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Sorption of Phenol from Aqueous Solution using Chicken Feathers

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Abstract

Concern is growing over the contamination of the water environments with organic pollutants, such as phenolic compounds because of their adverse effects on health and environment. In these studies, the ability to remove phenol from aqueous solution has been achieved using chicken feathers as an adsorbent. Batch studies were performed to evaluate the effects of process parameters such as initial concentration, contact time, adsorbent dosage, and temperature. Adsorption capacity for the adsorbent was dependent on the temperature since an increase in phenol removal efficiency with an increase in temperature was observed. Results have shown that an increase in the amount of adsorbent was followed by increased efficiency in phenol removal owing to a corresponding increase in adsorption sites. The equilibrium time for phenol removal was found to be 24 h. The experimental data were well represented by the Freundlich (R^2 = 0.9869) and the Langmuir (R^2 = 0.9997) isotherm models with data slightly better fitted to the Langmuir than the Freundlich isotherm model. The maximum sorption capacity was found to be 16.5 mg/g at 30°C and pH 8. Chicken feathers, an inexpensive and easily available material, can be an alternative to more costly adsorbents used for the removal of phenol from wastewater.

Key words: Adsorption; Chicken feathers; Isotherm; Phenol.

Introduction

Over the last decade, environmental pollution of aquatic resources by organic and inorganic substances has always been a universal concern. Among common organic substances found in industrial effluents are phenols and their derivatives that cause animal and human health problems (Mbui *et al*., 2002). Phenols, their derivatives, and the organic

compounds with two condensed rings belong to the most recurrent and harmful contaminants in the petroleum, petrochemical, plastics, dyes, pesticides and paper industries (Thawornchaisit and Pakulanon, 2007). Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health (USEPA, 1987). The majority of phenols are toxic substances and some are known or suspected carcinogens (Arellano-Cardenas *et al.*, 2005). It is important to remove phenols and aromatic compounds from contaminated industrial aqueous streams before they are discharged into public water bodies. Phenol is highly soluble in water and its presence in water sources, which is identiûed by various aspects such as taste, smell, and color; is harmful to organisms and causes human deaths even at low concentrations (Bevilaqua, 2002). Phenol is a dangerous stimulant and corrosive compound for skin, eye, and respiratory tract upon direct contact. Also, chlorophenol is produced during chlorination of water (Manshouri *et al.*, 2012). For this reason, a substantial number of phenols have been cited by the European Community Directive and the U.S. Environmental Protection Agency (EPA) (Keith and Telliard, 1979; EPA, 2004). The concentration of these phenolic compounds established in potable water should not exceed 10 mg L^{-1} (Hennion *et al.*, 1994).

Several techniques such as sedimentation, precipitation, osmosis, ultra-centrifugation, and micro-ûltration have been used with the purpose of keeping the concentrations of phenolic materials in drinking water within permissible limits. Phenolic compounds are generally eliminated by means of conventional techniques such as coagulation, solvent extraction (Arellano-Cardenas *et al.*, 2005), adsorption with activated charcoal (Taman and Okazaki, 1996; Haghseresht *et al.*, 2002), ionic exchange resins (Ramos *et al.*, 2005), photo catalytic degradation in suspensions of titanium oxide (Salaices *et al.*, 2004), oxidation with hydrogen peroxide (Li *et al.*, 1999) and biodegradation (Arcangeli and Arvin, 1995). Unfortunately, these technologies exhibit low efficiency in small contaminant concentrations and represent a big economic investment for developing countries, producing in some cases toxic residues that need later treatments (Navarro *et al.*, 2008a).

