Removal of Cu(II) from Water by Adsorption on Chicken Eggshell

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***Abstract*— The use of chicken eggshell as adsorbent for the removal of copper (II) from water was investigated in the present study. The effects of different parameters such as pH of the solution, agitation rate and contact time on the adsorption process were studied. The optimum conditions for Cu(II) adsorption by chicken eggshell were found to be at pH 7 with the agitation rate of 350 rpm. Equilibrium data were analyzed by Langmuir and Freundlich isotherm models and the data were fitted well to Freundlich isotherm model. The adsorption kinetics data were evaluated by the pseudo-first-order and pseudo-second-order models. The data were well correlated with the pseudo-second-order kinetic model, which indicated that chemisorption processes could be the rate-limiting step in the adsorption process. The results show that chicken eggshell has the potential to be used as biosorbent for adsorption of copper (II) from water.**

***Index Term*— Copper, chicken eggshell, adsorption isotherm, kinetic model**

I. INTRODUCTION

THE release of toxic substances in the wastewater from industrial activities such as mining, metal processing, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, etc. may cause serious effects on the environment and human health. It is because the toxic substances have a tendency to accumulate in the soil, sea water, fresh water and sediments due to their high dispersion from where they enter into the food chain [1]. Copper is one of the toxic heavy metals discharged into the environment due to industrial operations, anthropogenic activities and natural source of copper exposure [1]. In order to have a pollution-free environment, the toxic heavy metals should be removed from wastewater before its disposal.

Removal of toxic heavy metals from industrial wastewater has been practiced for several decades by the conventional physico-chemical removal methods, such as chemical precipitation, electroplating, membrane separation, evaporation and resin ionic exchange. However, these methods are usually are found to be inefficient and expensive, especially when treating wastewater with low concentration of heavy metals [2]–[4]. Therefore, alternative method has been attempted using low cost materials such as chicken eggshell to remove heavy metals by a simple adsorption process. Chicken eggshell can be used to adsorb heavy metal in wastewater due to its calcium carbonate content which is responsible for metal adsorption [5]. This alternative method will not produce chemical sludge, hence no secondary pollution and it is more efficient and easy to operate compared to other methods [1].

The objectives of this project are to study the effects of different operating parameters including pH, agitation rate and contact time on the adsorption efficiency of Cu(II) from water by chicken eggshell. Besides, the present study is also aimed to evaluate the equilibrium of adsorption process using Langmuir and Freundlich isotherms. Meanwhile, the kinetics of Cu(II) adsorption on chicken eggshell will also be analyzed using different models including the pseudo-first-order and pseudo-second-order kinetic models.

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II. MATERIALS AND METHODS

A. Materials

Copper sulfate ($CuSO_4$) was used for the preparation of stock standard solutions of Cu(II) in distilled water. For pH adjustment throughout the experiment, 0.1 M hydrochloric acid (HCl) and/or 0.1 M sodium hydroxide (NaOH) were used as necessary. All chemical used in the present study were of analytical grade from Merck, Germany. Atomic adsorption spectrometer (AAS Model HGA 850, USA) was used to measure the Cu(II) concentration.

B. Preparation of Adsorbent

The chicken eggshells were collected from kitchen waste and washed by deionized water for several times to remove the dirt particles. The eggshells were then dried overnight in the oven at 40°C. The dried eggshells were ground into small particles and stored in an airtight container for future use.

C. Effect of pH on Cu(II) Adsorption

The effect of solution pH on adsorption of Cu(II) was studied by mixing 0.5 g of adsorbent with 200 ml of copper solution of 50 mg/L concentration at different pH value (4 – 8) under 30°C. The pH was adjusted with 0.1 M NaOH or 0.1 M HCl solutions and measured by pH meter. Agitation was made at a constant stirring speed of 150 rpm for 180 minutes. The remaining concentration of Cu(II) after adsorption was measured using atomic adsorption spectrometer (AAS).

