REMOVAL OF Cu (II) IONS FROM AQUEOUS SOLUTION USING CALCIUM-ALUMINIUM/CARBON-DERIVED FISH BONES

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ABSTRACT

In this research, removal of Cu(II) ion was investigated using the adsorption process, which is widely known as simple operation, low cost, and high efficiency. Therefore, we have designed an adsorbent with the aim to increase its surface area and adsorptive capability. Calcium and aluminium were impregnated onto fish bones that were carbonized at 500°C for an hour, which is denoted as Ca-Al/CFB-500. The performance of Ca-Al/CFB-500 adsorbent to adsorb Cu²⁺ ions from solution was measured. The chemical and physical properties of Ca-Al/CFB-500 adsorbent were investigated by using X-ray diffraction (XRD), Infrared (IR) spectroscopy, N₂ adsorption-desorption, scanning electron microscopy (SEM) and Thermogravimetric (TG) analysis. The Ca-Al/CFB-500 is effective to act as an adsorbent for removing Cu²⁺ ions from solution, whereby the removal efficiency reached 98 % after 1440 min. The removal of Cu²⁺ ions from solution by Ca-Al/CFB-500 adsorbent was influenced by pH, whereby pH less than 3 was not favored. It is noticed that the removal of Cu²⁺ ions onto Ca-Al/CFB-500 follows the pseudo-second order model.

Keywords: adsorption, removal of Cu²⁺ ions, carbon-derived fish bone support, pseudo-second order model.

INTRODUCTION

The metal elements, which have density greater than 5 g cm⁻³ and high molecular mass, are well recognized as heavy metals. Numerous heavy metals, especially those highly soluble in water (pH < 5), could cause human health problems at excess use of copper (Cu), iron (Fe), nickel (Ni), zinc (Zn), and manganese (Mn). Generally, these soluble heavy metals undergo very fast entrance into the blood circulation system and then, they are thoroughly distributed to the whole body. As a result they can cause the following unpleasant effects, including vomiting, diarrhea, abdominal cramps, nausea, liver damage, kidneys damage and more seriously, leading to death [1].

Since Cu(II) ions are also leading to those adverse effects, many attempts have been taken to remove Cu (II) ions from water resources and wastewater, for examples, membrane filtration, ultrafiltration, ion exchange, solvent extraction, complexation, adsorption, coagulation, phytoextraction, chemical precipitation, chemical oxidation or reduction, evaporation and reverse osmosis. Adsorption is the most often used by researchers due to its high efficiency. On the contrary, other methods might involve a lot of reagents, high energy intensification, incomplete metal release, low selectivity, high operational costs and may not be environmentally friendly [2, 3]. The elimination of Cu (II) ions from aqueous solution over a variety of adsorbents has been investigated by several researches. The adsorbents used are comprised of pretreated fish bones [4], Kolubara lignite [5], agricultural by-products sawdust [6], activated carbon, silica, activated carbon composites, etc. [7]. Despite the fish bones were pretreated with NaOH, H₂O, H₂O₂, HNO₃ and C₂H₅OH, they were not efficient to act as adsorbents because of the long duration of the adsorption process.
Prompted by the aforementioned limitation, we have taken a step further to improve the efficiency of fish bone adsorbent by impregnating calcium (Ca) and aluminium (Al) onto carbon-derived fish bones that carbonized at 500°C. The prepared adsorbent is denoted as Ca-Al/CFB-500 and this abbreviation will be used throughout the manuscript. The inclusion of Ca and Al into the fish bones aims to increase the surface area and adsorption capacity by forming CaO and Al₂O₃ onto carbon-derived fish bones via the calcination process. It is worth noting that Cu(II) adsorptive equilibrium could be achieved in a shorter time duration with Ca-Al/CFB-500. The characterization of the adsorbent from carbon-derived fish bones impregnated with calcium and aluminum was performed using XRD, IR spectroscopy, SEM, TG analysis and N₂ adsorption-desorption. The removal process was studied by using the kinetic models and adsorption isotherms.

EXPERIMENTAL
Materials
The waste of Belida fish bones were collected from many companies around Samarinda, East Kalimantan, Indonesia. The fish bones were washed with boiling water until free of impurities. The fish bones are dried in an oven at 110°C for 24 h. Furthermore, they were crashed to powder and sieved (100 mesh). The fish bones powder (FB) was impregnated by calcium and aluminium (1000 µmol) and then carbonized (500°C, 1 h) in a furnace. It is abeled as Ca-Al/CFB-500.

Adsorbate
The stock of Cu²⁺ ion (1000 mg L⁻¹) was prepared by dissolving Cu(NO₃)₂·9H₂O (Merck) in distilled water. The stock solution was used to prepare solutions with another concentration of Cu²⁺ ion.