In recent years, biotechnological processes have attracted the attention of the scientiûc community for their variety of clean technologies for the removal of organic and inorganic contaminants from the environmental. Among them, biosorption has already tackled the problem of phenolic compounds removal from aquatic sources, using a variety of biomasses such as rice husk, eggshell, and chitosan (Munaf *et al.*, 1997; Koumanova *et al.*, 2002; Zheng *et al.*, 2004). Poultry chicken feathers representing about 6% of the total weight of a mature chicken are generated in huge quantities as a waste by product at commercial poultry plants that sometimes lead to environmental problems. Feather waste has been used as feedstuff for poultry and livestock. In addition, chicken feathers have been reported to be good adsorbents of heavy metals (Syama *et al.*, 1996; De la Rosa *et al.*, 2008). The biomass has shown a high efficiency in the elimination of Tartrazine, and other toxic dyes (Mittal *et al.*, 2007; Gupta *et al.*, 2006). Chicken feathers are semi-crystalline and structured by a non-porous network with pores of size in the range of 0.5 to 0.10 *ìm* (Kar and Misra, 2004). This biomass is predominantly constituted by the protein keratin, which can be assembled into á-helix (41%), â-sheet (38%) and disordered structures (21%) (Barone and Schmidt, 2006). FTIR analyses indicate that chicken feathers contain carboxylic groups that are capable of binding metal ions effectively (Kar and Misra, 2004).

Given the above advantages and characteristics, efforts have now been focussed towards introducing easily available and low cost biomaterials such as chicken feathers in phenol matter adsorption. Thus, the study was aimed at investigating the ability of chicken feathers for removing phenol from aqueous solutions. The effect of initial concentration, contact time, adsorbent dosage, and temperature were explored. The equilibrium sorption data were fitted to the Langmuir and the Freundlich sorption models.

Materials and methods

Preparation of the biosorbent

Chicken feathers were obtained from the Midlands State University Agricultural Department poultry section, Gweru, Zimbabwe. The chicken feathers were washed with a detergent, cleansed several times with distilled water, and dried in the sunlight for 1 day. Subsequently, feathers were treated with a solution of deionized water and ethanol (5:1

proportion) for 12 hours. This step was performed for total removal of organic materials in feathers. Finally, feathers were again washed with deionized water, dried, rachises removed, and soft barbs were cut to obtain fibers of about 0.5 cm in length. For the removal of moisture, the material obtained was kept in an oven at 100°C for 12 hours and activated adsorbent and stored in a vacuum desiccator until used (De la Rosa *et al.*, 2008).

Reagents and solutions

All other chemical reagents were of analytical grade 4-aminoantipyrine, $K_3Fe(CN)_6$, NH_40H, NH_4Cl, Phenol salt (Sky labs, Zimbabwe). A phenol stock solution was obtained by dissolving 1.0 g of phenol, in de-ionized water and diluted to 1 000 mL. Desired solutions of phenol were prepared using appropriate subsequent dilutions of the stock solution. The range in concentrations of phenol prepared from standard solution varied between 10 mg/L to 100 mg/L. Before mixing with the adsorbent, the pH of each test solution was adjusting the pH with 0.1 M H_3PO_4 or NaOH. All pH measurements were carried out with a pH meter (AZ pH/mV meter: model 8601).

Batch studies

Effect of adsorbent dosage

The effect of adsorbent dosage was studied by agitating 100 mL of 50 mg/L phenol solutions with different adsorbent doses (0.2 g, 0.4 g, 0.6 g, 0.8 g, 1.0 g) at equilibrium time and pH 8. The biosorbent was removed from the solution by filtration and the filtrate was analyzed for the residual concentrations of phenol using ultraviolet visible spectrophotometer. Briefly, the residual phenol concentrations were determined following the method of Gales and Booth (1976), which is based on spectrophotometric analysis of the developed color resulting from the reaction of phenol with 4-aminoantipyrine. A buffer solution with pH = 10.0 for phenols, was prepared by dissolving 70 g NH_4Cl in water and adding suitable amount of NH_40H in 1000 mL of distilled water. Solutions containing 2.0 g of 4-aminoantipyrine in 100 mL distilled water and 8.0 g $K_3Fe(CN)_6$ in 100 mL distilled water were prepared, as complexing reagents for phenol extraction into chloroform and subsequent spectrophotometric determination (Banat and Al-Asheh, 2001; APHA,1995). Absorbance was read at 510 nm (Navarro *et al.*, 2008b).

Effect of contact Time

The adsorption experiments were carried out at different contact times 30, 60, 180, 360, 720, 1 440, 2 880 min with a fixed adsorbent dosage at pH 8. The biosorbent was removed from the solution by filtration and the filtrate was analyzed for the residual concentrations of using Ultraviolet visible Spectrophotometer as described in section 2.3.1.

