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*Original Article*

# Removal of copper (II) ions from water by using chicken eggshell in fixed-bed columns

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## Abstract

The removal of Cu (II) ions from water by chicken eggshell powder adsorption was examined in a fixed-bed column. Kinetics data were satisfactorily described by a pseudo-second order chemisorption model. A 100% adsorption of Cu (II) ions at the initial copper concentration of 50 mg/L was obtained by using an eggshell amount of 8.0 g packed in the pilot-scale column with a height of 16 cm, and flow rate of 1.0 ml/min. Regarding co-adsorption with other metal ions, the Pb (II) ions reduced the adsorption of Cu (II) ions. However, the eggshell in fixed-bed column can remove Cu (II) ions from water by up to 83% in a mixed metal system. Then 0.5 M $BaCl_2$ with a flow rate of 0.5 mL/min can desorb about 60% of the Cu (II) ions. This process can be scaled up for the removal of heavy metal ions in actual wastewater treatment.

**Keywords**: copper, eggshell, fixed-bed column, adsorption, wastewater

## 1. Introduction

Heavy metals are an important type of environmental pollution. Without any treatment, the discharge of heavy metals causes concerns about community health, because this hazard component can contaminate the food chain (El-Sherif, Tolani, Ofosu, Mohamed, & Wanekaya, 2013). In industry, heavy metals are generated from the production processes. Although effluents are passed through the best treatment processes, still small contents can remain due to limitations of processing, and unfortunately contaminate the wastewaters. It is necessary to improve the wastewater treatment processes. The conventional physico-chemical methods used to remove metal ions include chemical precipitation, electroplating, membrane separation, evaporation, and resin ionic exchange (Kalyani, Rao, Saradhi, & Kumar, 2009). However, these methods are usually expensive. A cheaper process, such as adsorption, was found to be attractive not only when using synthesized materials (Chen & Chen, 2011; Chen *et al.*, 2020; Xiangxue, Xing, Jiaqi, & Hongtao, 2020) but also when using low-cost natural materials such as chicken eggshells (Rohaizar, Hadi, & Sien, 2013; Kristianto, Daulay, & Andreas, 2019), oyster shells (Wu, Chen, Clark, & Yu, 2014; Xu, Liu, Oh, Park, 2019), chestnut shells (Çetinkaya, Targan, Tirtom, 2018), Bornean oil palm shells (Chong, Chia, Ahmad, 2013), natural zeolite (Sabadash, Mylanyk, Matsuska, & Gumnitsky, 2017) and clay (Melnyk, Bessarab, Matko, & Malovanyy, 2015), to reduce contents of heavy metals. Moreover, this approach provides a good performance and is easier to operate compared to other alternatives.

Among the mentioned adsorbents, eggshells are a waste from cooking. We can get them free from restaurants or bakeries. The $CaCO_3$ species in an eggshell makes it suited for metal adsorption (Arunlertaree, Kaewsomboon, Kumsopa, Pokethitiyook, & Panyawathanakit, 2007; Tsai *et al.*, 2006). In this work, the adsorption of Cu (II) ions from aqueous solution by eggshells was examined using a fixed-bed column. The adsorption kinetics were studied. The conditions for Cu (II) ions adsorption and desorption as well as the effects of other two-valent metal ions namely Pb (II), Fe (II), Zn (II), and Mn (II) were also assessed.

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## 2. Materials and Methods

### 2.1 Preparation of adsorbent

The eggshells were washed with tap water several times and washed afterwards with distilled water. They were left to dry overnight in ambient air. The dried eggshells were milled to a particle size of 212 µm for the batch system and to 300-600 µm for the fixed-bed column. They were then dried at 105 ºC for 1 hour. The eggshell powder was stored in a desiccator at room temperature (~27 ºC) before use in the experiments.

