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Low cost biosorbent for the removal of Cu (II) from aqueous solution

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ABSTRACT

In developing countries where cost is often an important factor, many studies were done to determine the effectiveness and reliable factors in removing heavy metals from waste waters using low cost adsorbent. Thus, this study was focused on hen egg shell as an alternative adsorbent in order to remove copper metal ion. Batch experiments were conducted to determine the factors affecting adsorption of copper. The operating variables studied were initial concentrations, pH, biosorbent dosage and biosorbent particle size. Equilibrium isotherm data were analyzed using the Langmuir, Freundlich and Redlich-Peterson isotherms. The Freundlich model yields a much better fit than the other two models. In order to investigate the mechanism of sorption, kinetic data were modelled using the pseudo- first-order and pseudo-second-order equation was the best applicable model to describe the sorption process. © 2010 Trade Science Inc. - INDIA

KEYWORDS

Eggshell powder;
Biosorption;
Isotherms;
Kinetic studies;
Heavy metals.

INTRODUCTION

Heavy metals are important environmental pollutants threatening the health of human populations and natural ecosystems. Metal contamination is a persistent problem in many contaminated soils. The most commonly occurring metals are Cd, Cu, Ni, Pb, Cr and Hg. The potential sources of heavy metals are Mining, Metallurgical, electroplating, battery manufacturing and Petrochemical industries. The presence of metals in ground water can also pose a significant threat to human health and ecological systems^[1-3].

Removal of heavy metals from waste water is usually achieved by physical and chemical processes which include precipitation, coagulation, membrane separa-

tion, ion simple design with a sludge free environment and can involve low investment in terms of both initial cost and land required. Usage of activated carbon is recognized as highly effective adsorbent in removing heavy metals but it consist high operation cost. However, efforts have been done to develop and improvise new adsorbent as alternative to activated carbon. In recent years, a number of adsorption materials, such as rice husk, coconut husk, sugar industry waste, red mud, green algae and saw dust were used in heavy metal removal from waste waters^[4,5].

In this study, egg shell is used as an adsorbent to remove the copper metal ion in waste water. Experimental parameters affecting biosorption process such as pH, contact time, biomass dosage and temperature

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were studied. The equilibrium biosorption data were evaluated by Langmuir, Freundlich and Redlich Peterson isotherm models. The biosorption mechanism was also investigated in terms of kinetics.

EXPERIMENTAL PROCEDURE

Preparation of eggshell powder for biosorbent

The hen *eggshells* used in the present study were collected from the college of Engineering hostels, Andhra University, Visakhapatnam. The collected hen egg shells were washed with deionized water several times to remove dirt particles. The washing process was continued till the wash water contains no dirt. The washed egg shells were then completely dried in sunlight for 10 days. The resulting product was directly used as biosorbent. The dried egg shells were then powdered using domestic mixer. In the present study the powdered materials in the range of 75-283.5 μ m. average particle size were then directly used as biosorbent without any pretreatment.

Preparation of metal solutions

Copper solutions of desired concentration have been prepared by dissolving the appropriate amount of $\text{CuSO}_4 \cdot 8\text{H}_2\text{O}$ in distilled water. All chemicals used in this study were of analytical grade.

Batch biosorption procedure

Sorption experiments were carried out using batch method. In order to optimize the experimental conditions, the batch studies were performed for different metal concentrations (20-100mg/l), contact times (1-180min), pH (2-6), biosorbent size (75- 218 μ m) and biosorbent dosage from (0.1-0.5gm). The solutions (30ml of 20mg/l) including the metal ions and biosorbent were shaken during optimum contact time in an orbital shaker at 120 rpm. After the contents of the flask were filtered through 0.2 μ m filters, the metal concentration of the filtrate was analyzed using Atomic Absorption Spectrophotometer (GBC Avanta Ver 1.32, Australia) at a wavelength 228.8nm for cadmium metal.

The biosorption percent was calculated as follows:

$$\% \text{ Biosorption} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

Where C_i and C_f are the initial and final concentrations

respectively.

The amount of sorption at equilibrium, Q (mg g^{-1}), was calculated by:

$$Q = (C_o - C_f) \times \frac{V}{M} \quad (2)$$

Where Q is the metal uptake (mg/g); C_o and C_f are the initial and equilibrium metal concentrations in the solution (mg/L), respectively; V is the solution volume (L); and M is the mass of biosorbent (g).

