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Announcement
The Scientific committee of ICOSMEE 2019 proudly announces the accepted abstracts in Batch 2 include in the conference. Kindly find check your status in your account and download your letter of Acceptance

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THE 2nd INTERNATIONAL CONFERENCE ON SCIENCE, MATHEMATICS, ENVIRONMENT AND EDUCATION 2019
Best Western Premier, Solo City, Indonesia

Welcome Message from the Conference Chairperson
It is with great pleasure to invite you to participate in the 2nd International Conference on Science, Mathematics, Environment and Education (ICOSMEE), which will be held on 26 – 28th July 2019 in Universitas Sebelas Maret, Surakarta, Indonesia. This is a biannual conference encompasses a wide spectrum of topics including the state-of-art and recent trend in different innovative research in science, mathematics, environment and education which will be covered through plenary lectures, oral and poster presentations.
The 21st century and the fourth industrial revolution (Industry 4.0) are two issues closely related and have a great impact to education. It is beyond doubt that education is at the heart of preparing present and future generation to thrive. An education system designed for the industrial economy is now being automated requires transformation, from a system based on facts and procedures to one that actively applies knowledge to collaborative problem solving. Thus, we present this year theme:

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Publication of 1st ICoSMEE
Journal of Chemical Technology and Metallurgy
[Volume 54 Iss. 4, 2019](#)
Journal of Physics Conference Series Scopus Indexed Volume 1022
International Journal of Paedagogy and Teacher Education (IJPTE DOAJ Indexed)
[IJPTE Focus Issue January 2018](#)
[IJPTE Focus Issue July 2018](#)
[ICoSMEE Regular Proceedings ISBN: 978-602-51856-0-1](#)

"Innovative Research in Science, Mathematics, Environment and Education for Sustainable Life"
By joining with the ICoSMEE, we will bring together educators and researchers to further research ideals and foster new ideas and relationships.
We look forward to seeing you in Surakarta on 26 - 28th July 2019
Sri Mulyani
Chairperson of The 2nd ICoSMEE

Aims and Scope
The conference aims to provide forum to share and discuss ideas and new development in science, math, environment and education.
The scopes of our conference that will be discussed are:
a. Physics, Instrumentation, and Energy
b. Chemistry and Material Science
c. Biology
d. Natural Science
e. Mathematics, Applied Mathematics, Statistics, Computer Science
f. Environment, Human Ecology
g. Physics Education
h. Chemistry Education
i. Biology Education
j. Mathematics Education
k. Environmental Education, Education for Sustainable Development
l. Science Education
m. STEM Education

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CERTIFICATE

is awarded to

Mukhamad Nurhadi

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Presenter

entitled

*Removal Of Cu (II) Ions From Aqueous Solution Using Carbon
Derived Fishbone Supported Calcium And Aluminum*

in The 2nd ICoSMEE (International Conference on Science,
Mathematics, Environment and Education) 'Faculty of Teacher Training
and Education', Sebelas Maret University

Surakarta, 26-28 July 2019

Dean,



Dr. Mardiyana, M.Si.

Chair,



Dr. rer.nat. Sri Mulyani, M.Si.



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

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ABSTRACT

In this research the performance of Ca-Al/CFB-500 adsorbent to adsorb Cu²⁺ ion from solution has been investigated. The chemical and physical properties of Ca-Al/CFB-500 adsorbent were investigated by using X-ray diffraction (XRD), Infrared (IR) spectroscopy, nitrogen adsorption-desorption, scanning electron microscopy (SEM) and Thermogravimetric (TG) analysis. The adsorbent of Ca-Al/CFB-500 was very good for removing Cu²⁺ ion in solution. The Cu²⁺ ion removal reached 98% after the adsorption process was carried out 1440 min. The removal of Cu²⁺ ion from solution by Ca-Al/CFB-500 adsorbent was influenced by pH condition especially the pH less than 3. The adsorption of Cu²⁺ ion onto Ca-Al/CFB-500 follows the pseudo second order model.

Keywords: Adsorption; removal Cu²⁺ ion; pseudo second order model.

INTRODUCTION

Heavy metals are metal elements which have a density greater than 5 g cm⁻³ and high molecular weight. Copper (Cu) element is one kind of essential heavy metals which highly

soluble in water at pH less than 5 and to be dangerous to a human when excess. In the human body, the Cu element very fast entrance into the blood circulation and distributed to the whole body. The effect of the excess of Cu metal in the human body can cause vomiting, diarrhea, abdominal cramps, nausea, liver damage, kidneys damage and lead to death [1].

Many researchers have tried various elimination methods to remove heavy metal from water resources and wastewater such as membrane filtration, ultrafiltration, ion exchange, solvent extraction, complexation, adsorption, coagulation, phytoextraction, chemical precipitation, chemical oxidation or reduction, evaporation and reverse osmosis. Adsorption method was often used by many researchers due to simple, low cost, easy of handling, high adsorption capacity and low maintenance. Otherwise, other methods have several disadvantages such as requiring a lot of reagent and energy, incomplete metal release, low selectivity, high operational costs and not being environmentally friendly [2, 3].