### 2.2 Batch adsorption experiments

#### 2.2.1 Adsorption of Cu (II) ions

The batch experiment was preliminarily studied. The stock standard solutions of Cu (II) ions were prepared using $CuSO_4$. The initial Cu (II) ion concentrations varied within 5.0-50.0 mg/L. At room temperature, 50 mL of different Cu (II) ion solutions were mixed with 1.0 g of eggshell and stirred at 200 rpm. After due time, the adsorbent was filtered using a filter paper (No.5). The Cu (II) contents in the supernatant were determined by using an atomic absorption spectrometer, AAS (Perkin Elmer model 3110) using $\lambda_{Cu}$ = 324.8 nm. The amount of metal adsorbed by eggshell powder was calculated using the following equation (1):

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

Here $q_e$ is the metal uptake (mg/g); $C_0$ and $C_e$ are the initial and equilibrium metal concentrations in the solution, respectively (mg/L); V is the solution volume (L); and m is the mass of adsorbent (g).

#### 2.2.2 Adsorption kinetics

The kinetics of Cu (II) ion adsorption were determined using batch adsorption. The solution with 5 mg/L of Cu (II) ions was agitated with 1 g of eggshell powder at 200 rpm for 360 min. The remaining concentration of Cu (II) ions after adsorption was measured by AAS.

### 2.3 Fourier transform infrared spectroscopy

The ground eggshell powder was analyzed using Fourier-transform infrared spectrometer, FTIR (Bruker model Alpha). The eggshell powder was thoroughly mixed with KBr. The mixture was ground and then pressed with a special press to give a disk of standard diameter. The sample was scanned for IR spectrum in the range of 400–4000 $cm^{-1}$.

### 2.4 Fixed-bed column experiments

#### 2.4.1 Eggshell dose and flow rate for Cu (II) ion adsorption

A 100 mL sample of 50 mg/L Cu (II) ion solution was passed through the adsorbent (0.5-8 g) in a fixed-bed column (glass tube, i.d. of 1 cm) with a flow rate of 1.0 mL/min. The solution from the column was collected and analyzed every 10 min. The flow rates 1.0-3.0 mL/min were tested using the selected eggshell dosage. The adsorption efficiency of metals can be calculated from equation (2), as follows

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

#### 2.4.2 Cu (II) ion desorption

After the Cu (II) ion adsorption process had achieved 100% saturation, distilled water, NaCl, $BaCl_2$, and KCl were tested for desorbing Cu (II) ions out of the fixed-bed column. Among $Ca^{2+}$, $Mg^{2+}$, and $Ba^{2+}$ chloride species, the $BaCl_2$ was chosen for testing. This is because the size of $Ba^{2+}$ is larger than of $Ca^{2+}$ and $Mg^{2+}$ ions. Therefore the hydrated ionic radii of $Ba^{2+}$ tends to be smaller than that of the other ions, and be highly efficient for elution. A 100 mL of 0.5 M salt solution was passed through the column with the flow rate of 1.0 mL/min. The solution from the column was collected and analyzed every 10 min. A suitable eluent was selected, and different concentrations and flow rates were studied.

### 2.5 Effects of common ions

$Pb(NO_3)_2$, $FeSO_4$, $MnSO_4$, and $ZnSO_4$ were used to prepare stock standard solutions of Pb (II) ions, Fe (II) ions, Mn (II) ions, and Zn (II) ions, respectively. The adsorption of Cu (II) ions together with the other ions (100 mL of 50 mg/L metals solution, 8 g of eggshell, and flow rate of 1 ml/min) was studied using binary blends and all mixed metals solution. The solutions from the column were analyzed by AAS ($\lambda_{Pb}$ = 217 nm, $\lambda_{Fe}$ = 248.3 nm, $\lambda_{Mn}$ = 279.5 nm, $\lambda_{Zn}$ = 213.9 nm).

## 3. Results and Discussion

### 3.1 Batch adsorption of Cu (II) ions

#### 3.1.1 The contact time and initial concentration

As shown in Figure 1, the adsorption increases rapidly due to the availability of active sites on the adsorbent surface during the first stage. It can be attributed to the mutual attraction between the negatively charged surface of the adsorbent and positive metal ions. Afterwards, the adsorption rate slowed down and adsorbed amount leveled off, because the active sites became occupied and an equilibrium was reached (Elabbas *et al.*, 2016; Khoo & Esmaeili, 2018). The repulsive forces between the adsorbed and bulk metal ions, led to a slow-down in adsorption rate.

