid particles per unit volume of solution that contains the solute.

Effect of initial phenol concentration

The effect of the initial phenol concentration on its uptake, which would give an indication of the sorption capacity of feathers, was studied using three initial concentrations: 10, 50, and 100 ppm. The results (Fig. 3) showed that an increase in the initial phenol concentration resulted in an increase in the uptake of phenol. This is because the increase in the initial phenol concentration would increase the mass transfer driving force and thus the uptake of phenol. However, it is important to mention here that at higher phenol concentration, the percentage of phenol removal becomes lower.

Effect of initial pH

The effect of initial pH on the adsorption of phenol by chicken feathers was studied by adjusting the solution pH with 0.1-M HCl or 0.1-M NaOH, using different phenol concentrations. The studied initial pH values were 2, 5, and 8. The pH at which adsorption was carried out has a strong influence on the uptake of phenol (Fig. 4). The change in pH is expected to influence the ionization of both the sorbate and the sorbent. In terms of the sorbent, it was reported that extremes of acidity or alkalinity would affect the ionization of charged amino acid side chains in the keratin protein (Bailey and Bailey 1981). The sorbate phenol is a weak organic acid with a pK_a value of about 10. When phenol dissociates, a negative phenoxide ion is produced. According to the Henderson–Hasselbach equation (Watts 1998), the ionization of phenol is highly affected by the pH value. The concentration of the phenol form decreases with increased pH and the concentration of the phenoxide salt (ionized) form increases as the pH is raised. The two forms exist at equal concentration at a pH of 10. Inspection of Fig. 4 shows that phenol adsorption increases as the pH rises. This means that the amount of phenol adsorbed is correlated to the proportion of phenoxide salt (ionized) form in solution. Therefore, it is believed that ionic interactions had occurred between the negatively charged phenoxide ion and the positively charged amine groups in the feathers.

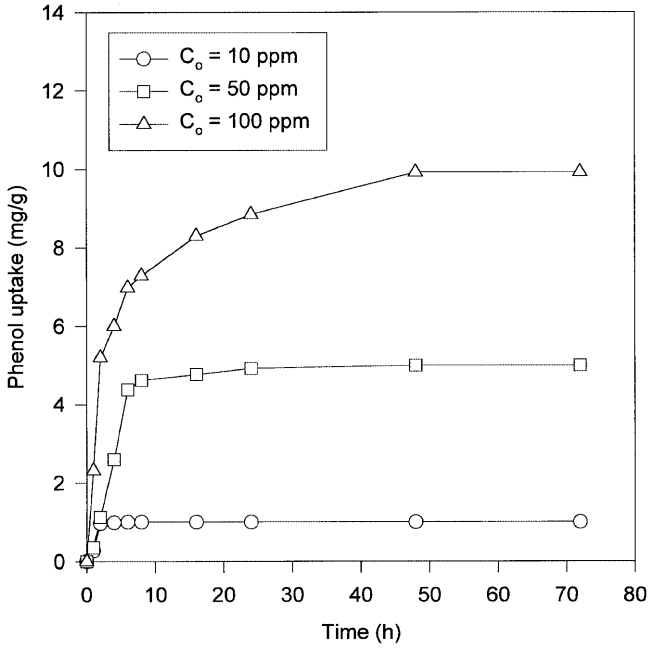

Fig. 3. Effect of initial phenol concentration on phenol uptake, using a 4-mg/mL sorbent concentration