Removal Cu (II) ions from solution by using adsorbent have been investigated by several researches. The adsorbent that have been used to remove Cu (II) ions from solution such as; pretreated fish bones[4], Kolubara lignite [5], Agricultural by-products sawdust[6], activated carbon, silica and silica activated carbon composite[7].

Previous research, the removal Cu (II) ions use fish bones pretreated with NaOH, H₂O, H₂O₂, HNO₃ and C₂H₅OH as adsorbent was not efficient due to need a long time duration in adsorption process. In this study, the removal of Cu (II) ions from aqueous solution was investigated by using carbon derived fish bones supported calcium and aluminum need a short time duration to achieve equilibrium. The supporting calcium and aluminum onto fish bones was aimed to increase adsorption capacity by forming CaO and Al₂O₃ onto carbon derived fish bones after calcinations process. The adsorbent from carbon derived fish bones supported calcium and

aluminum was characterized by the XRD, FTIR, SEM, TGA and N₂ adsorption and checked to the kinetic model and adsorption isotherm into adsorption process.

EXPERIMENTAL

Materials

The fish bones materials were collected from waste of Belida fish from East Kalimantan, Indonesia. The waste of Belida fish bones was washed with boiling water to separate bone and impurities. The fish bones dried in an oven at 110 °C for 24 hours. Furthermore, it was crushed and sieved to get a powder with size of 100 mesh and it was labeled FB. The fish bones powder was impregnated by calcium and aluminium (1000 µmol) and then it carbonized in a furnace at 500 °C for 1 hour. The results are labeled Ca-Al/CFB-500.

Adsorbate

Cu(NO₃)₃ · 9H₂O (Merck) was used to prepare stock solution of Copper. That compound was dissolved in distilled water until concentration of Cu²⁺ ion 1000 mgL⁻¹. Another concentration of Cu²⁺ ion which used in experiment was prepared by diluting of the stock solution.

Characterizations

The XRD, FTIR, SEM, TGA and N₂ adsorption test were used to characterize the samples. The X-ray diffraction (XRD) pattern which recorded with a Bruker AXS Advance D8 diffractometer using Cu K_α radiation ($\lambda = 1.5405 \text{ \AA}$, 40 kV and 40 mA) was used to investigate the crystallinity of the samples. The functionalize groups in the samples were investigated from IR spectra which recorded on a Shimadzu Fourier transform infrared spectrometer, with a

spectral resolution of 2 cm^{-1} , scans 10 s, at temperature $20 \text{ }^\circ\text{C}$. The scanning electron microscopy (SEM), JEOL JSM-6701F instrument with an accelerating voltage of 15 kV were used to determine the morphology of the surface in the samples. The thermal gravimetric Analysis (TGA) data which collected by STA Linseis PT1600 instrument with heat rate $10 \text{ }^\circ\text{C min}^{-1}$ and target temperature $900 \text{ }^\circ\text{C}$ were used to predict the amount of carbon in the samples. The N_2 adsorption at 77 K using a Quantachrome instruments version 11.0 was used to calculate the surface area of the samples and the pore size distribution was determined with the Barrett-Joyner-Halenda (BJH) model.

Batch adsorption studies

The sorption performance of the samples was investigated by contacting 0.5 g sample with 50 mL Cu^{2+} (100 mgL^{-1}) in 250 mL Erlenmeyer flasks at room temperature under stirring for duration time of 5, 10, 15, 30, 60, 120, 240, 480, 720 and 1440 min. The suspension was centrifuged to separate solid and filtrate. The filtrate was analyzed for metal ion concentration by using Atomic absorption Spectrophotometric analysis (Analysis 200 AA, Perkin Elmer, USA). The effect of pH for sample performance to metal sorption was tested in the range of 1.0 – 6.0. The mixing 0.1 M HCl and 0.1 M NaOH was used to arrange of the pH of metal solution. The amount of metal adsorption in the adsorbent was determined by the equation[8]:

$$\text{Metal adsorption (\%)} = \frac{(C_i - C_f)}{C_i} \quad (1)$$

where C_i and C_f are initial and final concentration of metal ion (mgL^{-1}) in the solution [9].

RESULT AND DISCUSSION

Fig. 1 showed the XRD pattern of Ca-Al/CFB-500. The crystalline phase of hydroxyapatite dominated onto the sample which shows the angles corresponding to the peak positions at $2\theta = 25.9, 31.8, 39.8, 46.8, 49.6, 53.4$ and 64.4 . [10]. The average size of hydroxyapatite crystal is calculated by using the Debye-Scherrer equation[11]:

$$T = \frac{K\lambda}{\beta \cdot \cos\theta} \quad (2)$$

where T is the average of crystal size, K is the shape factor (0.9), λ is the X-ray wavelength (0.15406 nm), β is the line broadening at full width at half maximum (FWHM = 0.002651) on the $2\theta = 31.224$ scale in radians and θ is the Bragg angle of the peak in degrees. The average crystal size of hydroxyapatite was estimated to be 50.37 nm.