When considering the initial Cu (II) ion concentration, it can be noted that the rate of Cu (II) ion removal increased when the initial concentration was stepped up from 5 to 50 mg/L. The initial Cu (II) ion concentration at 50 mg/L gave the highest Cu (II) ion adsorption, which leveled to a constant when the contact time reached 180 min. Therefore, in this batch experiment, a contact time of 180 min was sufficient to reach an equilibrium. The eggshell can

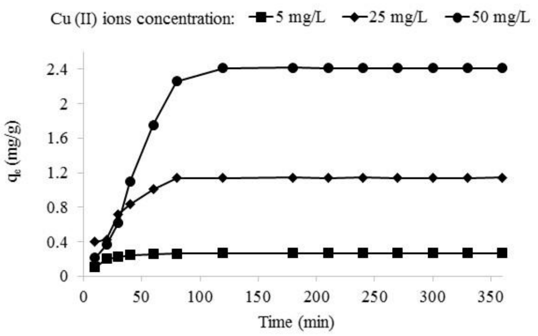


Figure 1. Effects of contact time and initial concentration on the adsorption of Cu (II) ions

adsorb Cu (II) ions maximally to 0.26, 1.14, and 2.42 mg/g for the initial concentrations of 5, 25, and 50 mg/L, respectively. The metal uptake did not change significantly at a low concentration. The further adsorption tests in a fixed-bed column are conducted with an initial Cu (II) ion concentration at 50 mg/L.

### 3.1.2 Adsorption kinetics

The mechanism of Cu (II) ion adsorption by eggshell powder and the potential rate-controlling steps were investigated with pseudo-first order and pseudo-second order kinetic models. The linear forms of the two models can be represented by equations (3) and (4), respectively.

$$\log\left(q_e - q_t\right) = \log q_e \frac{k_1}{2303} t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

Here $q_t$ is the adsorption capacity at time t (mg/g), $k_1$ is the first-order reaction rate constant ($min^{-1}$), and $k_2$ represents the second-order reaction rate constant (g/mg.min).

The plots linearizing pseudo-first order and pseudo-second order models are shown in Figure 2. It can be seen that the coefficient of determination ($R^2$) of the pseudo-first order kinetic model ($R^2$=0.7636, Figure 2(a)) is less than that obtained for the pseudo-second order kinetic model ($R^2$=0.9993, Figure 2(b)). It is clear that the adsorption of Cu (II) ions is well fit with the pseudo-second order kinetics model. This model describes the adsorption on the adsorbent as time-independent. The adsorption rate depends on the number of active sites on the surface of adsorbent. Similar results for the adsorption of Cu (II) ions have been reported in some prior studies (Ali, Ibrahim, & Madhloom, 2016; Rohaizar *et al.*, 2013). This suggests that chemisorption could be the rate-limiting step in the overall adsorption process.

### 3.2 FTIR analysis of eggshell powder

The eggshell powder was characterized by the FTIR technique. The most significant peak was observed at 1417 $cm^{-1}$, suggesting the presence of carbonate minerals within the