D. Effect of Agitation Rate on Cu(II) Adsorption

The effect of agitation rate on Cu(II) adsorption was investigated by adding 0.5 g of adsorbent into 200 ml of copper solution of 50 mg/L concentration at optimum pH determined previously. The solution was agitated using water bath shaker at different stirring rates (150 – 350 rpm) under constant temperature of 30°C. The remaining concentration of Cu(II) after adsorption was measured using AAS.

E. Equilibrium Studies of Cu(II) Adsorption

A series of solutions containing different initial concentrations of Cu(II) ions (in the range of 50 – 350 mg/L) was prepared and employed for the batch adsorption studies at 30°C to check the applicability of the Langmuir and Freundlich adsorption isotherms under optimum conditions obtained previously. The remaining concentration of Cu(II) after adsorption was measured using AAS and the amount of adsorption at equilibrium, q_e (mg/g) was calculated by:

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

where C_0 and C_e (mg/L) are the liquid-phase concentration of copper at initial and equilibrium, respectively, V (L) is the volume of the solution and W (g) is the mass of dry adsorbent used. The adsorption efficiency of Cu(II) can be calculated as:

$$\text{Adsorption percentage} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

F. Kinetics Studies of Cu(II) Adsorption

The kinetics studies of Cu(II) adsorption were carried out by batch adsorption at optimum conditions evaluated previously. The samples were taken at preset time intervals up to 180 minutes under temperature of 30°C. The remaining concentration of Cu(II) after adsorption was measured using AAS and the amount of adsorption at time t, q_t (mg/g) was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (3)$$

where C_t (mg/L) is the liquid-phase concentrations of Cu(II) solutions at any time, t.

III. RESULTS AND DISCUSSION

A. Effect of pH on Cu(II) Adsorption

Solution pH is one of the most important parameters controlling adsorption of heavy metals from aqueous solutions because wastewater from various sources will have different pH values. Therefore, in this study the effect of pH on removal of Cu(II) was examined in the pH range of 4 – 8. The concentration of Cu(II), the amount of chicken eggshells and contact time were kept constant at 50 mg/L, 0.5 g and 180 minutes, respectively.

Fig. 1 shows that the adsorption capacities of Cu(II) increased significantly as the pH increased from 4 – 7 and approached a plateau at pH range of 7 – 8. The adsorption capacities reached almost 100% at higher pH. At lower pH, little adsorption could be ascribed to the hydrogen ions competing with metal ions for adsorption site [6].

The effect of pH can be explained by ion-exchange mechanism of adsorption in which the important role is played by carbonate groups on the chicken eggshells that have cation-exchange properties. At lower pH values, copper adsorption was inhibited due to the competition between hydrogen and copper ions on the adsorption sites, which restricts the approach of metal cations. As the pH increased, the carbonate groups in chicken eggshells would be exposed, increasing the negative charges on the adsorbent surface, attracting the metal cations and allowing the adsorption onto the adsorbent surface [7].

B. Effect of Agitation Rate on Cu(II) Adsorption

Agitation rate plays an important role in the adsorption process and the effect of agitation speed on adsorption capacity of copper has been studied by varying the agitation speed from 150 – 350 rpm. The copper adsorption percentage at different agitation speeds by chicken eggshells is shown in Fig. 2.

It has been observed that the percentage of copper adsorption increased with increasing agitation speed due to the proper contact between the metal ions in solution and the adsorbents binding sites that promotes effective transfer of copper ions to the adsorbents sites. Results indicated that the Cu(II) adsorption by chicken eggshells reached almost 100% at 350 rpm. At lower speed, the adsorbent will accumulate at bottom and result in burial of various active sites under the above layers of adsorbent [8].