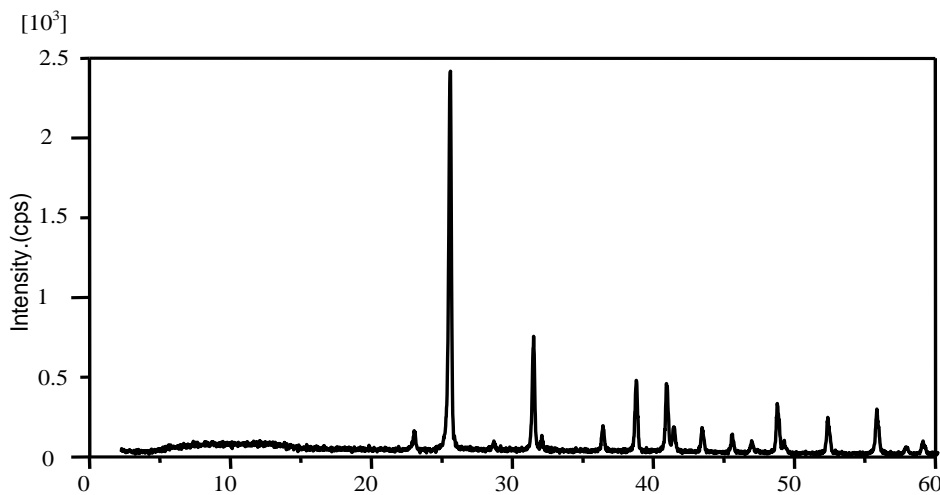


Fig. 1. XRD pattern of Ca-Al/CFB-500

The IR spectra for the surface functional groups of CFB-500 and Ca-Al/CFB-500 were shown in Fig. 2. Both spectra show the IR absorption a broad peak at around 3436 cm^{-1} and 1632 cm^{-1} which indicated to hydroxyl stretching mode which correlated adsorbed water in the sample [12]. Carbonization process caused the appearance of peaks at around 2925 and 2851 cm^{-1} were assigned to the absorption of organic material as C–H group symmetric and asymmetric

stretching mode. The carbonate ion substitution in the sample was shown by the absorption peak at around 2129 and 877 cm^{-1} [9]. And the phosphate groups on the sample were showed by the peak at around 679 and 591 cm^{-1} . The carbonate ion and the phosphate groups indicate the hydroxyapatite in the sample.

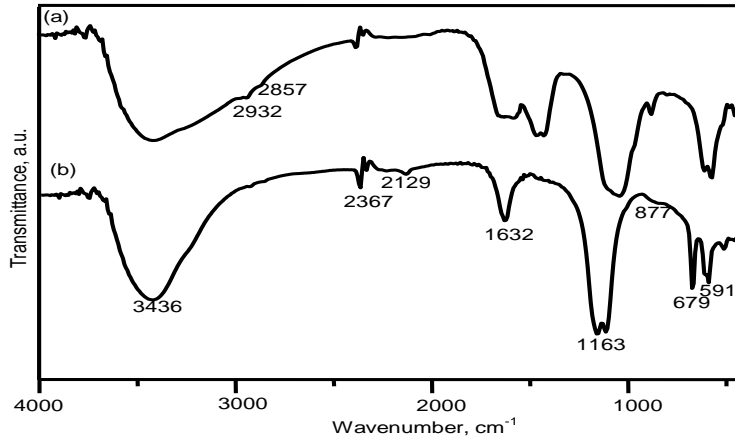


Fig. 2. IR spectra of of (a) CFB-500 and (b) Ca-Al/CFB-500

Fig. 3 shows the N_2 adsorption-desorption isotherms and pore size distributions of FB and Ca-Al/CFB-500. Both isotherms are III type in the IUPAC classification which indicated no identifiable monolayer. The pore size distribution of FB sample indicated the presence of uniform pores with pore radius $\sim 17 \text{ \AA}$. The pore radius, pore volume and surface area of Ca-Al/CFB-500 sample were 17.3 \AA , 0.061 cc/g and $26.9 \text{ m}^2/\text{g}$, respectively.

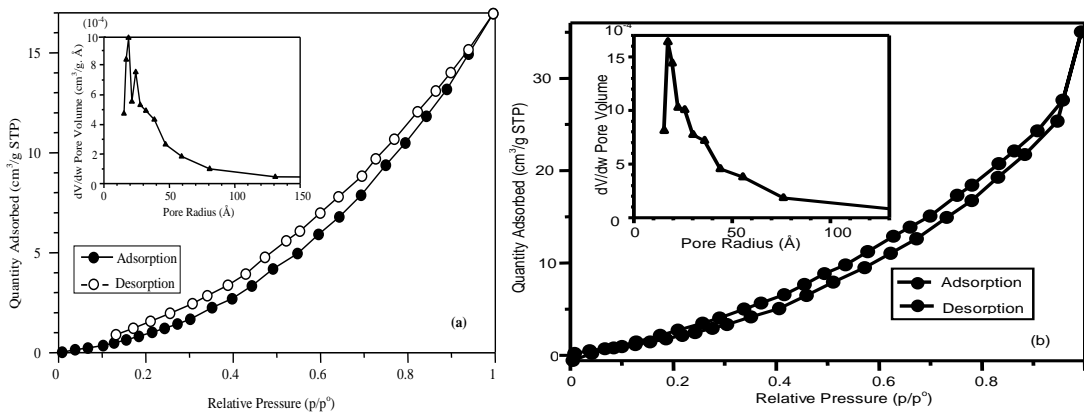


Fig. 3. N_2 adsorption-desorption isotherms and pore size distribution of Ca-Al/CFB-500

The morphology of Ca-Al/CFB-500 was determined by scanning electron microscopy (SEM). The SEM image in Fig. 4, it can be seen that the morphology of Ca-Al/CFB-500 has roughness surfaces and splinters shape.

