Adsorption and desorption of Zn(II) and Cu(II) on Ca-alginate immobilized activated rice bran

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Abstract. Ca-alginate immobilized activated rice bran has been used for adsorption of Zn(II) and Cu(II) from aqueous solution. The effect of the pH, kinetics model, adsorption isotherm and desorption on the adsorption performance was investigated. Activated rice bran was immobilized by the entrapment in alginate beads. The adsorption strength of Ca-alginate immobilized activated rice bran was compared to Ca-alginate and non-immobilized activated rice bran. The concentrations of adsorbed ions were analyzed using Atomic Absorption Spectrophotometer (AAS). The result showed that pH of 4.0 and the contact time of 120 min are the optimum condition for adsorption of Zn(II) and Cu(II). The adsorption kinetic of Zn(II) and Cu(II) followed the pseudo-second-order model with adsorption rate constant 4.9 x 10^{-2} and 3.14 g.mg^{-1}.min^{-1}, respectively. The both adsorption processes obeyed Langmuir isotherm with adsorption capacity of 2.03 and 2.42 mg.g^{-1} of adsorbent, respectively. The strength of Zn adsorption on Ca-alginate immobilized activated rice bran (86.63%) was more effective compared to Ca-alginate beads (60.96%) and activated rice bran (43.85%). The strength of Cu adsorption was 80.00%, 61.50% and 22.10%, respectively. The desorption of Zn(II) and Cu(II) showed that recovery percentage of the adsorption was 76.56% and 57.80% with the condition of using HCl 0.1 M as desorption agent for 1 hour.

1. Introduction
The heavy metal pollution in natural water arises from mainly acid mine drainage and waste water released by industries, agricultural effluents, and various sources. These heavy metals such as Cu, Pb, Hg, Ni, Zn and Cd are toxic to the living system that is very important for environmental quality.

Some methods such as ion exchange, adsorption, membrane separation, solvent extraction, chemical precipitation, reverse osmosis, evaporation and electrodialysis have been used for metal removing from wastewater [1]. Since trace heavy metals should be removed in wastewater, adsorption may provide an effective alternative method for a low cost for the removal of heavy metals from wastewater [2].

Biosorption of heavy metals is proven to be quite effective for the removal of metal ions at low concentration from wastewater with a low cost treatment, potential for sorbent regeneration, high velocity of adsorption and desorption, and environmental friendly manner [3, 4]. Algae, fungi, yeast and bacteria are some of the microorganisms capable on sorption of toxic heavy metal ions from dilute aqueous solution [4, 5].

Rice bran is a by-product of the rice milling industry and found in a big amount that cause disposal problem. The rice bran has been successfully used to remove metal from waste water with the relatively low-cost process [6, 7].
Alginate is one of the most common biopolymers used for immobilization of material like kaolin/zeolite, microorganism or bacteria or biomass [5, 8, 9]. Alginate is the ammonium or alkali salt of chains of 1,4 linked β-D-manuronic and α-L-guluronic acid residues. Alginate becomes a negatively charged anionic polymer on acidification with the formation of –COO- groups. After reaction with calcium salts, alginate can form gels so that it can retain its shape and size unchanged. Calcium ions can be bound to the polymer by simple ionic bridging with two carboxyl groups. These –COO- groups have interaction with metal ions in waste water and calcium ions can be readily exchanged with the metal ions in the waste water [10]. In this experiment, alginate is used as immobilized activated rice bran to remove Cu(II) and Zn(II) from water.

The process of biosorption can be economical if sorbent can be used in a continuous adsorption-desorption cycle. Biosorbent should be cheap, reusable, both uptake and release of metals ions should be efficient and rapid, and desorption process should be metal-selective [5].

2. Materials and methods

2.1. Materials

Rice bran, Na-alginate from Sigma-Aldrich, CaCl$_2$, 2H$_2$O, ZnSO$_4$, 7H$_2$O, CuCl$_2$, 2H$_2$O, HNO$_3$, KNO$_3$, Na$_2$EDTA, NaOH, HCl, CH$_3$COOH, H$_3$PO$_4$, Na$_2$HPO$_4$ were supplied by Merck. All chemicals were analytical reagent grade. Distilled water was used in the preparation of standard and all solution.

2.2. Methods

2.2.1. Preparation of activated Rice Bran. The rice bran was weighed and washed with 30 mL of HCl 0.1 M two times, centrifuged at 2800 rpm for 15 min, then washed with distilled water. Activation of rice bran was treated by addition of 150 mL NaOH 0.1 M were and soaked for 24 h. The solution was then centrifuged at 2800 rpm for 15 min again and washed with distilled water for three times. Water was removed by filtration. Biomass thus was dried at 50 °C and used for adsorption investigation.