RESULTS AND DISCUSSION

The influence of several operating conditions such as sorbent dosage, initial metal ion concentration, contact time and solution pH on the sorption capacity was investigated.

Effect of contact time

Time course profiles for the biosorption of copper from each metal solution of 20 mg/L are shown in Figure 1. The data obtained from the biosorption of cadmium ions on the *eggshell powder* showed that a contact time of 60 min was required to achieve an optimum adsorption and there was no significant change in concentration of the metal ion with further increase in contact time. Therefore, the uptake and unadsorbed copper concentration at the end of 60 min are given as the equilibrium values, q_{eq} (mg/g) and C_{eq} (mg/L). For further studies of biosorption with other variable parameters, with this *eggshell powder* as biosorbent, this optimum time of 60 min has been chosen for contact period.

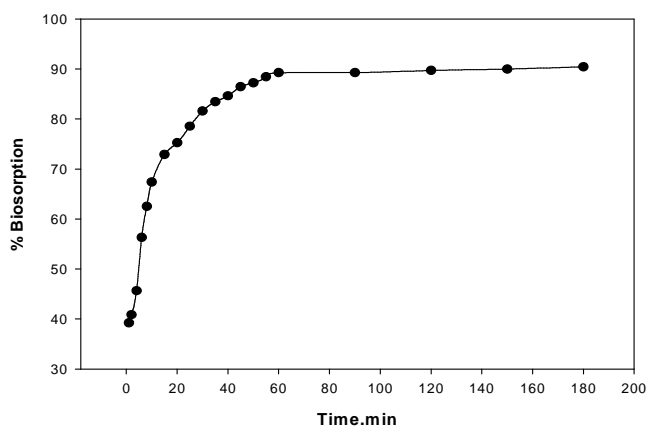


Figure 1 : Effect of contact time on biosorption of copper by eggshell powder for 20 mg/L of metal and 0.1g/30ml of biomass concentration

Effect of initial metal ion concentration

Experiments were undertaken to study the effect of the initial metal ion concentration on kinetics of copper removal from the solution. The results obtained were shown in Figure 2 & 3. The obtained curves show that the metal uptake increases with increase in initial concentration of metal ion while the percentage biosorption of copper decreases with an increase in initial metal ion concentration. The increase of metal uptake is a result of the increase in the driving forces i.e. concentration gradient, with an increase in the initial copper ion concentration (from 20 to 100 mg/L). However, the percentage biosorption of copper ions on *eggshell powder* was decreased from 89.25 to 74.84%. Though an increase in metal uptake was observed, the decrease in percentage biosorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percentage biosorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of copper displays an opposite trend. At lower concentrations, all copper ions present in solution could interact with the binding sites

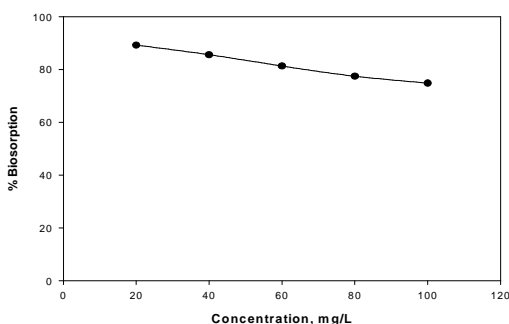


Figure 2 : Effect of initial metal ion concentration on the biosorption of copper by eggshell powder at 0.1g/30ml of biomass concentration.

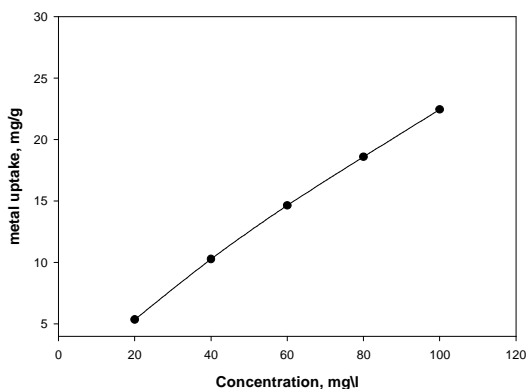


Figure 3 : Effect of initial metal ion concentration on the metal uptake for 0.1g/30ml biosorbent concentration.

and thus the percentage biosorption was higher than those at higher initial copper and cadmium ion concentrations. At higher concentrations, lower biosorption yield is due to the saturation of biosorption sites. As a result, diluting the wastewaters containing high metal ion concentrations can increase the purification yield.