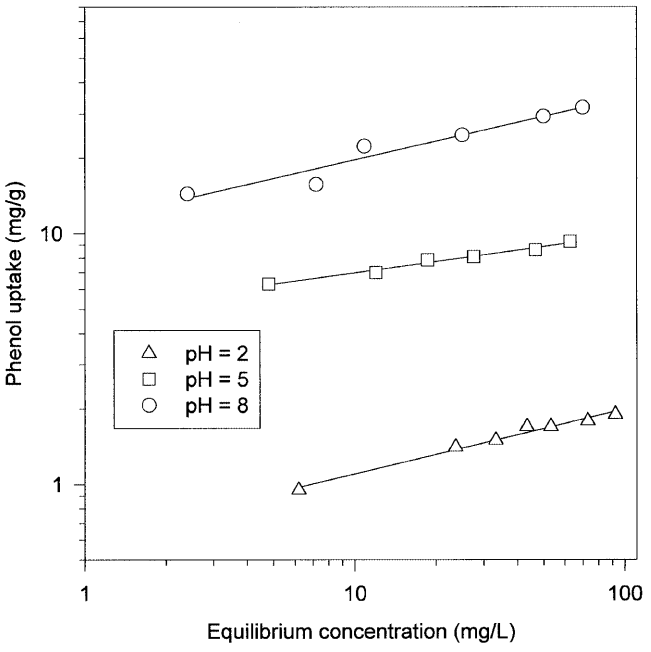

Fig. 4. Relationship between equilibrium phenol concentration and uptake, at various pH values, using a 4-mg/mL sorbent concentration

In Fig. 4, the results of pH effect were well represented by the linearized Freundlich equation

$$\log q = \log K + \frac{1}{n}\log C \qquad (1)$$

where q is the equilibrium solid-phase concentration (mg/g), C is the equilibrium liquid-phase concentration (mg/L), and K and $1/n$ are the Freundlich constants. The linear plot of log q versus log C at different pH values (Fig. 4) elucidates the applicability of the Freundlich model in representing the equilibrium data of phenol sorption by chicken feathers. From the slope and intercept of these lines, the values of K and $1/n$ were calculated. These constants at the three pH values are shown in Table 1. Table 1 shows that K increases with the increase in the initial pH value. This reflects the increase in the sorption capacity of chicken feathers with the increase in the solution initial pH value. The slope of the plots ($1/n$) could indicate that the intensity of sorption

Table 1. Freundlich constants for the sorption of phenol by chicken feathers at various pH values

pH	K	$1/n$	R^2
2	0.61	0.258	0.982
5	4.96	0.148	0.981
8	11.15	0.247	0.941

was virtually the same regardless of the pH value. The R^2 values, which are a measure of the goodness of fit, indicate that Freundlich model can adequately describe the experimental data.

Effect of temperature

The effect of temperature on the uptake of phenol by chicken feathers is shown in Fig. 5. For the system under investigation, the uptake of phenol increases with the increase in temperature. This improvement is partly due to the increase of phenol dissociation and adsorption rate with temperature, and perhaps partly due to the stretching of feathers' keratin with temperature. The later factor may expose more functional groups for adsorption.

The equilibrium data at different temperatures were well represented by the Freundlich model as revealed by the regression coefficient, R^2, shown in Table 2. The constant K of the Freundlich isotherm model (Table 2) shows an increase in the sorption capacity of chicken feathers with increased temperature. The following linearized Langmuir isotherm model also represents these equilibrium data at different temperatures:

$$\frac{1}{q} = \frac{1}{q_m} + \left(\frac{1}{q_m b}\right)\frac{1}{C} \tag{2}$$

where q_m and b are constants related to the maximum adsorption capacity and enthalpy of adsorption, respectively. These constants were calculated from the slope and intercept of the linear plots of $1/q$ versus $1/C$ (Fig. 6) at various temperatures. The Langmuir model fits the

Table 2. Freundlich constants for the sorption of phenol by chicken feathers at various temperatures

Temperature (°C)	K	$1/n$	R^2
20	3.22	0.404	0.976
35	4.14	0.69	0.991
45	6.05	0.69	0.961