Effect of initial phenol concentration

The adsorption experiments were carried out at increasing concentration of phenol 10 mg/L, 20 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L in 100 mL of phenol solution in 250 mL Erlenmeyer flask at optimum contact time, pH 8 and optimum adsorbent dosage. The biosorbent was removed from the solution by filtration and the filtrate was analyzed for the residual concentrations of using Ultraviolet visible Spectrophotometer as described above.

Effect of temperature

Optimum biosorbent concentration and optimum contact time were used to monitor the temperature effect on adsorption. The adsorption experiments were carried out at different temperature values: 20°C, 30°C, 45°C, and 65°C with a fixed adsorbent dosage at optimum contact time and pH 8. The biosorbent was removed from the solution by filtration and the filtrate was analyzed for the residual concentrations of using Ultraviolet visible Spectrophotometer as described above.

Adsorption Equilibrium

The phenol concentration retained in the adsorbent phase was calculated according to the mass balance of the equation as given below:

$$q_e = \frac{V(C_0 - C_e)}{W} \qquad (1)$$

Where C_0 and C_e are the initial and the equilibrium phenolic solution concentrations (mg/ L), V is the volume of the phenolic solution (L), and W is the mass of the adsorbent (g). Two replicates were done per sample and the mean value determined.

Results and Discussion

Effect of dosage

Adsorbent dose is an important parameter in the biosorption of

pollutants from aqueous solution owing to its effect on the amount of pollutant ions removed per unit mass of the adsorbent (Miretzky *et al.*, 2008). The effect of sorbent concentration on the removal of phenol from solution is presented in Fig. 1.

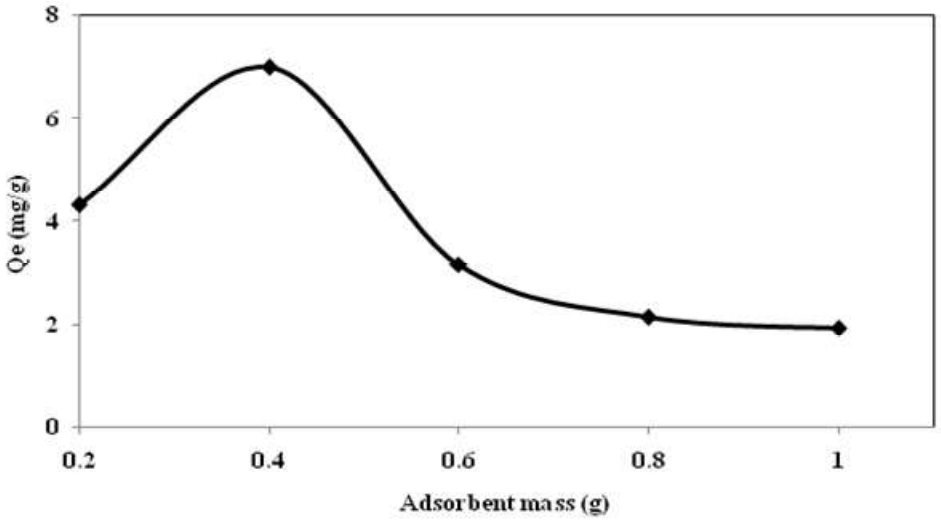

Fig. 1: Effect of adsorbent dosage

The removal of phenol increased with an increase in biosorbent concentration because of an increasing adsorption surface area. The maximum biosorption efficiency was obtained at 0.4 g of chicken feather, but further increase in biosorbent concentration decreased the maximum removal of phenol because of saturation of biosorbent surfaces. The increase in the sorbent concentration at a fixed phenol concentration grants more available sorption sites for phenol and thus more phenol removal (Banat and Al-Asheh, 2001).

Effect of contact time

Contact time plays an important role in the efficient removal of pollutants using biomaterials. Agitation time gives an insight into a sorption process, provides information on the minimum time required for considerable adsorption to take place (La Rosa *et al.*, 2008). The contact time was evaluated as one of the important

parameters affecting the biosorption efficiency. The adsorption experiments were carried out for different contact times with a fixed adsorbent dosage concentration at pH 8. Fig. 2 shows the biosorption efficiency of phenol by chicken feathers as a function of contact time. The phenol uptake was found to increase with increase in contact time up to 24 h and after that time no significant sorption of phenol was noticed. The fast initial phenol biosorption rate is attributed to the surface binding and the slower sorption is attributed to the interior penetration (Kumari *et al*., 2011). 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 24 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 (Banat and Al-Asheh, 2000).