C. Analysis of Adsorption Isotherm

The equilibrium study is important for an adsorption process as it shows the capacity of the adsorbent and the adsorption isotherm is normally applied to describe the adsorption mechanism for the interaction of cations on the adsorbent surface. In the present study, experimental data were analyzed to examine the adsorption isotherm using Langmuir and Freundlich models. The Langmuir isotherm is applicable to monolayer adsorbate coverage on the adsorbent surface [9], whereas the Freundlich isotherm is an empirical model that considers heterogeneous adsorption on the adsorbent surface [10]. The linearized equations for the Langmuir and Freundlich isotherms are expressed as (4) and (5), respectively:

$$\frac{C_e}{q_e} = \left(\frac{1}{bq_m}\right) + \frac{C_e}{q_m} \tag{4}$$

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \tag{5}$$

where C_e is the adsorbate concentration at equilibrium (mg/L), q_e is the adsorption capacity at equilibrium (mg/g), b is the adsorption equilibrium constant (L/mg) related to the apparent energy of adsorption, q_m is the maximum adsorption capacity of absorbent (mg/g), n indicates the bond energies between metal ion and the adsorbent, and k_F (L/g) is related to bond strength [2].

The linear plots of Langmuir and Freundlich equations representing Cu(II) adsorption by the chicken eggshells are illustrated in Figs. 3 and 4. The adsorption constants of Langmuir and Freundlich equations and their correlation coefficients (R^2) are presented in Table I. The value of R^2 is a measure of the goodness-of-fit of experimental data on the isotherm models [2]. Results showed that the adsorption process by chicken eggshells was better represented by the Freundlich equation compared to the Langmuir isotherm, where the R^2 values were found to be 0.9818 and 0.7360, respectively. This indicated that the uptake of copper on chicken eggshells was happened through heterogeneous adsorption.

From Table I, the k_F constant of Freundlich isotherm, which expresses the selective uptake of copper and affinity of adsorbent was 13.8995 L/g, whereas the $1/n$ value was found to be 0.6473. Generally, the value of $1/n$ that is related to the distribution of site bonding energies is ranging between 0.2 – 0.7 [11]. If $1/n$ is higher than 1, it indicates that the surface areas of adsorbent covered by the metal ions increase, and the energies of adsorption will decrease [11].

D. Analysis of Adsorption Kinetics

The kinetic study of metal ion adsorption is important to give insight into the adsorption rate, provide information on the contact time required for considerable adsorption to take place and also the factors affecting or controlling the adsorption rate. The adsorption of Cu(II) by chicken eggshells at different contact time is shown in Fig. 5. The adsorption occurred rapidly at the first 15 minutes and almost 100% adsorption efficiency of Cu(II) was attained after 60 minutes.

In order to investigate the mechanism of Cu(II) adsorption by chicken eggshells and the potential rate-controlling steps, two of the most commonly used kinetic models, pseudo-first-order and pseudo-second-order kinetic models were employed to evaluate the adsorption of Cu(II). The linear form of equations for the pseudo-first-order and pseudo-second-order kinetic models can be represented by (6) and (7), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{7}$$

where q_t is the adsorption capacity at time t (mg/g), k_1 is the first-order reaction rate constant (L/min) and k_2 represents the second-order reaction rate constant (g/mg.min). The plots of pseudo-first-order and pseudo-second-order models are illustrated in Figs. 6 and 7, respectively. A comparison of the reaction rate constants and R^2 values estimated from the pseudo-first-order and second-order equations is presented in Table II.

From Table II, the R^2 value for the pseudo-second-order model was higher than the pseudo-first-order model. This showed that the adsorption of copper on chicken eggshells was well-fitted to the pseudo-second-order kinetics model compared to the first-order model. It can be concluded that the pseudo-second-order kinetics model provides a good correlation for the adsorption of Cu(II) on chicken eggshells and it also suggests that the chemisorption process could be the rate-limiting step in the adsorption process. Similar conclusion was also reported for the adsorption of heavy metal ions by other adsorbents such as modified groundnut husks, oil palm fibres, waste tea leaves and tree leaves waste [12].