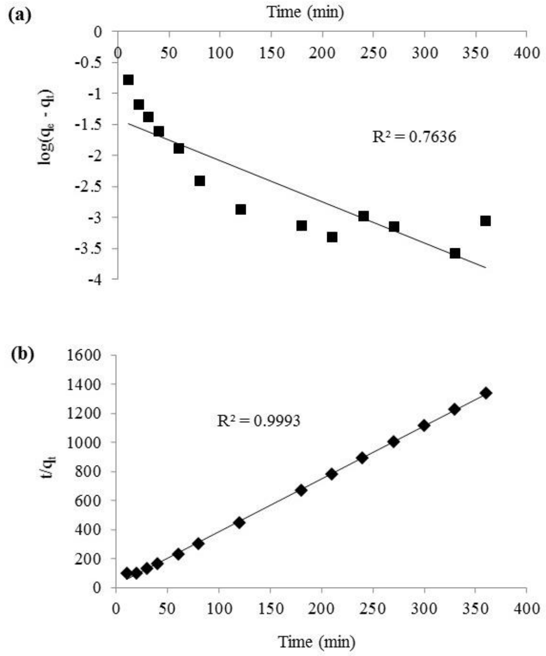


Figure 2. Test for Cu (II) adsorption kinetics model: (a) Pseudo-first order; and (b) Pseudo-second order

matrix. There are also two observable peaks at about 712 $cm^{-1}$ and 875 $cm^{-1}$, which are associated with in-plane and out-plane deformation modes, respectively, of the $CaCO_3$ molecules. The presence of amines and amides in the eggshell membrane was also found, exhibiting peaks at 3200–3500 $cm^{-1}$. The main functional groups of the eggshell powder before and after Cu (II) ion adsorption were not significantly changed.

### 3.3 Fixed-bed column adsorption of Cu (II) ions

The eggshell dose and flow rate were studied for the Cu (II) ions adsorption. Actually, a small particle size gives more specific surface area, which increases the opportunity to adsorb metal ions (Zhang *et al.*, 2017). However, the eggshell particle size of 300-600 µm was used for the fixed-bed column. This is because the flow could be clogged when the eggshell powder with particle diameter smaller than 600 µm was employed. The eggshell amount of 0.5-8.0 g was packed in the column with a height of 1.0-16.0 cm, respectively. The amount of eggshell that can adsorb copper (II) ions (50 mg/L, 100 mL) was considered. The results of Cu (II) ion adsorption are shown in Figure 3. It was found that the ability to adsorb Cu (II) ions tends to increase with the quantity of eggshells used, as would be expected simply from considering availability of adsorbent, but also because the residence time of solution with Cu (II) ions in the column increased. This corresponded to the adsorption kinetics described in Section 3.1.2. The adsorption rate depends on the vacant sites in the adsorbent. The eggshell amount of 8.0 g can adsorb the Cu (II) ions up to 100 %, being equivalent to 0.620 ± 0.20 mg/g.

The effects of flow rate were studied on Cu (II) ion adsorption. The flow rate of 1.0-3.0 mL/min was passed

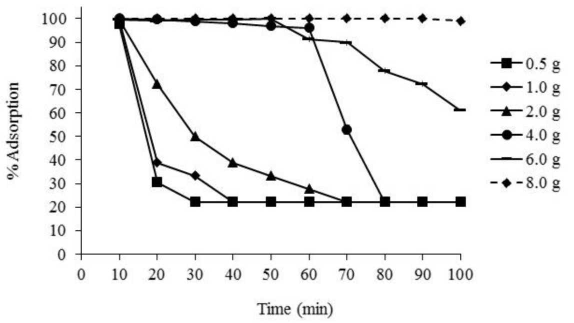


Figure 3. Effects of eggshell dose on Cu (II) ion adsorption

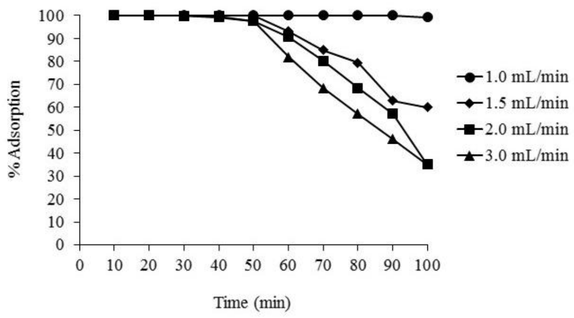


Figure 4. Effects of flow rate on Cu (II) ion adsorption

through 8 g of eggshell powder, for considering the adsorption of copper (II) ions (50 mg/L, 100 mL). The results are shown in Figure 4, and it is noted that the Cu (II) ion adsorption capacity decreased with an increased flow rate, since the residence time between the Cu (II) ions and the adsorbent decreased. A low flow rate promotes chemisorption and an increased residence time would increase the removal of Cu (II) ions.