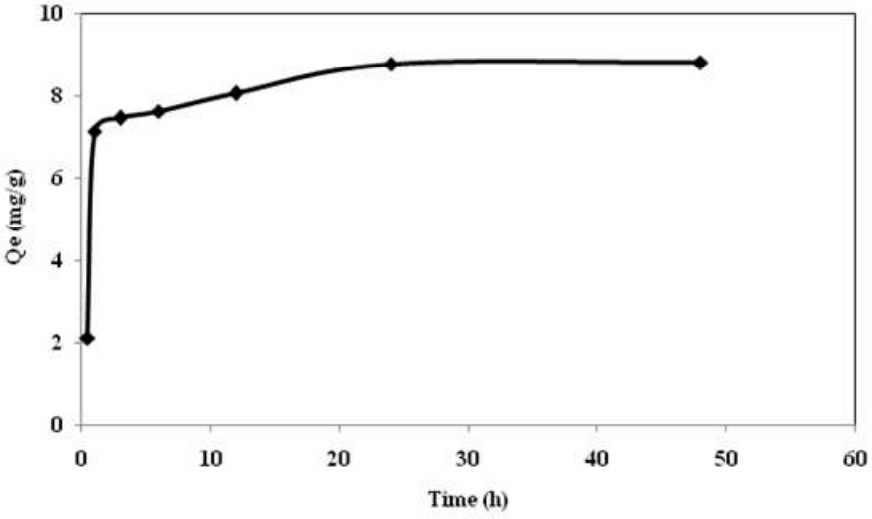

Fig. 2: Effect of contact time

Effect of initial phenol concentration

The feasibility and efficiency of a biosorption process depends not only on the properties of the biosorbents, but also on the concentration of the species

ion solution. The initial ion concentration provides an important driving force to overcome all mass transfer resistances of the ion between aqueous and solid phase (Aksu and Akinpar, 2000). The effect of the initial phenol concentration on its uptake, gives an indication of the sorption capacity of feathers. Fig. 3 exhibits that the adsorption of the phenol increases with increasing initial phenol concentration. This is because the increase in the initial phenol concentration would increase the mass transfer driving force and thus the uptake of phenol (Rubin *et al.*, 2006).

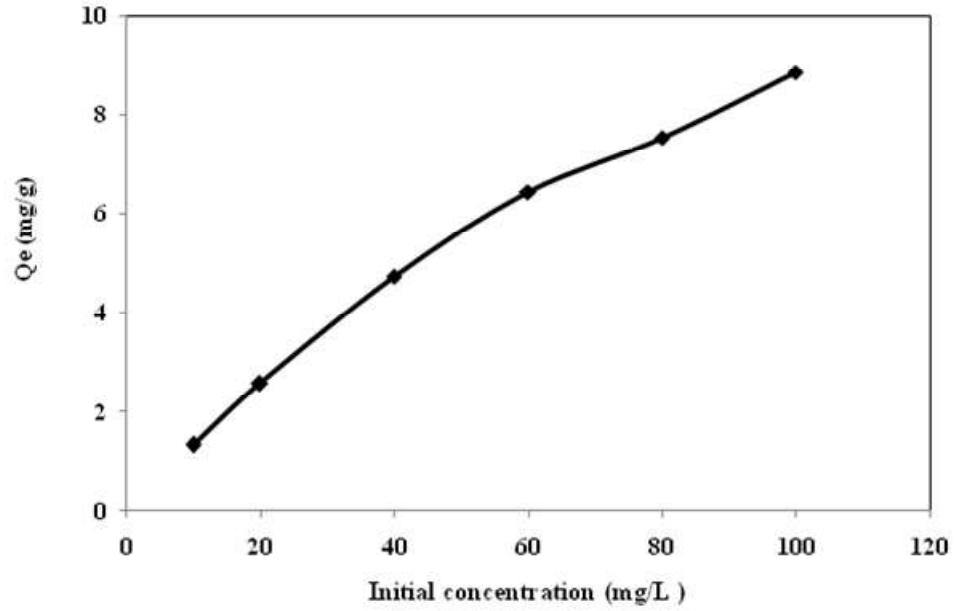

Fig. 3: Effects of initial concentration

Effect of Temperature

Temperature has two major effects on the adsorption process. An increase in temperature will increase the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbate particles because liquid viscosity decreases as temperature increases and the other one is that it effects the equilibrium capacity of the adsorbate depending on whether the process is exothermic and endothermic (Al-Qodah, 2006). The effect of temperature on the uptake of phenol by chicken feathers is shown in Fig. 4. As seen from Fig. 4, 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 (Banat and Al-Asheh, 2000). The later factor may expose more functional groups for adsorption and thus increase of more available active sites in the sorbent (Manshouri *et al.*, 2012).