IV. CONCLUSION

The removal of Cu(II) from water by using chicken eggshells has been experimented under several conditions such as at different pH, agitation rate and contact time. The optimum pH for copper adsorption was found at pH 7, whereas the optimum agitation rate was determined at 350 rpm. From the analysis of adsorption equilibrium, the correlation regression coefficients showed that the adsorption process was better defined by Freundlich equation. Results also indicated that adsorption kinetics of Cu(II) adsorption on chicken eggshells followed the pseudo-second-order kinetic model where the chemisorption process may be the rate-limiting step in the adsorption process. This study shows that chicken eggshells have high potential to be used as low-cost adsorbent for the removal of copper from water.

Since the metals uptake by chicken eggshells is highly dependant on the number of active binding sites or functional groups on the adsorbents, further research can be attempted to enhance the existing results by modifying the chicken eggshell adsorbents using acids or bases. As a result of chemical modification, it is expected that the number of active binding sites or functional groups on the adsorbents might be increased to improve the adsorption capacity of adsorbents.

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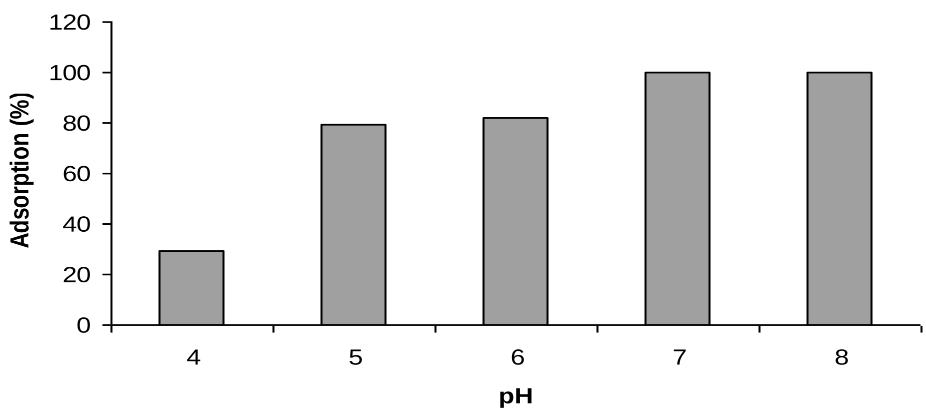