Influence of pH

The effect of solution pH on the amount of mercury sorbed was studied by varying the initial pH under constant process parameters at equilibrium conditions. From Figure 4, it was observed that the sorption was strongly pH-dependent.

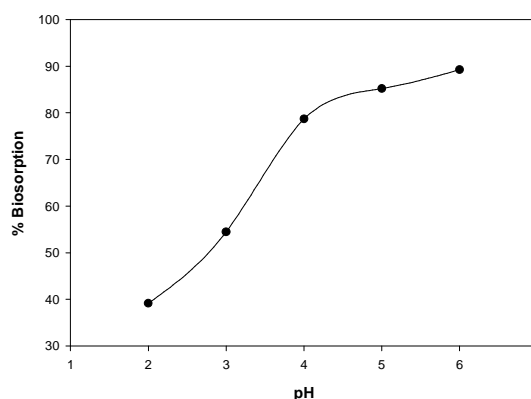


Figure 4 : Effect of pH on copper biosorption by eggshell powder for 20 mg/L of metal and 0.1g/30ml of biomass concentration

It is well known that the pH of the medium affects the solubility of metal ions and the concentration of the counter ions, on the functional groups of the biomass cell walls. Thus pH is an important parameter on biosorption of metal ions from aqueous solution since it is responsible for protonation of metal binding sites, calcium carbonate solubility and metal specification in the solution. It was found that copper and cadmium uptake by eggshells was a function of solution pH. As shown in Figure 4, the uptake of free ionic cadmium depends on pH. The biosorption of metallic ion observed to increase with increase in pH (Figure 4). The effect of pH studied at room temperature ($30 \pm 1^\circ\text{C}$) at an initial metal ion concentration 20 mg/L. This increase in pH resulted in an increase of k (rate constant).

The equilibrium sorption capacity was higher at pH 6 and it was lower at low pH values. The effect of pH can be explained by ion exchange mechanism of sorption in which carbonate groups that have cation-ex-

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change properties play the important role, at lower pH values cadmium removal was inhibited possibly as a result of competition between Hydrogen and metal ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force.

Effect of biosorbent dosage

The sorption of copper by hen egg shell sorbent was studied by changing the quantity of sorbent in the test solution while maintaining the initial metal ions concentration (20 mgL⁻¹), temperature (20 °C), stirring speed (120 rpm), contact time (60 min), and pH (pH 5) constant. The effect of sorbent dosage on the amount of copper sorbed at equilibrium is shown in Figure 5. The biosorption plot shows an increase in % biosorption with an increase in biosorbent dosage. This is because of the availability of more binding sites for complexation of metal ions.

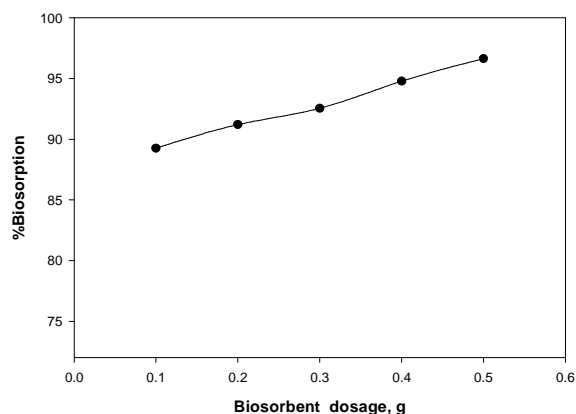


Figure 5 : Effect of eggshell powder dosage on biosorption of copper for 20mg/L of metal concentration

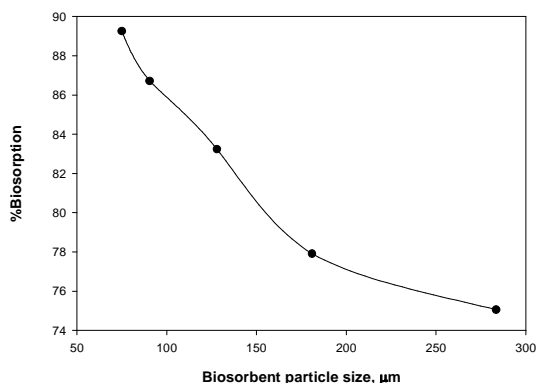


Figure 6 : Effect of eggshell powder particle size on adsorption of copper for 20mg/L of metal and 0.1g/30ml of adsorbent concentration

Effect of biosorbent particle size

Fixing the initial concentration of solution at 20 mg/L, pH 6, the fixed volume of 30 ml solution is allowed for 60 min with 0.1 g each of the varied size of particles of biosorbent ranging from 75 to 283.5 μm, the plot (Figure 6) drawn for the variation of the percentage biosorption against particle size, shows that with increase in particle size the biosorption decreases. This is due to less surface area available with increased particle size, thus reducing the biosorption.