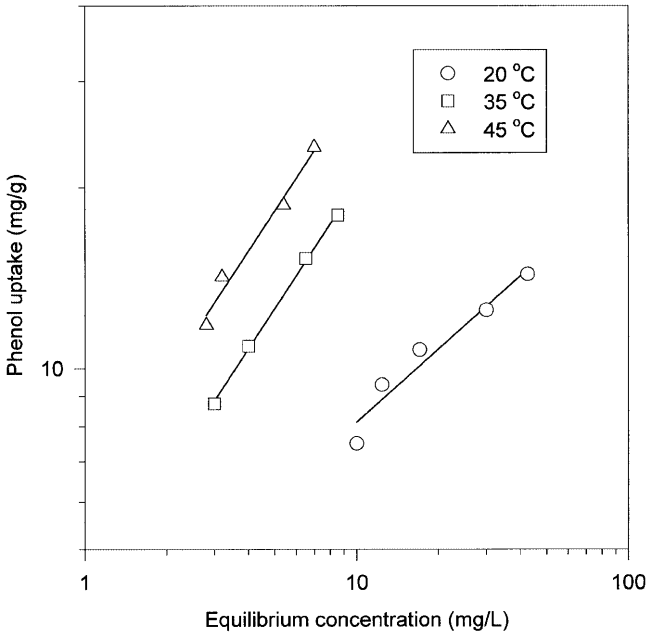

Fig. 5. Relationship between equilibrium phenol concentration and uptake at various temperatures, using a 4-mg/mL sorbent concentration

experimental data, as shown by the R^2 values given in Table 3, well. Application of the Langmuir model to the equilibrium data indicates the monolayer coverage of chicken feathers by phenol. The value of q_m (Table 3) increases with the increase in temperature, which again means, as in the Freundlich model, that sorption capacity increases with temperature. The values of b can be used to calculate the change in enthalpy (H), free energy (G), and entropy (S) of adsorption using the following equations (Viraraghavan and Kapoor 1994; Eligwe et al. 1999):

$$\ln b = \ln b' - \frac{\Delta H}{RT} \tag{3}$$

$$\Delta G = -RT\ln b \tag{4}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{5}$$

where R is the universal gas constant, T is the temperature (in degrees K), and b' is the adsorption energy constant. The value of H, as calculated from the plot of $\ln b$ versus $1/T$ (Fig. 7), was found to be $+13.2$ kJ/mol. The positive value of H indicates that adsorption of phenol by chicken feathers was endothermic in nature.

Table 3. The Langmuir constants and the thermodynamic parameters at different temperatures for the adsorption of phenol by chicken feathers

Temperature (K)	q_m (mg/g)	b (L/mg)	R^2	ΔG (kJ/mol)	ΔS (kJ/kmol K)
293	19.46	0.067	0.981	6.57	22.63
308	42.07	0.087	0.992	6.24	22.60
318	54.61	0.103	6.02	22.59	

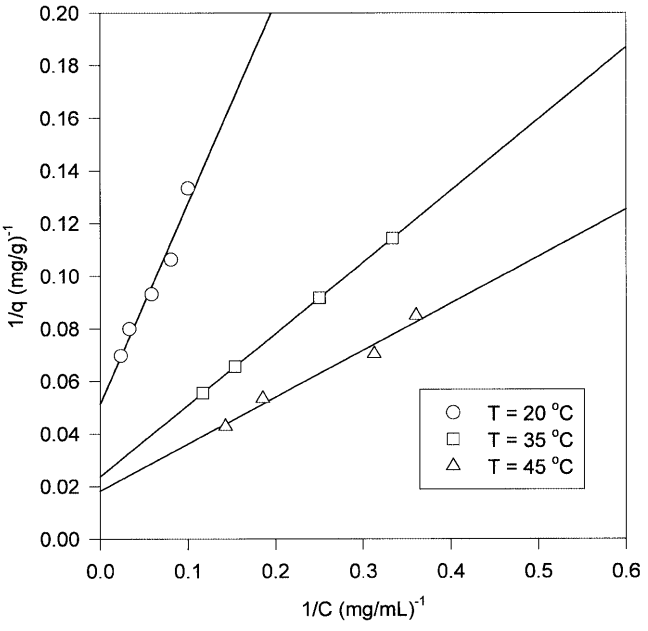

Fig. 6. Linearized Langmuir plots for equilibrium phenol concentration and uptake at various temperatures