Characterizations
The characterization of the adsorbent was carried out by using XRD, FTIR, SEM, TGA and N₂ adsorption-desorption test. The crystallinity was investigated by XRD pattern recorded with a Bruker AXS Advance D8 diffractometer using Cu Kα radiation (λ = 1.5405 Å, 40 kV and 40 mA). The Shimadzu IR spectrometer was used to record IR spectra. The surface morphology of the samples was investigated by using SEM instrument (JEOL JSM-6701F, 15 kV). The amount of carbon in the samples was determined by TG Analysis (STA Linseis PT1600) with heat rate 10 °C min⁻¹ and target temperature 900°C. The surface area and pore size distribution of the samples were calculated based on N₂ adsorption-desorption data at 77 K (Quantachrome 11.0).

Batch Adsorption Studies
The adsorbent (0.5 g) was contacted with 50 mL Cu²⁺ ion solution (100 mg L⁻¹) in 250 mL Erlenmeyer flasks at room temperature under stirring for 5, 10, 15, 30, 60, 120, 240, 480, 720 and 1440 min. The solid adsorbent and filtrate were separated by centrifugation. The concentration of Cu²⁺ ions in the filtrate was detected by Atomic Absorption Spectrophotometry (Analysis 200 AA, Perkin Elmer, USA). The extent of metal removal was determined by the equation [8]:

\[
\text{Metal adsorption (\%)} = \left( \frac{C_i - C_f}{C_i} \right) \times 100
\]

where \( C_i \) is initial concentration and \( C_f \) is the final concentration of Cu(II) in the solution [9].

RESULTS AND DISCUSSION
Fig. 1 shows the XRD pattern of Ca-Al/CFB-500. The peak positions at 2θ = 25.9, 31.8, 39.8, 46.8, 49.6, 53.4 and 64.4 indicated that the crystalline phase of hydroxyapatite dominated onto the sample [10]. The average crystal size of hydroxyapatite was estimated to be 50.37 nm.

The functional groups onto CFB-500 and Ca-Al/CFB-500 surfaces are shown by IR spectra in Fig. 2. The O–H stretching mode, which correlated adsorbed water in the sample, appeared at both spectra with broad peak at around 3436 cm⁻¹ and 1632 cm⁻¹ [12]. The peaks at around 2925 cm⁻¹ and 2851 cm⁻¹, which indicated as the
the absorption of organic material as C–H group symmetric and asymmetric stretching mode, can prove the effect of carbonization process. The carbonate ion substitution in the sample was shown by the absorption peak at around 2129 cm\(^{-1}\) and 877 cm\(^{-1}\)\[^9\]. The phosphate groups on the sample were shown by the peak at around 679 cm\(^{-1}\) and 591 cm\(^{-1}\). The carbonate ion and the phosphate groups indicate the hydroxyapatite in the sample.

Fig. 3 shows the physisorption isotherms and pore size distributions of FB and Ca-Al/CFB-500. Both physisorption isotherms are type III in the IUPAC classification which indicated no identifiable monolayer. The pore radius, pore volume and BET surface area were 17 Å, 0.029 cc/g and 16.0 m\(^2\)/g for FB and 17.3 Å, 0.061 cc/g and 26.9 m\(^2\)/g for Ca-Al/CFB-500, respectively.

The surface morphology of Ca-Al/CFB-500 was investigated based on the SEM image illustrated in Fig. 4. The surface morphology of Ca-Al/CFB-500 has roughness surfaces and splinters shape.

The TG analysis curve of Ca-Al/CFB-500 is shown in Fig. 5. The weight losses of the sample are shown in two-step temperature ranges. The TG analysis displayed a drastically weight loss ~ 21.76 % in the temperature range 33.3°C - 146.8°C (first step) which indicated with the evaporation of the water adsorbed on samples. In the temperature range 200°C - 500°C (second step), the weight lose of 2.0 % is caused by the decomposition of organic compounds. The carbon content in the sample also can be determined by the weight lose percentage in the second step.
The effect of the contact time on the removal of Cu\(^{2+}\) ion onto Ca-Al/CFB-500 adsorbent is shown in Fig. 6. Adsorbent rapidly adsorbed Cu\(^{2+}\) ion within the first 5 min with adsorption capacity of 45.8 mg g\(^{-1}\). This is because there are many active sites and empty pores available on the adsorbent surface. Adsorption capacity progressively increased from 53.8 mg g\(^{-1}\) to 79.3 mg g\(^{-1}\) within the contact time from 10 to 480 min. The Cu\(^{2+}\) ion adsorption capacity achieved 92 mg g\(^{-1}\) when the adsorption process was done for 720 min and after around 1440 min it reaches 99.3 mg g\(^{-1}\). The increasing of Cu\(^{2+}\) ion adsorption capacity was negligible (~7 mg g\(^{-1}\)) within duration of contact time from 720 to 1440 min, indicating that the adsorption process of Cu\(^{2+}\) ion reached equilibrium.