2.2.2. Immobilization of Activated Rice Bran Biomass. Na-alginate was prepared for immobilization of activated rice bran. Na-alginate solution 3% (w/v) was prepared with distilled water. Then, 1.6 g of activated rice bran was added to the alginate solution. The solution was drawn through needles and introduced into 0.1M CaCl$_2$, 2H$_2$O. The alginate beads were allowed to treat for 30 min, then were dried and stored at 4 °C for the next use. The characterization of Ca-alginate immobilized activated rice bran was performed by FT-IR.

2.2.3. Adsorption and desorption studies. The adsorption of Cu(II) and Zn(II) on the Ca-alginate immobilized activated rice bran was investigated. The effect of pH (range 3-5), contact time (10-240 min), initial concentrations of Cu(II) and Zn(II) (20 to 300 mg/L) on the adsorption rate and capacity were studied. The comparation between activated rice bran, Ca-alginate and Ca-alginate immobilized activated rice bran were carried out under the optimal condition. In order to study metal desorption, the adsorbed Cu(II) and Zn(II) in Ca-alginate immobilized activated rice bran were rinsed by sequential desorption of H$_2$O, 1M KNO$_3$, 0.5 M HNO$_3$, 0.1 M Na$_2$EDTA, respectively. The adsorbed Cu(II) and Zn(II) were rinsed by direct desorption of 0.5 M HNO$_3$ and 0.1 M HCl for 1 h. The concentration of Cu(II) and Zn(II) were analyzed by 3110-perkin Elmer atomic absorption spectrophotometer.

3. Results and discussion

3.1. Characterization of Ca-alginate immobilized activated rice bran

FTIR spectra of Ca-alginate immobilized activated rice bran are shown in Figure 1. The combination of Ca-alginate and rice bran FTIR spectrum showed the characteristic peaks at 3448 cm$^{-1}$ (OH
stretching), 1635 and 1427 cm$^{-1}$ (COO$^-$ asymmetric and symmetric stretching), 1088-1034 cm$^{-1}$ (C-O-C antisymmetric stretching), and carboxyl and carboxylate at about 1427 and 1635 cm$^{-1}$. From rice bran, -Si-O from silanol group at 879 and 439 cm$^{-1}$, siloxane (Si-O-Si) at 1000-1100 cm$^{-1}$ was found. Based on the FTIR analysis, the immobilization of rice bran in Ca-alginate will increase the adsorption of active group of Ca-alginat and free rice bran on Cu(II) and Zn(II).

![Figure 1. FTIR spectra of ca-alginate immobilized activated rice bran](image)

3.2. Effect of pH on Cu(II) and Zn(II) adsorption

The effect of pH on the Cu(II) and Zn(II) adsorption by Ca-alginate immobilized activated rice bran was studied and the observed results are shown in Figure 2. Test was undertaken with different initial pH values of Cu (II) and Zn(II) solutions in water. There was an increase in adsorption capacity with increasing pH from 3.0 to 4.0 and a decrease in pH 4.0. The pH 4.0 is found to be highest efficiency for the Cu(II) and Zn(II) adsorption. At acidic pH, protonation of the adsorbent influenced the adsorption capacity. The proton concentration in solution is high and competes with free Cu(II) and Zn(II) for adsorption sites on surface of adsorbent. This effect becomes minor with increasing pH in the solution.

![Figure 2. Effect of pH on Cu(II) and Zn(II) adsorption](image)
3.3. Adsorption kinetic study

The contact time on Cu(II) and Zn(II) adsorption by Ca-alginate immobilized activated rice bran was investigated and the experimental results are showed in Figure 3. In order to find out the optimum contact time, adsorption of Cu(II) and Zn(II) have been carried out for 240 minutes. The equilibrium of both metal adsorptions is achieved after 120 min. The adsorption rate was initially fast due to availability of binding sites and after that the change of rate became constant.

In order to explain the adsorption kinetics, four common kinetic models, which are the first order, second order, pseudo-first order and pseudo-second-order kinetic model were tested. All the parameters were determined and listed in Table 1. The best kinetic model was selected based on the linear regression correlation coefficient \( R^2 \). Furthermore, the correlation coefficient \( R^2 \) for pseudo-second-order model was much closer to 1 than other models. These results confirmed that the adsorption of Cd (II) and Zn (II) ions onto alginate immobilized activated rice bran can be represented by pseudo-second-order kinetic model.

| Kinetic Model       | Equation                           | Cu(II) adsorption          | Zn(II) adsorption          |
|---------------------|------------------------------------|-----------------------------|-----------------------------|
|                     |                                    | \( k \) \( R^2 \)          | \( k \) \( R^2 \)          |
| First order         | \( \ln C_a = -k_1t + \ln C_0 \)   | 3.3 x 10^{-3} min^{-1}      | 5.03 x 10^{-3} min^{-1}     | 0.973 | 0.782 |
| Second order        | \( (1/C_a) = k_2t + (1/C_0) \)    | 1.0 x 10^{-4} M.min^{-1}    | 1.3 x 10^{-4} M.min^{-1}    | 0.984 | 0.783 |
| Pseudo-first order  | \( \log (q_e - q_t) = \log q_e - (k_3/2.303)t \) | 3.22 x 10^{-3} min^{-1}      | 5.02 x 10^{-3} min^{-1}     | 0.974 | 0.782 |
| Pseudo-second order | \( t/q_t = 1/(k_4q_e^2) + (1/q_e)t \) | 3.14 g.mg^{-1}.min^{-1}     | 4.9 g.mg^{-1}.min^{-1}      | 0.999 | 0.999 |