### 3.4 Fixed-bed column desorption of Cu (II) ions

In the Cu (II) ions adsorption process, the initial concentration of 50 mg/mL, 100 mL, eggshell powder of 8.0 g and flow rate of 1.0 mL/min gave 100 % adsorption of the Cu (II) ions. After that, the effects of eluent type, concentration of eluent, and flow rate, on Cu (II) ion desorption were studied.

Distilled water, and 0.5 M of NaCl, $BaCl_2$, and KCl solutions were selected for the investigation of Cu (II) ion desorption. The comparison of eluent types showed that the 0.5 M $BaCl_2$ gave the highest elution with desorption by 43.76 % (Figure 5) because the ionic strength of $BaCl_2$ is greater than of the other solutions. Therefore, the $BaCl_2$ solution was chosen to tests of the effects of concentration.

The 100 mL $BaCl_2$ aliquots at concentrations of 0.1, 0.3, and 0.5 M were selected for finding an appropriate concentration to remove the Cu (II) ions from the eggshell powder. Higher concentrations than 0.5 M were not studied because $BaCl_2$ solubility limits the range. The %desorption of Cu (II) ions decreased when the concentration of $BaCl_2$ was decreased. Increasing the concentration of $BaCl_2$ gave a higher ionic strength, which increased Cu (II) ion desorption. Thus, high concentration of the eluent was suitable for desorption.

The flow rate of desorption was adjusted to 0.5, 0.8, and 1.0 mL/min. This showed that a low flow rate gave a high %desorption, since the solution was retained for a longer time in the column, giving more opportunity to $Ba^{2+}$ species to replace adsorbed Cu (II) ions. The flow rate of 0.5 mL/min gave the highest %desorption of Cu (II) ions of 59.27 %.

### 3.5 Effects of common ions

The 50 mg/L, 100 mL solutions of Pb (II), Fe (II), Zn (II), Mn (II), and Cu (II) ions were used to study the effects of interference by other ions. The binary metal solution results are shown in Figure 6. The results show that eggshell powder the adsorbs Pb (II) ions better than Cu (II) ions. The Cu (II) ions, Fe (II) ions, and Mn (II) ions were similarly

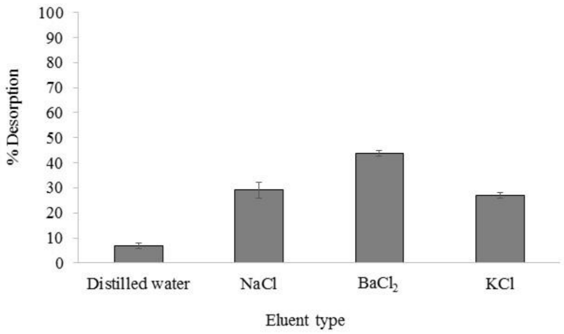


Figure 5. Effects of eluent type on Cu (II) ion desorption

adsorbed by the eggshell powder, while Zn (II) ions were adsorbed less than Cu (II) ions. In the case of the mixed metal ion systems presented in Figure 7 and Table 1, the ability to adsorb Cu (II) ions by the eggshells was decreased. The rank order of adsorption preferences was as follows: Pb (II) ions, Mn (II) ions, Fe (II) ions, Cu (II) ions, and Zn (II) ions. This is because the adsorption is inversely proportional to the hydrated ionic radii of the metal ions. The Pb (II) ions are larger than the other ions. The Pb (II) produced low charge density to bind with water molecules, causing smaller hydrated ionic radius (Chen, Ma, Chen, & Xian, 2010). Thus the highest activity of Pb (II) for adsorption was obtained.

However, the eggshell powder in fixed-bed column can remove Cu (II) ions from water by up to 82.9% in the mixed metal system. Therefore, the results confirm that chicken eggshell powder in a fixed-bed column has potential for use as a sorbent to adsorb various heavy metal ions.