Fig. 1. Effect of pH on the adsorption of Cu(II) by chicken eggshells

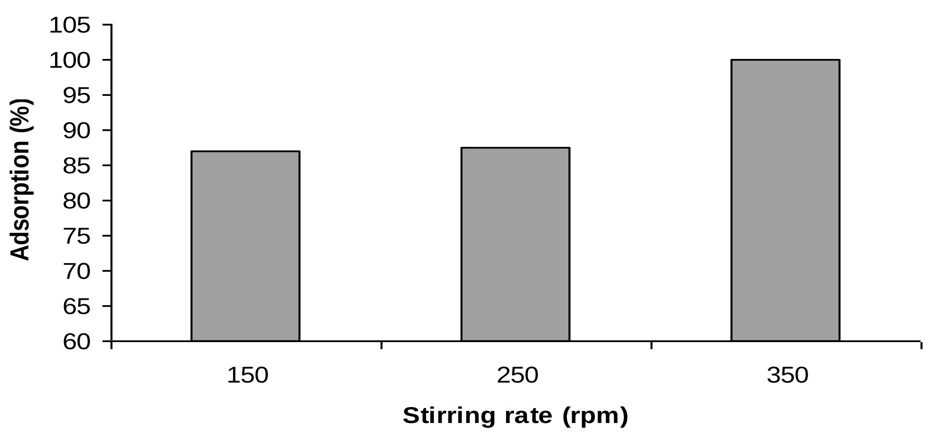

Fig. 2. Effect of stirring rate on the adsorption of Cu(II) by chicken eggshells

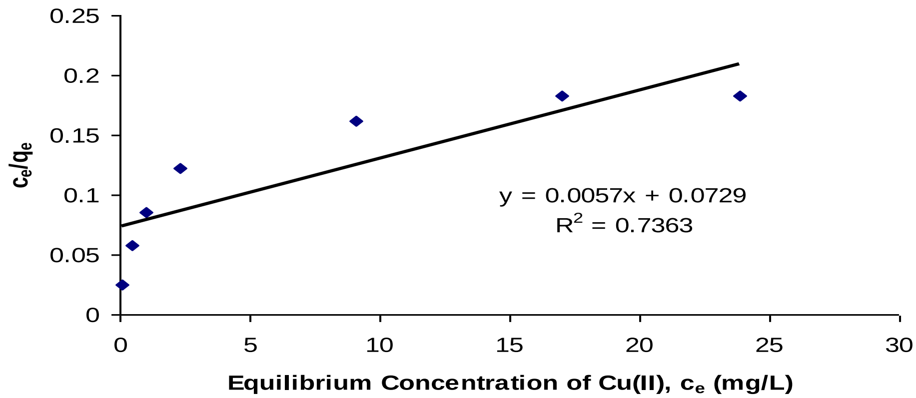

Fig. 3. Linear plot of Langmuir isotherm for the adsorption of Cu(II) by chicken eggshells

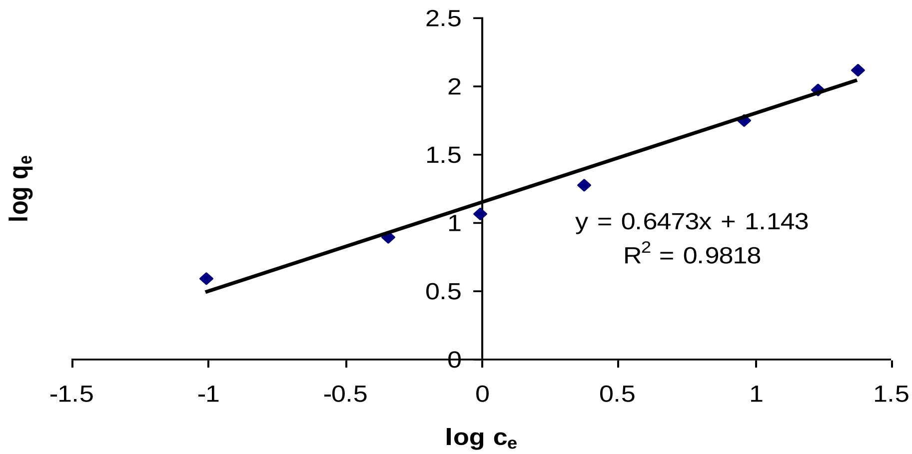

Fig. 4. Linear plot of Freundlich isotherm for the adsorption of Cu(II) by chicken eggshells