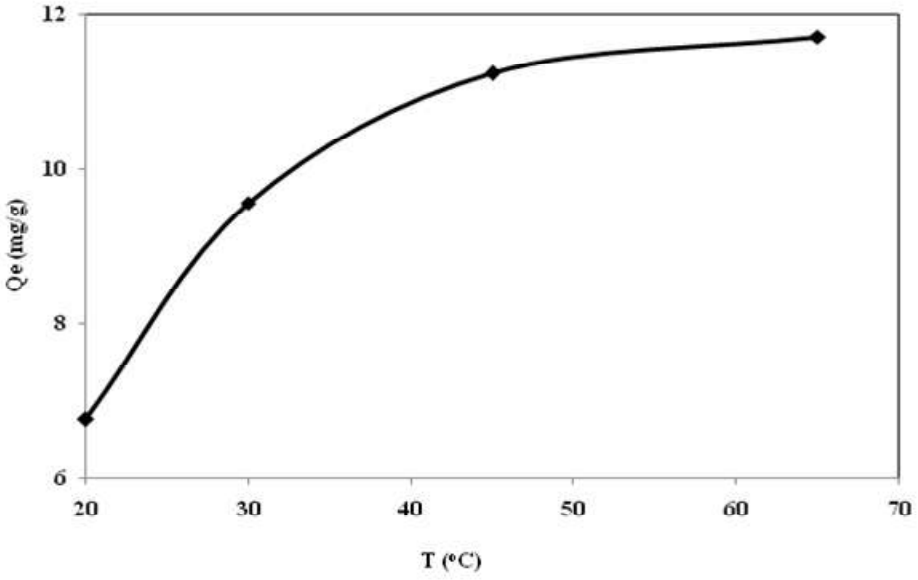

Fig. 4: Effect of temperature

Adsorption isotherms

The capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which are usually the ratio, at equilibrium between the quantity adsorbed and that of the unadsorbed in solution at fixed temperature. The Freundlich and Langmuir isotherm models are the most frequently employed models. In this work both, models were used to describe the relationship between the amount of phenol and its equilibrium concentrations. Standard procedures used by various authors (Mahvi *et al.*, 2004; Rengaraj *et al*, 2002) were employed in the use of these isotherm models.
The general form of Freundlich isotherm is:

$$q_e = K_f C_e^{\frac{1}{n}} \qquad (2)$$

where K_f (mg/g) stands for adsorption capacity and *n* for adsorption intensity. The logarithmic form of Eq. (2) is:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (3)$$

Where: qe is the equilibrium solid-phase concentration (mg/g), Ce is the equilibrium liquid-phase concentration (mg/L), and K and 1/n are the Freundlich constants of which K is the adsorption capacity (mg/g) and 1/n is the intensity of adsorption The constants (K and 1/n) obtained from the intercept and slope, respectively, and determined from the intercept and slope, respectively of linear plot of log q_e vs. log Ce.
The Langmuir isotherm is represented in the following equation:

$$q_e = \frac{q_{max}\, bC_e}{1 + bC_e} \qquad (4)$$

Where: q_{max} (mg/g) and b (L/mg) are the Langmuir constants. These constants evaluated by the intercept and slope of the linear plot of the experimental data of $1/q_{max}$ vs. 1/C (Mahvi *et al.*, 2004).

Table 1 shows the values of Langmuir and Freundlich constants. The higher regression values showed that the equilibrium data for phenol fitted well to both the Langmuir and Freundlich isotherms in the studied concentration ranges. Based on the correlation coefficients (R^2), the equilibrium data was slightly better fitted in the Langmuir than the Freundlich adsorption isotherm (Table 1).