## 4. Conclusions

The adsorption of Cu (II) ions by chicken eggshell powder was investigated. Kinetics data were satisfactorily described by a pseudo-second order chemical sorption model. A long adsorption bed coupled with a low flow rate can promote the adsorption of Cu (II) ions from water. A concentrated $BaCl_2$ solution with a low flow rate was suitable for Cu (II) ion desorption from the eggshell powder. The adsorption of mixed metal showed that the removal of Pb (II) ion was favored over the other tested ions. Although the Pb (II) ions reduced the adsorption of Cu (II) ions, eggshell powder in a fixed-bed column was still able to remove Cu (II) ions from water by up to 83%. This work demonstrated the ability of chicken eggshells for use as an adsorbent of heavy

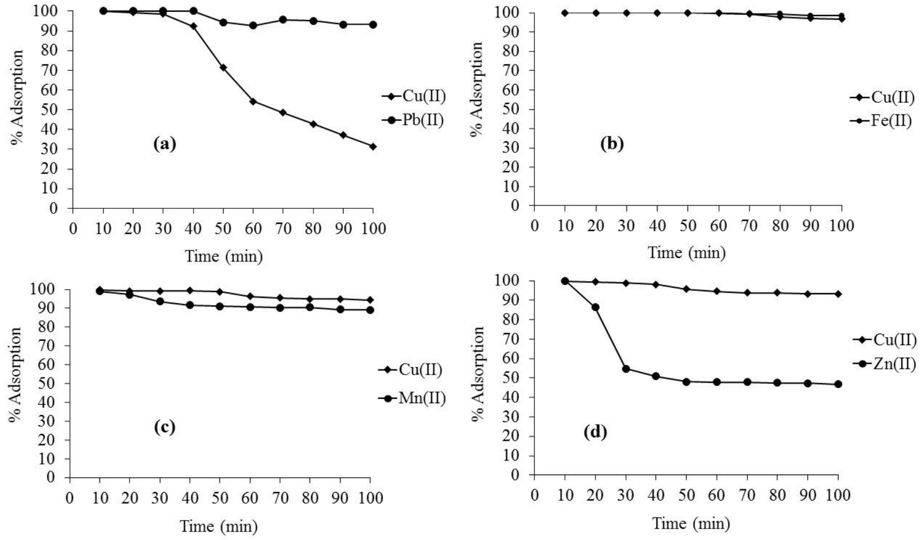


Figure 6. Effects of other common ions on Cu(II) ion adsorption in binary solution: (a) Cu (II) ions and Pb (II) ions; (b) Cu (II) ions and Fe (II) ions; (c) Cu (II) ions and Mn (II) ions; and (d) Cu (II) ions and Zn (II) ions

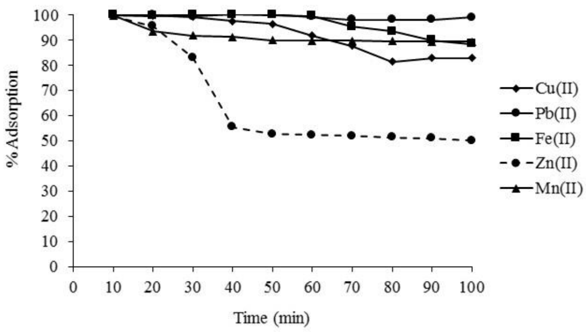


Figure 7. Effects of other common ions on Cu (II) ion adsorption from a solution with multiple metal ions

Table 1. The Cu (II) ion adsorption in the mixed metal solution system

| Metal ion | % Adsorption |
|---|---|
| Cu (II) | 82.9 |
| Pb (II) | 99.0 |
| Fe (II) | 88.5 |
| Zn (II) | 50.1 |
| Mn (II) | 89.3 |

metal ions. The procedure can be scaled up for actual wastewater treatment. Moreover, this system could be developed for pre-concentrating some metal ions before quantitative analysis.

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