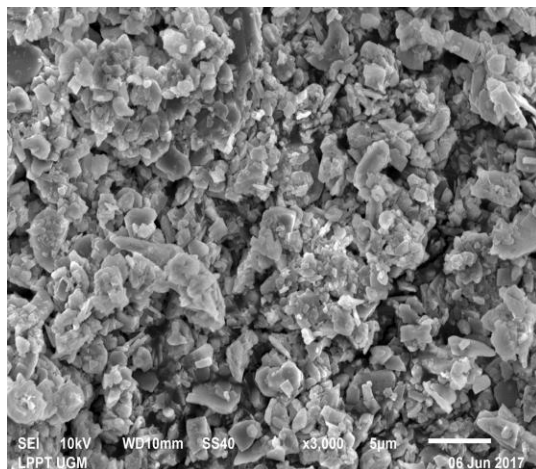


Fig. 4. SEM images of Ca-Al/CFB-500

The TG analysis plot of Ca-Al/CFB-500 was shown in Fig. 5. The weight losses of the samples were shown in two step temperature ranges. The TGA plot of Ca-Al/CFB-500 displayed a drastically weight loss $\sim 21.76\%$ in the first temperature range $33.3 - 146.8\text{ }^{\circ}\text{C}$ which correlated with the evaporation of the water adsorbed on samples. In the second temperature range $200 - 500\text{ }^{\circ}\text{C}$, the TG analysis plot saw weight lose 2.0% which associated with the decomposition of organic compounds. Decreasing of weight lose percentage in the second temperature range also can be associated with carbon contain in the sample.

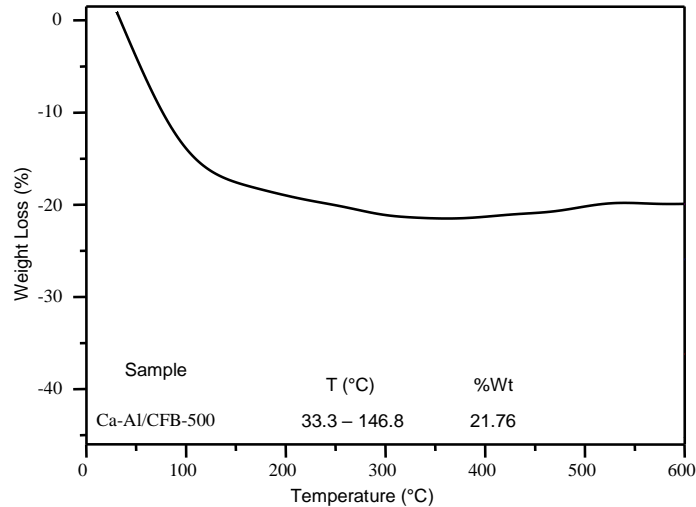


Fig. 5. TG analysis of of Ca-Al/CFB-500

Fig. 6 shows the histogram of the effect of contact time on the adsorption of Cu^{2+} ion onto Ca-Al/CFB-500 adsorbent. Adsorbents rapidly adsorbed Cu^{2+} ion within the first 5 min of contact time with adsorption capacity of 46%. This was caused amount of active site and empty pore still many available onto adsorbent surface. Adsorption capacity progressively increased from 53 to 80% within duration contact time 10 to 480 min. The Cu^{2+} ion adsorption achieves 91% when the adsorption process was done for 720 min. The Cu^{2+} ion adsorption capacity achieves 98% after the adsorption process was carried out around 1440 min. The increasing of Cu^{2+} ion adsorption capacity very small (~7%) within duration of contact time from 720 to 1440 min, this condition is indicated that the adsorption process of Cu^{2+} ion reaches equilibrium.