Table 1: Parameters of Freundlich and Langmuir isotherm models

	Freundlich			**Langmuir**		**Separation Factor**
K (mg/g)	1/n (mg/L)	R^2	Q_e (mg/g)	b (L/mg)	R^2	0.52
0.467	0.7234	0.9869	16.5	0.0184	0.9997	

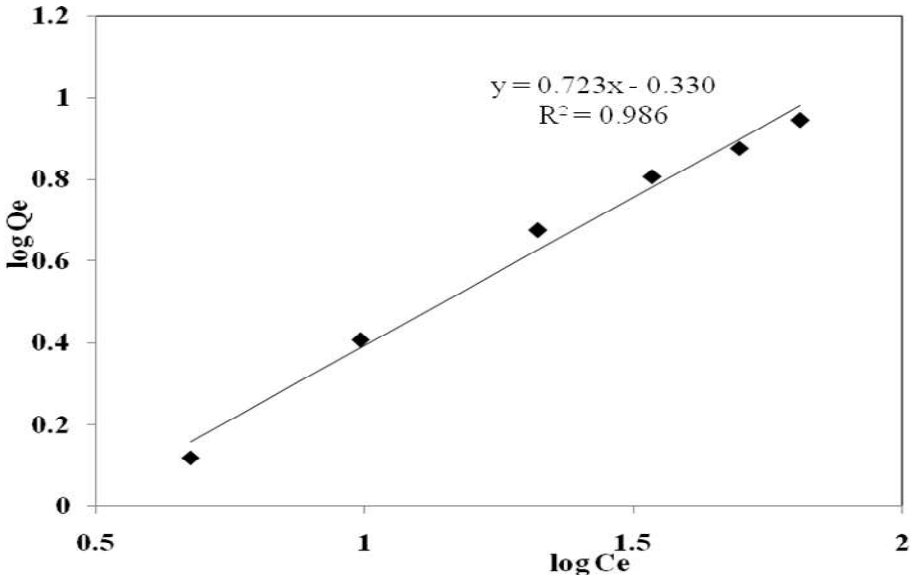

Fig. 5: Freundlich isotherm for phenol adsorption using chicken feathers

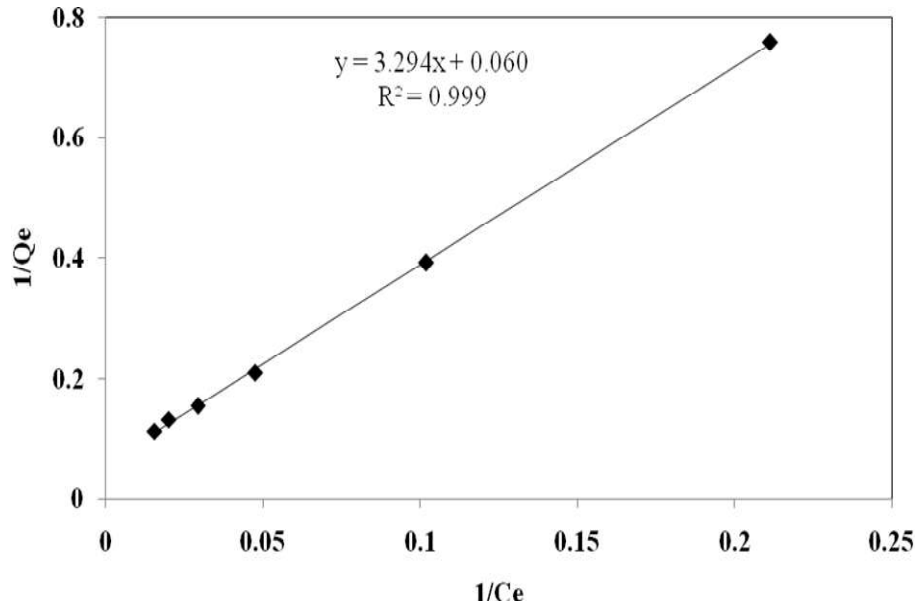

Fig. 6: Langmuir isotherm for phenol adsorption using chicken feathers

The adsorption intensity, 'n' was found to be 1.38 for chicken feathers. It was observed that the n-value satisfies the condition(s) of heterogeneity, i.e., $1< n < 10$ as well as $0 < 1/n < 1$. A relatively lower 'b' value (< 0.03) implies low surface energy in the system, thus indicating a probable stronger bonding between phenol and sorbent (Aksu and Yener, 2001). In fact, fairly low to moderate 'b' values have been reported in many of the sorbent-phenol systems, involving palm-seed-coat, activated-carbon, bentonite, and rice husk (Banat *et al*., 2000, Rengaraj *et al.*, 2002; Mahvi *et al*., 2004;).