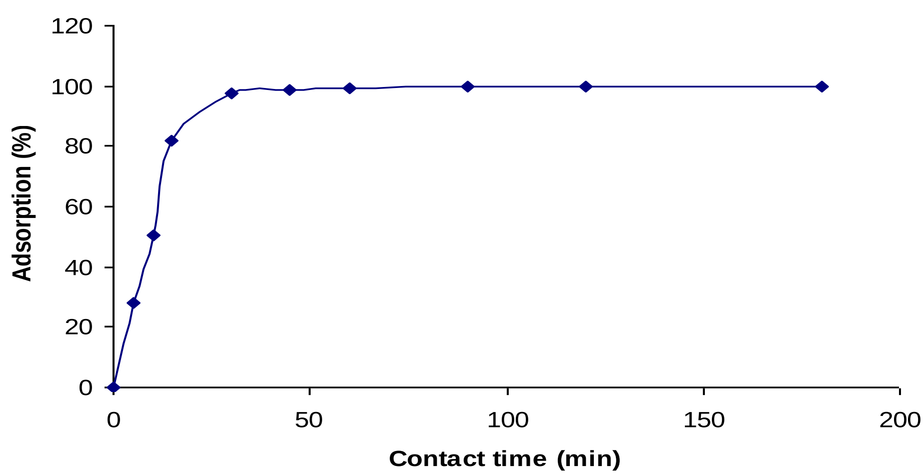

Fig. 5. Effect of contact time on the adsorption of Cu(II) by chicken eggshells

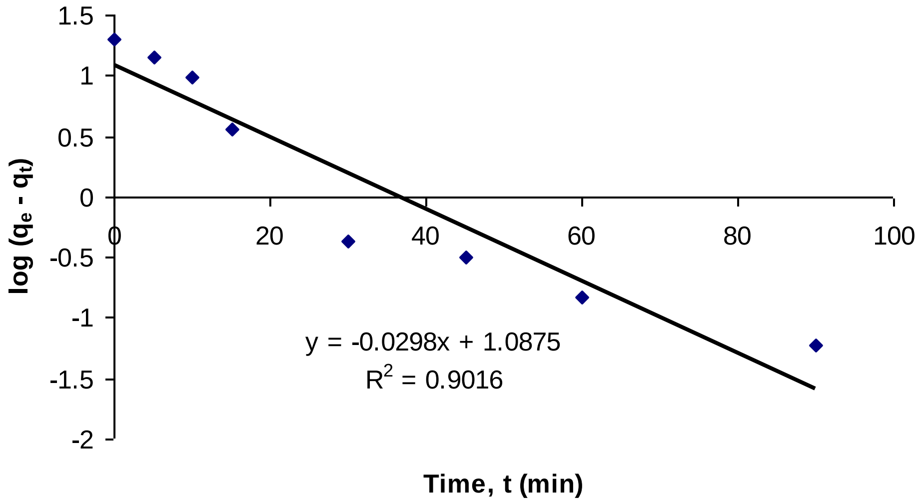

Fig. 6. Linear plot of pseudo-first-order kinetic model for the adsorption of Cu(II) by chicken eggshells

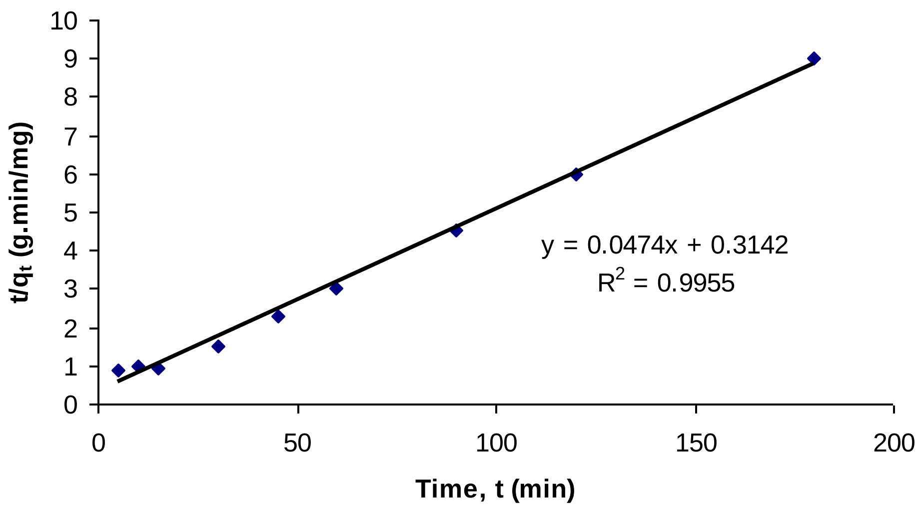

Fig. 7. Linear plot of pseudo-second-order kinetic model for the adsorption of Cu(II) by chicken eggshells

TABLE I
ISOTHERM PARAMETERS FOR THE ADSORPTION OF CU(II) BY CHICKEN EGGSHELLS

Langmuir isotherm			Freundlich isotherm		
R^2	q_m (mg/g)	b (L/mg)	R^2	$1/n$	k_F (mg/L)
0.7363	175.4386	0.0782	0.9818	0.6473	13.8995

TABLE II
PARAMETERS OF KINETIC MODELS FOR THE ADSORPTION OF CU(II) BY CHICKEN EGGSHELLS

Pseudo-first-order model		Pseudo-second-order model	
k_1 (L/min)	R^2	k_2 (g/mg.min)	R^2
0.0686	0.9016	0.00715	0.9955