The effect of pH on Cu\(^{2+}\) ion removal was shown in Fig. 7. The experiments were carried out with Cu\(^{2+}\) ion solution (100 mg/L; 50 mL) with 0.5 g Ca-Al/CFB-500 adsorbent at room temperature with duration of the contact time 1 h at different pH (pH 1 ~ 6). The Cu\(^{2+}\) ion adsorption process was unaffected in the pH range of 3 - 6. Absorption at pH less than 3 was not favorable as the excess H\(^+\) ion may cause a competition in absorption between the positively charged sites (H\(^+\)) and the Cu\(^{2+}\) ion [13].

The Lagergren rate equation was used to determine the adsorption rate constant of the first-order rate. It equation can be written [14]:

\[
\ln(q_e - q_t) = \ln q_e - k_1 \cdot t
\]

where \(q_e\) and \(q_t\) are the amount of Cu\(^{2+}\) ion adsorbed (mg g\(^{-1}\)) at equilibrium and at time t (min), and \(k_1\) is the rate constant of first order rate Cu\(^{2+}\) ion adsorption (min\(^{-1}\)).

The slope of plot of \(\ln(q_e - q_t)\) versus t which shown in Fig. 8(a), was used to calculate the linear relationship (R\(^2\)), \(k_1\), and \(q_e\), such as 0.6392, 0.0018 min\(^{-1}\) and 37.148 mg g\(^{-1}\). Based on the value of the experimental \(q_e\) (90.86 mg g\(^{-1}\)) does not agree with the calculated value obtained from linear plot.

The adsorption rate constant of the second order rate also was tested by the Lagergren which the equation was expressed as follows[14]:

\[
t/q_t = 1/(k_2 \times q_e^2) + t/q_e
\]

where \(k_2\) is the rate constant of the second order rate Cu\(^{2+}\) ion adsorption (g mg\(^{-1}\) min\(^{-1}\)). The plotting \(t/q_t\) vs \(t\) which is shown in Fig. 8(b) was used to calculate the value of the linear relationship (R\(^2\) = 0.9943), \(k_2\) (0.0007) and \(q_e\) (90.09 mg g\(^{-1}\)) of the second order kinetics. The experimental \(q_e\) (90.864 mg g\(^{-1}\)) showed good
agreement with the calculated value obtained from the linear plot. This shows that the adsorption of Cu$^{2+}$ ion onto Ca-Al/CFB-500 adsorbent follows a second order reaction.

The effectiveness of Cu$^{2+}$ ion adsorption was investigated by the following linear forms of Freundlich isotherm. The Freundlich isotherm is expressed as follows [13]:

$$\log q_e = \log k_f + \left(\frac{1}{n}\right) \log C_e$$

(5)

where $k_f$ is the roughly a measure of adsorption capacity and $n$ is the effectiveness indicator of adsorption. From Fig. 9 can be determined $1/n$ and $k_f$ which calculated from slope and intercept of linear plot log $C_e$ vs log $q_e$. The value of $n$ and $k_f$ were 1.01 and 246, respectively. Due to the value $n > 1$, it can be concluded that the adsorption of Cu$^{2+}$ ion onto Ca-Al/CFB-500 adsorbent was effective.

CONCLUSIONS

Fish bones are available as by-product waste from the fish processing industry. In this study, fish bones were undergone carbonization and impregnated with calcium and aluminium. Carbon-derived fish bones impregnated with calcium and aluminium (Ca-Al/CFB-500) was proven effective to be used as a sorbent to remove heavy metals. The adsorption capacity was investigated as a function contact time and pH. The results of this research showed that Ca-Al/CFB- 500 could remove Cu$^{2+}$ ion effectively due to an increase of surface area from 16.0 m$^2$ g$^{-1}$ to 26.9 m$^2$ g$^{-1}$. Besides, the highest removal capacity Cu$^{2+}$ ion was reached, 99.3 mg g$^{-1}$, after the adsorption process was carried out around 1440 min. The removal Cu$^{2+}$ ion from solution by Ca-Al/CFB-500 adsorbent can be used with high removal capacity by pH condition more than 3. The coefficient of determination of adsorption of Cu$^{2+}$ ion onto Ca-Al/CFB-500 was well-fitted to the pseudo-second order model.

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