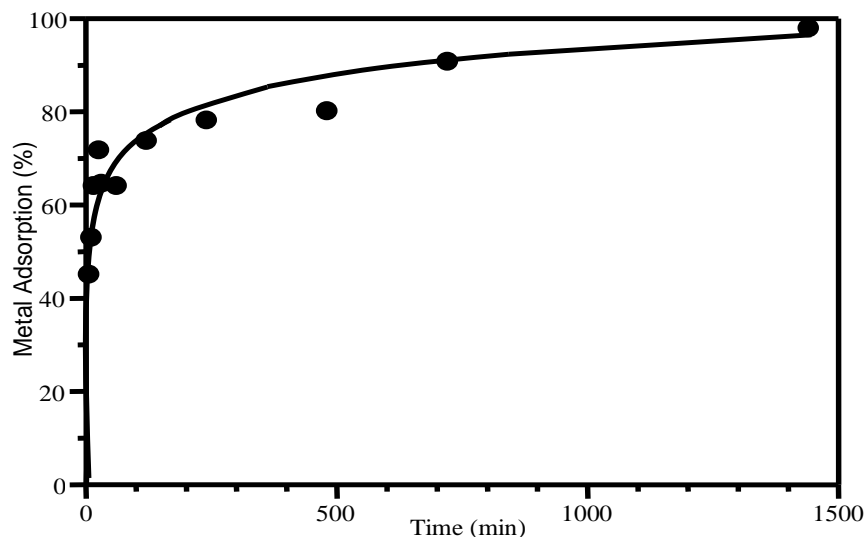


Fig. 6. Metal adsorption of Ca-Al/CFB-500

The graph of the effect solution pH on Cu^{2+} ion adsorption was shown in Fig. 7. The experiments were carried out in Cu^{2+} ion solution (100 mg/L; 50 mL) with 0.5 g Ca-Al/CFB-500 adsorbent at room temperature with duration of contact time 1 h at different pH solution (pH 1 ~ 6). The Cu^{2+} ion adsorption process was unaffected in the pH range of 3 – 6. Adsorption at pH less than 3 was not favorable as the excess H^+ ion may have caused competition in absorption between the positively charged sites (H^+) and the Cu^{2+} ion [13]. The effect of solution pH more than 7 was not done due to Cu^{2+} ion in base solution will be precipitated to be $\text{Cu}(\text{OH})_2$.

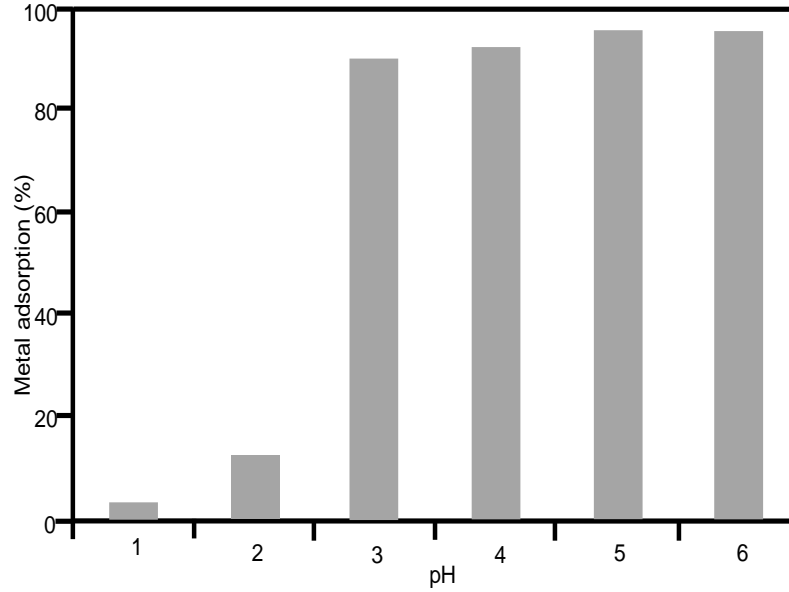


Fig. 7. The effect of pH to Metal adsorption

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

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \quad (3)$$

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} . Base on the value of the experimental q_e (90.864 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]:

$$t/q_t = 1/(k_2 \times q_e^2) + t/q_e \quad (4)$$

where k_2 is the rate constant of second order rate Cu^{2+} ion adsorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$). The plotting t/q_t vs t which 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 linear plot. This shows that the adsorption of Cu^{2+} ion onto Ca-Al/CFB-500 adsorbent follow a second order reaction.

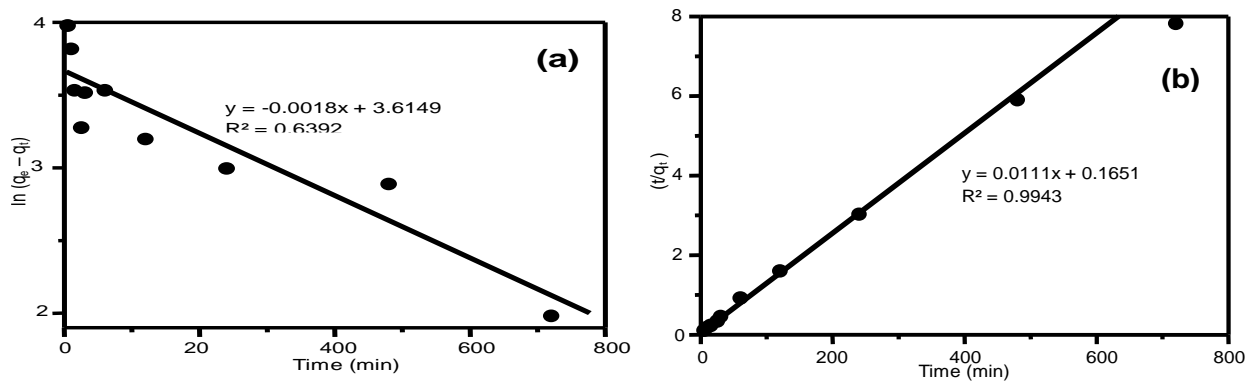


Fig. 8. (a) Pseudo first order of metal adsorption of Ca-Al/CFB-500, (b) Pseudo second order of metal adsorption of Ca-Al/CFB-500

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]:

$$\log q_e = \log k_f + (1/n) \log C_e \quad (5)$$

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 $n > 1$, so can be concluded the adsorption Cu^{2+} ion onto Ca-Al/CFB-500 adsorbent was effective.