The Langmuir model makes several assumptions, such as monolayer coverage and constant adsorption energy while the Freundlich equation deals with heterogeneous surface adsorption. The applicability of both Langmuir and Freundlich isotherms to the chicken feathers implies that both monolayer adsorption and heterogeneous surface conditions exist under the experimental conditions used. This observation is not rare as similar findings have been reported before (Aksu and Gonen, 2003; Mohd Din *et al*., 2008, Vazquez *et al*., 2007, Annadurai *et al*., 2002). This phenomenon can be further explained by understanding the surface chemistry of chicken feathers used in this study. The presence of active functional groups with different intensity and non-uniform distribution may cause differences in the energy level of the active sites available on the chicken feather surface thus affecting its adsorption power. Active sites with higher energy level tend to form hetero layer phenolic compounds coverage with robust support from strong chemical bonding whilst active sites with lower energy level will induce monolayer coverage due to electrostatic forces (Mandi *et al*., 2009). The essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called the equilibrium parameter, R_L, defined as:

$$R_L = \frac{1}{1 + aC_o} \qquad (5)$$

where b is the Langmuir constant, C_0 is the initial phenolic compounds concentration (g/L) and R_L values indicate the type of isotherm to be irreversible (R_L =0), favorable ($0< R_L <1$), linear (R_L =1), or unfavorable (R_L >1) (McKay *et al*.,1987; Ho *et al*., 2002). The results show that the adsorption of phenol onto chicken feathers is favorable and has an R_L value (0.52) between 0 and 1 (Table 1). The

comparison of maximum monolayer adsorption capacity of phenol onto various chicken feathers is given in Table 2. The maximum adsorption capacity values listed in Table 2 show that chicken feathers, without any activation, have a lower capacity for phenol uptake to that of acacia bark powder but an approximately equal capacity to that of activated carbon and marine sea weed. It is evident from Table 2 that chicken feathers adsorption capacity is better than that of other potential adsorbents such as bentonite, tendu leaf and ostrich feathers. Chicken feathers, therefore, show promise for the removal of phenol from aqueous solutions

Table 2: The maximum adsorption capacity (Qm) of various adsorbents

Adsorbent	Q_m (mg/g)	Temperature /^{0}C	Reference
Natural clay	15	23	Djebbar *et al*, 2012
Tendu leaf	7.69	25	Nagda *et al.*, 2007
Ostrich feather	2.16	30	Manshouri *et al.*, 2012
Sea weed	16.8	30	Navarro *et al.*, 2008
Activated carbon	17.39	25	Abdulkarim *et al.*, 2002
Rice husk ash	15.25	25	Mbui *et al.*, 2002
Acacia bark powder	94.33	25	Navada, 2011
Bentonine	1.7	25	Banat *et al.*, 2000
Chicken feathers	16.5	30	Present study

Conclusion

Chicken feathers, a residue released in a substantial amount in the poultry sector, were used as an adsorbent. The material under consideration is not only economical but is a waste product. Hence, its use as an adsorbent would on one hand solves the problem of its disposal and on other hand provides an effective adsorbent for the treatment of phenolic wastewaters. Results from adsorption studies revealed that the adsorption capacity of the sorbent was temperature dependent showing an increase in phenol removal efficiency with an increase in temperature. From the results, it was observed that by increasing the

amount of adsorbent, the efficiency of removal of phenol would be increased owing to a corresponding increase in adsorption sites. The equilibrium time for phenol removal was found to be 24 h. The experimental data were well represented by the Freundlich (R^2 = 0.9869; K = 0.467 mg/g; n = 1.38 L/mg) and the Langmuir (R^2 = 0.9997; Q_e = 16.5 mg/g; b = 0.0184 L/mg) isotherms with data slightly better fitted in the Langmuir than the Freundlich isotherm model.

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