Sorption equilibrium

In order to optimize the design of a sorption system to remove metal ions from solutions, it is important to establish the most appropriate correlation for the equilibrium curve. Experimental data were fitted to the well-known and widely applied isotherm models of Langmuir, Freundlich and Redlich Peterson. The linear equations are given below:

Langmuir Isotherm Equation:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{bq_{max}} + \frac{1}{q_{max}}C_{eq} \quad (3)$$

Freundlich Isotherm Equation:

$$\log q_{eq} = \log K_f + m \log C_{eq} \quad (4)$$

Redlich-Peterson Equation:

$$\ln \left(A \frac{C_{eq}}{q_{eq}} - 1 \right) = g \ln C_{eq} + \ln B \quad (5)$$

The linearized Langmuir, Freundlich and Redlich-Peterson isotherms obtained at room temperature are shown in Figure 7

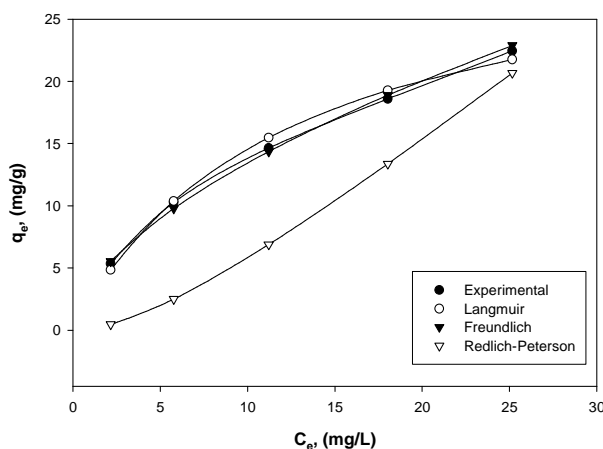


Figure 7 : Equilibrium curves for copper on to eggshell powder.

From Langmuir isotherm, the biosorption affinity constant (b) and maximum capacity (q_{\max}) of the ions copper to form a complete monolayer on to the surface of the *eggshell powder* was estimated as 0.083 l/mg, 32.02 mg/g respectively.

For Freundlich isotherm the constants related to the biosorption coefficient (K_f) and intensity (m) were 3.571, 0.5759 for copper.

From Redlich-Peterson isotherm the constants A (L/mg), B (L/mg) and Redlich-Peterson isotherm exponent (g) were 1.145, 8.953 and -0.9686 for copper.

The correlation coefficients obtained from the Langmuir, Freundlich and Redlich-Peterson isotherm models were 0.983, 0.9962 and 0.2937 for copper respectively. Freundlich equation was more suitable for the experimental data of copper. A comparison of the maximum capacity, q_{\max} , of *eggshell powder* with other adsorbents was given in TABLE 1. The biosorbent capacity of *eggshell powder* was relatively high when compared with other adsorbents. Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups and surface area.

TABLE 1 : Comparison of the biosorption capacity of present work for Copper metal with those reported in the literature.

Biosorbent	Biosorption		Reference
	pH	capacity (mg/g)	
Modified bark	4.5	1.04	39
Modified tannin	4.5	1.43	10
Granular biomass	5.5	55	11
Olive stone waste	5.5	0.002025	12
Fly ash	2-9	1.38	13
Marine green macro alga	6.0	6.12	14
Grape stalk waste	5.5	10.10445	15
Papaya wood	5.0	0.49	16
Ascophyllum nodosum	4.5	22.58	17
Pseudomonas sp.	4.0	163.93	18
Activated sludge	5.5	31.775	19
Ulva fasciata sp.	5.0	26.88	9
Hen egg shell	6	32.02	Present study

Biosorption kinetics

Kinetics is one of the major parameters to evaluate biosorption dynamics and the kinetic constants can be used to optimize the residence time of a biosorption process. In order to examine the controlling mecha-

nism of the biosorption process, kinetic models are used to test the experimental data. In this study, the equilibrium data were analyzed using two simplest kinetic models, pseudofirst-order and pseudo-second-order model.