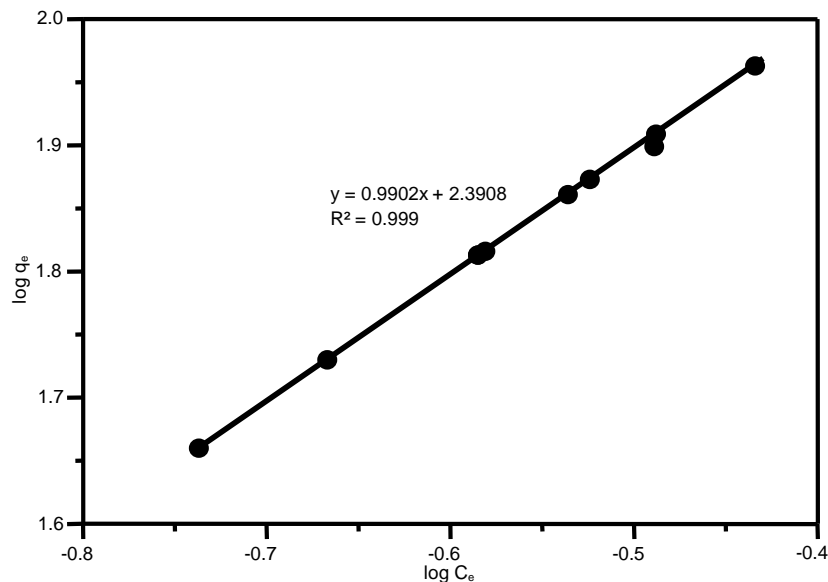


Fig. 9. Fitting adsorption with Freundlich isotherm

CONCLUSIONS

Fish bones are abundant available as by-product waste from the fish processing industry. In this study, fish bones were modified to be carbon and supported with calcium and aluminium. Carbon-derivate fish bones supported calcium and aluminium (Ca-Al/CFB-500) can be used as sorbent to remove heavy metal. The adsorption capacity was investigated as a function contact time and pH. The results of this research showed that Ca-Al/CFB-500 can be promoted as adsorbent for removing Cu^{2+} ion from solution. The highest removal capacity Cu^{2+} ion was reached 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 adsorption of Cu^{2+} ion onto Ca-Al/CFB-500 was effective and follows the pseudo second order model.

ACKNOWLEDGEMENTS

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REFERENCES

1. M. Nurhadi, R. Kusumawardani, I.I. Widiyowati, Wirhanuddin, H. Nur, Utilization of fish bone as adsorbent of Fe³⁺ ion by controllable removal of its carbonaceous component, *J. Physics: Conf. Series*, 1022, 2018, 012031
2. H. K. Lima, Hasan, T. T. Tenga, M. H. Ibrahima, A. Ahmad, H. T. Chee, Adsorption and Removal of Zinc (II) from Aqueous Solution Using Powdered Fish Bones, *APCBEE Procedia* 1, 2012, 96 – 102.
3. E. M. Zayeda, H.H. Sokkerb, H. M. Albishric, A. M.Faragd, Potential use of novel modified fishbone for anchoring hazardous metal ions from their solutions *Ecol. Eng.* 61, 2013, 390–393.
4. B. Kizilkaya, A. A. Tekinay, Y. Dilgin, Adsorption and removal of Cu (II) ions from aqueous solution using pretreated fish bones, *Desalination*, 264, 2000, 37–47.
5. S. Milicevic, T.B., S. Martinovic , M. Vlahovic , and B.B. Vladan Milosevic. Removal of copper from aqueous solutions by low cost adsorbent-Kolubara lignite, *Fuel Process. Technol.*, 95, 2012, 1–7.
6. S. Larous , A-H. Meniai, Removal of Copper (II) from Aqueous Solution by Agricultural By-Products Sawdust, *Energy Procedia* 18, 2012, 915 – 923
7. A.K. Mona Karnib, H. Holail, Z. Olama, Heavy Metals Removal Using Activated Carbon, Silica and Silica Activated Carbon Composite, *Energy Procedia*, 50, 2014, 113 – 120.

8. L. Wang, Application of activated carbon derived from 'waste' bamboo culms for the adsorption of azo disperse dye: kinetic, equilibrium and thermodynamic studies, *J. Environ. Manage.*, 102, 2012, 79 - 87.
9. R. Donat, A. Akdogan, E. Erdem, H. Cetisli, Thermodynamics of Pb²⁺ and Ni²⁺ adsorption onto natural bentonite from aqueous solutions, *J. Colloid Interface Sci.* 286, 2005, 43–52.
10. R. Chakraborty, D. Roy Chowdhury, Fish bone derived natural hydroxyapatite-supported copper acid catalyst: Taguchi optimization of semibatch oleic acid esterification. *Chem. Eng. J.*, 215–216, 2013, 491–499.
11. S. Patel, J. Han, W. Qiu, W. Gao, Synthesis and characterisation of mesoporous bone char obtained by pyrolysis of animal bones, for environmental application. *J. Environl. Chem. Eng.*, 3, 2015, 2368–2377.
12. M. Nurhadi, Modification of Coal Char-loaded TiO₂ by Sulfonation and Alkylsilylation to Enhance Catalytic Activity in Styrene Oxidation with Hydrogen Peroxide as Oxidant, *Bull. Chem. React.Eng. Catal.*, 12(1), 2017, 55-61.
13. M. Nurhadi, I.I. Widiyowati, Wirhanuddin, S. Chandren, Kinetic of Adsorption Process of Sulfonated Carbon-derived from *Eichhornia crassipes* in the Adsorption of Methylene Blue Dye from Aqueous Solution, *Bull. Chem. React.Eng. Catal.*, 14(1), 2019, 17-27.
14. W. C. Wanyonyi, J.M. Onyari, P.M. Shiundu, Adsorption of Congo Red Dye from Aqueous Solution Using Roots of *Eichhornia Crassipes*: Kinetic and Equilibrium Studies *Energy Procedia*, 50, 2014, 862-869.