3.4. Equilibrium Adsorption Study

Adsorption of Cu(II) and Zn(II) by Ca-alginate immobilized activated rice bran is due to surface phenomena that would follow either Freundlich or Langmuir isotherm models. The Langmuir model makes several assumptions, the metal adsorption is a process occurring on homogenous surface and
form monolayer coverage, while Freundlich model is based on physicochemical adsorption on heterogeneous surfaces. The Langmuir model gives the best representation and showed in Table 2. Regression correlation coefficients for Cu(II) and Zn(II) adsorption by Ca-alginate immobilized activated rice bran are very high. According to the Langmuir isotherm model, the value of adsorption capacity ($Q_{\text{max}}$) appears to be higher for the Cu(II) than Zn(II). Ca-alginate immobilized activated rice bran shows good performance of Cu(II) and Zn(II) adsorption. Both Ca-alginate and rice bran have negatively charge on the functional groups that attract the cationic metals. This contributed to high sorption capacity for alginate immobilized rice bran.

| Parameter | $Q_{\text{max}}$ (mg·g$^{-1}$) | $R^2$ |
|-----------|--------------------------------|-------|
| Cu(II)    | 2.42                          | 0.969 |
| Zn(II)    | 2.03                          | 0.967 |

3.5. The effectivity of Ca-Alginate/rice bran to adsorb Cu(II) and Zn(II)

The effectivity of Cu(II) and Zn(II) adsorption between activated rice bran, Ca-alginate, and Ca-alginate immobilization activated rice bran were carried out under the optimal condition. Figure 4 showed that the strength of Zn(II) and Cu(II) adsorption on Ca-alginate immobilized activated rice bran (79.97% for Cu(II), 86.63% for Zn(II)) were more effective compared to Ca-alginate beads (61.51%, 60.96%) and activated rice bran (43.85%, 22.03%). It is because of alginate and rice bran have an active site that can be interact with Cu(II) or Zn(II). The combination of both can increase the active site so that the Cu(II) and Zn(II) adsorption will be more effective.

3.5. Desorption efficiency of Cu(II) and Zn(II) absorbed by Ca-alginate immobilized activated rice bran

Adsorbent generation by desorption of adsorbed metal is necessary in order to minimize the process cost. Optimum desorption was achieved by a proper selection of pollutants, which depends on the type of adsorbent and the mechanism of adsorption. The absorbed Cu(II) and Zn(II) in Ca-alginate immobilized activated rice bran were rinsed by sequential desorption of H$_2$O, 1M KNO$_3$, 0.5 M HNO$_3$, 0.1 M Na$_2$EDTA, respectively. Those desorption agents are responsible for adsorption of Cu(II) and Zn(II) through entrapment, ion exchange and complexation mechanism [5]. During desorption studies, maximum desorption of adsorbed Cu(II) was recorded. The results shown in Figure 5 indicates that high recoveries were possible for the Cu(II) and Zn(II) by using HNO$_3$. It indicates that adsorption
process involves electrostatic interaction between negative charges of the adsorbent and cationic metal.

In this study, the desorption efficiency was tested by 0.1 M HCl compare to 0.5 M HNO₃ for 1 h. The results that showed in Figure 6 indicate that HCl effective to desorb Cu(II), and Zn(II) compare to HNO₃. The recovery of Cu(II) and Zn(II) were found to be 57.89% and 76.56%, respectively.

Figure 5. Sequential desorption of adsorbed Cu(II) and Zn(II)

Figure 6. Effectivity desorption of adsorbed Cu(II) and Zn(II) by HNO₃ and HCl

4. Conclusions
Ca-alginate Immobilized activated rice bran can be used as adsorbents for the removal of Cu(II) and Zn(II) from the aqueous medium. The maximum adsorption capacity of adsorbent was achieved at pH 4 and contact time 120 min. Kinetic adsorption of Zn(II) and Cu(II) can be described by the pseudo-
second-order kinetic model with adsorption rate constant $4.9 \times 10^{-2}$ and $3.14 \text{ g.mg}^{-1}.\text{min}^{-1}$. The Zn(II) and Cu(II) adsorption process obeyed Langmuir isotherm with adsorption capacity of 2.03 and 2.42 \text{ mg.g}^{-1} of adsorbent. Compared with free activated rice bran and Ca-alginate only, the Ca-alginate immobilized activated rice bran showed improved performance to adsorb Cu(II) and Zn(II) and could be used as an efficient adsorbent system for the wastewater treatment. The desorption of Zn(II) and Cu(II) showed that recovery percentage of the adsorption was 76.56% and 57.89% with the condition of using HCl 0.1 M.

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