The linear form of the pseudo-first-order rate equation^[6] is given as

$$\log(q_{\text{eq}} - q) = \log q_{\text{eq}} - \frac{K_1}{2.303} t \quad (6)$$

Where q_{eq} and q (mg/g) are the amounts of the metal ions sorbed at equilibrium (mg/g) and t (min), respectively and K_1 is the rate constant of the equation (min^{-1}). The biosorption rate constants (K_1) can be determined experimentally by plotting (Figure 8) of $\log(q_{\text{eq}} - q)$ versus time was made for *eggshell powder* for initial copper concentration, 20 mg/L. The intercept of the above plot should equal to $\log q_{\text{eq}}$. However, if q_{eq} from intercept does not equal to the equilibrium copper uptake then the reaction is not likely to be first order, even this plot has high correlation coefficient with the experimental data. Correlation coefficients were found to be 0.9793 for copper. Based on these results it can be concluded that the biosorption of copper on to *egg shell powder* does not fit a pseudo-first-order kinetic model. Therefore, the pseudo-first-order model is not suitable for modeling the biosorption of copper on to *eggshell powder*. Experimental data were also tested by the pseudo-second-order^[7] kinetic model which is given in the following form

$$\frac{t}{q} = \frac{1}{K_{II} q_{\text{eq}}^2} + \frac{1}{q_{\text{eq}}} t \quad (7)$$

Where t is the contact time (min), q_{eq} (mg/g) and q (mg/g) is the amount of metal adsorbed at equilibrium and at any time, t . This model is more likely to predict kinetic behavior of biosorption with chemical sorption being the rate-controlling step. The linear plots of t/q versus t for the pseudo-second-order model at 200°C were shown in Figure 9. The R^2 values are very high 0.9978. In addition, the theoretical $q_{\text{e,cal}}$ values are closer to the experimental $q_{\text{e,exp}}$ values. In the view of these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the biosorption of copper onto egg shell in contrast to the pseudo-first-order model. This conclusion is in agreement with literature^[8,9].

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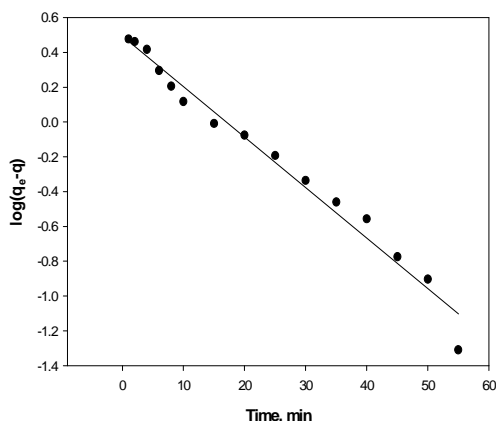


Figure 8 : Pseudo first order adsorption of copper by eggshell powder for 20mg/L of metal and 0.1g/30ml of biomass concentration.

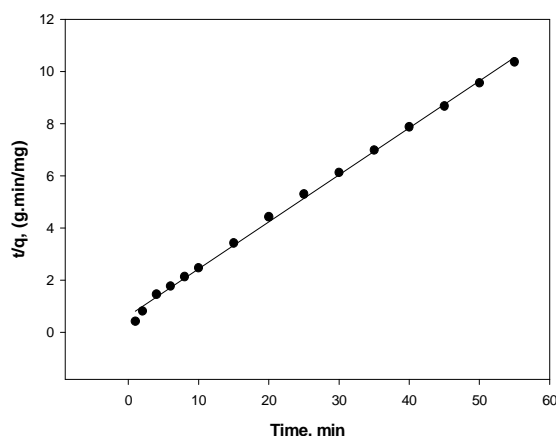


Figure 9 : Pseudo second order adsorption of copper by eggshell powder for 20mg/L of metal and 0.1g/30ml of biomass concentration

CONCLUSIONS

The present work shows that hen egg shell can be used as a sorbent for the removal of Cu(II) ions from aqueous media. Experimental data indicated that the sorption capacity was dependent on operating variables such as sorbent dosage, sorbent size, solution pH, contact time, and initial metal concentration. The process was strongly pH-dependent. Kinetic measurements showed that the sorption process was uniform and rapid. Modeling of sorption kinetics showed good agreement of experimental data with the pseudo-second-order kinetic equation for different initial metal concentrations. The Freundlich model yielded a much better fit than the other models. The maximum sorption capacity was determined to be 32.02mgg⁻¹.

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