ICoSMEE Publication : Category A

List of papers that will be proposed to the Journal of Chemical Engineering and Metallurgy (JCTM)

No.	First Author	Title
1	Cindy Claudia Christanti	Effect Of Methyl-Tributyl-Ammonium Methyl Sulphate Addition On Hardness And Corrosion Resistance Of Ni-W Alloy
2	Tarmizi Taher	Adsorption Behavior Of Cr (VI) From Aqueous Solution By Fe-pillared Acid Activated Indonesian Bentonite
3	Endang Susilowati	Synthesis Of Colloidal Silver Nanoparticles Assisted By Microwave Irradiation And Their Stability During Storage
4	Witri Wahyu Lestari	Green Synthesis Of Composite Material MIL-100(Fe)/Indonesian Active Natural Zeolite (ANZ) As Enhanced CO ₂ Capture Material
5	Mela Yuliyanti	Development Of Antiseptic Liquid Detergent Using The Mahogany Seed Extract (Swietenia Mahagoni) As A Foaming Agent And Antibacterial Substance
6	Mohammad Masykuri	Characteristic Morphology Surface and Biodegradation Test of Composite Rigid Foam Polyurethane/Clay
7	Mukhamad Nurhadi	Removal Of Cu (II) Ions From Aqueous Solution Using Carbon Derived Fishbone Supported Calcium And Aluminum
8	Andi Haryanto	Photocatalytic Activity Of CuBDC And UiO-66 MOFs For Methyl Orange Degradation
9	Jaidan Jauhari	Synthesis And Characteristics Of Polyacrylonitrile (PAN) Nanofibrous Membrane Using Electrospinning Method
10	Ashadi	The Removal of Organic Pollutant from Aqueous Solution by Modified Activated Carbon Surface
11	Durrotunnisa Fathia Rahma	Hydrophilicity Test Of Zinc Oxide Nanoparticle Using Xilene-Water For Ibuprofen Adsorption Study
12	Moh Ali Khafidhin	Novel Mixed Matrix Membranes Based on Polyethersulfon and MIL-96(Al) For CO ₂ Gas Separation
13	Lina Mahardiani	One Pot Synthesis Of Carboxylated Activated Carbon For Water Purification: A Kinetic Study
14	Sri Mulyani	The Effect Of NPK Fertilizer Amount On The Quality Of Super Absorbent Polymer Hydrogel Based Oil Palm Empty Fruit Bunch As An NPK Fertilizer Carrier
15	Neza Rahayu Palapa	Kinetic Aspect of Direct Violet Adsorption on M ₂ ⁺ /M ₃ ⁺ (M ₂ ⁺ : Zn; M ₃ ⁺ :Al,Fe,Cr) Layered Double Hydroxides
16	Sulistyo Saputro	The Usage Of Rice Husk Waste And Natural Zeolite For Pb ²⁺ Adsorbent And It's Analysis Using Solid-phase Spectrophotometry
17	Aldes Lesbani	Preparation Of Ni-Al LDH: Influence Of Intercalated Polyoxometalate Anion (SiW ₁₂ O ₄₀) ₄ - On The Interlayer Gallery Distance

Revision Note

Journal: Journal of Chemical Technology and Metallurgy

Title: **Removal of Cu (II) Ions from Aqueous Solution over Calcium-Aluminium/Carbon-derived Fish Bones**

Manuscript Reference No.:

Reviewer's comments:

p.1

What is the correct name of the adsorbent:

Carbon Derived Fish Bones Supported Calcium and Aluminium (in the title)

or

Carbon-derivate fish bones supported calcium and aluminium (Ca-Al/CFB-500) (in the conclusions)

The abbreviation should be defined in the abstract.

We thank reviewer for your meticulousness in pointing out the inconsistency of the use of the adsorbent name and its denotation.

Herein, we decide to adopt this title (with minor amendment), “**Removal of Cu (II) Ions from Aqueous Solution over Calcium-Aluminium/Carbon-derived Fish Bones**”, whilst the abbreviation that will be used throughout the manuscript is **Ca-Al/CFB-500**.

The abbreviation is defined in the abstract and introduction sections. The descriptions are as the followings:

Abstract (Page 1, Line 12-16)

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.

Introduction (Page 3, Line 51-60):

Prompting 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.

p.2

It is difficult to follow the text because of the language. Example: *'This was caused amount of active site and empty pore still many available onto adsorbent surface'*.