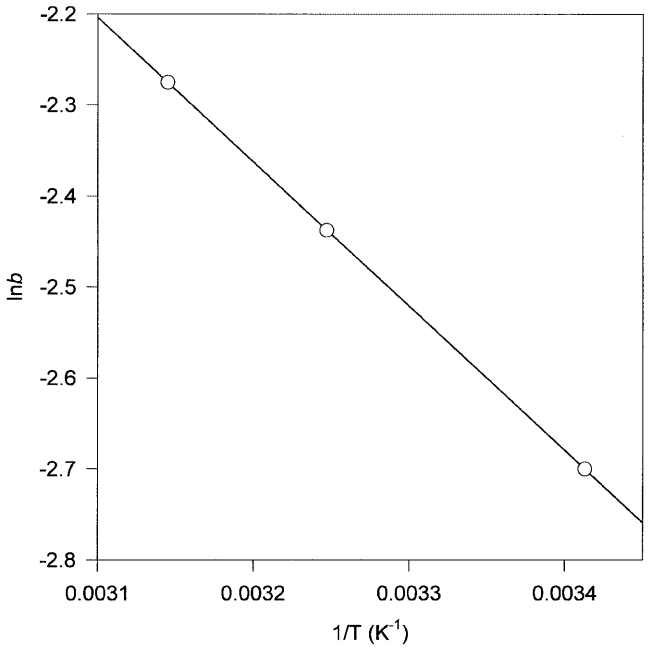

Fig. 7. Plot of ln b versus $1/T$ for sorption of phenol by chicken feathers

Table 4. The maximum adsorption capacity (q_m) of various adsorbents

Adsorbent	q_m (mg/g)	Temperature	Source
Powdered activated carbon (Filtrasorb)	206	Room temp.	Mckay and Bino (1985)
Powdered activated carbon (4 types)	136–200	20 °C	Seidel et al. (1985)
Powdered activated carbon from apricot stone shells	32–120	Room temp.	Daifullah and Sirgis (1998)
Granular activated carbon	21	Room temp.	Daifullah and Sirgis (1998)
Carbonized polymers (Ambersorb XE-340)	90	Room temp.	Vliet et al. (1980)
Polymeric adsorbent (Amberlite XAD-2)	40	Room temp.	Vliet et al. (1980)
Organo-clay ($HDTMA^+$–Smectite)	99	20 °C	Mortland et al. (1986)
Organo-clay ($HDPY^+$–Smectite)	109	20 °C	Mortland et al. (1986)
Bentonite	1.7	25 °C	Banat et al. (2000)
Spent oil shale	5	30 °C	Darwish et al. (1996)
Chicken feathers	19.5	20 °C	Present study

Since adsorption is endothermic, the degree of adsorption will increase at higher temperature and decrease at lower temperatures. This is in agreement with what was found in Fig. 6. Values of G and S at different temperatures are listed in Table 3. The positive value of G (endergonic) indicates that for adsorption to occur energy should be supplied to the system, while the positive values of S indicate the possibility of the adsorption process.

Comparison between chicken feathers' and other adsorbents' ability to remove phenol from aqueous solutions was made, based on the maximum adsorption capacity of each adsorbent. The maximum adsorption capacity values listed in Table 4 show that chicken feathers, without any activation, have a lower capacity for phenol uptake to that of powdered activated carbon (PAC) but an approximately equal capacity to that of granular activated carbon (GAC). It is clear from Table 4 that chicken feathers' adsorption capacity is better than that of other potential adsorbents such as bentonite and spent oil shale. Chicken feathers, therefore, show promise for the removal of phenol from aqueous solutions. For the process to be practical, chicken feathers after adsorption have to be regenerated with a suitable desorbent. There are a number of solvents such as acetone and methanol that could be tested for this purpose.

Conclusions

The ability of chicken feathers to remove phenolic compounds, represented by phenol as a model component, from aqueous solutions was confirmed. At low initial phenol concentration, no residual phenol in the aqueous solution was detected after attaining equilibrium. The capacity of chicken feathers to remove phenol was enhanced by an increase in temperature and pH. Increasing the adsorbent concentration resulted in the increase of phenol removal, owing to a corresponding increase in adsorption sites. The experimental data were

well represented by the Freundlich and Langmuir isotherm models. The Langmuir isotherm model was used to study the process thermodynamics, which showed that phenol adsorption by chicken feathers was endothermic in nature.

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