Adsorption capacity is usually defined as mg/g adsorbent, not as %.

Please, consider the paragraphs: ‘The amount of metal adsorption’ (eq.1), ‘where q_a and q_t are the amount of Cu^{2+} ion adsorbed (mg g^{-1})’ (eq.3), ‘adsorption capacity of 46%’ (in the text after Fig.5).

The amount of adsorption capacity is re-calculated with mg g^{-1} as the unit. Below is the description for Figure 6 (Page 10, Line 151-159).

The effect of contact time on the removal of Cu^{2+} ion onto Ca-Al/CFB-500 adsorbent is shown in Fig. 6. Adsorbents rapidly adsorbed Cu^{2+} ion within the first 5 min of contact time with adsorption capacity of 45.8 mg g^{-1} . This is because there are plentiful of active sites and empty pores available on adsorbent surface. Adsorption capacity progressively increased from 53.8 to 79.3 mg g^{-1} within duration contact time 10 to 480 min. The Cu^{2+} ion adsorption achieved 92 mg g^{-1} when the adsorption process was done for 720 min. The Cu^{2+} ion adsorption capacity achieved 99.3 mg g^{-1} after the adsorption process was carried out around 1440 min. The increasing of Cu^{2+} ion adsorption capacity was negligible ($\sim 7 \text{ mg g}^{-1}$) within duration of contact time from 720 to 1440 min, indicating that the adsorption process of Cu^{2+} ion reached equilibrium.

Many of the sentences are revised and highlighted with yellow colour in the manuscript.

p.3 Please, define the novelty – the adsorbent, the adsorptive properties, in comparison with other adsorbents?

The novelty is described as follows:

Fish bones are widely pretreated with NaOH, H₂O, H₂O₂, HNO₃ and C₂H₅OH as to increase their surface functionality in capturing the pollutants, however, those alkaline and acidic pre-treatments are not much assisting the adsorptive capability. It is because these pre-treated fish bones acquire long duration the pollutants removal process.

Due to this shortcoming, we would like to close the gap by synthesizing a composite material with high surface area and good adsorptive capability. Herein, we proposed to impregnate fish bone with both calcium (Ca) and aluminium (Al) onto carbon-derived fish bones that carbonized at 500 °C (Ca-Al/CFB-500). The encapsulation of Ca and Al onto carbonized 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.

p.6 I recommend addition of text concerning p.3

We do agree to add some description in the paragraph of page no.3 as to enhance the readable quality. In previous manuscript, the synthesis method might not be presented concisely, withal, the problem statement and novelty might be vague as well. Thus, we put in our efforts to give a comprehensive and informative descriptions as below **Page 3, Line 45-60**:

On that account, elimination of Cu (II) ions from aqueous solution over a variety of adsorbents have been investigated by several researches. Those adopted adsorbents used are comprised of pretreated fish bones [4], Kolubara lignite [5], agricultural by-products sawdust [6], activated carbon, silica, activated carbon composites, and so forth [7]. Despite of the fish bones were pretreated with NaOH, H₂O, H₂O₂, HNO₃ and C₂H₅OH, they are not efficient to act as adsorbents thus far as its long duration during the adsorption process.

Prompting 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 encapsulation of Ca and Al onto fish bones aims to increase the surface area and adsorption capacity by forming CaO and Al₂O₃ onto carbon-derived fish bones via the calcinations process. Worth noting that Cu(II) adsorptive equilibrium could be achieved in a shorter time duration over Ca-Al/CFB-500. The characterizations of adsorbent from carbon-derived fish bones impregnated calcium and aluminum were investigated using XRD, IR spectroscopy, SEM, TG analysis and N₂ adsorption-desorption. The removal process was checked by using the kinetic models and adsorption isotherms.

p.7 I recommend shortening or better formulation of the text in the Introduction

The suggestion is taken with high appreciation. We do hope that the flow of ideas is clearly stated and at ease of reading now. The sentences re-structuring is made for the whole passage in the introduction section. We have adopted the inverted pyramid style of writing to convey the main idea of our research work.

Firstly, we introduce several kinds of heavy metals and their potential risks to human beings, thus many attempts have been adopted to remove those heavy metals, including Cu(II). Next, in spite of many types of removal processes have been adopted, adsorption is frequently adopted due to its simple operation, low costs, easy of handling, and high efficiency. It is succeeded by introducing some adsorbents and fish bone is one of them. However, fish bone is low in adsorption efficiency, thus urging our research group to working on it to improve the Cu(II) removal efficiency using our adsorbent, *i.e.* Ca and Al impregnation onto carbon-derived fish bone calcined at 500 °C, denoted as Ca-Al/CFB-500.

Please refer to introduction at [Page 2-3, Line 28-60](#).

p.8. The English writing is with very different quality in the different paragraphs of the paper. Example for a bad quality is the following:

'Many kind of essential heavy which highly soluble in water at pH less than 5 and to be dangerous to a human when excess such as copper (Cu), ferum (Fe), nickel (Ni), zinc (Zn), and manganese (Mn). In the human body, copper (Cu) element very fast entrance into the blood circulation and distributed to the whole body'

We apologize for the quality presented previously and now, we try to improve it to a better one, as shown in the following paragraph

[Page 1, Line 29-36].

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

1 **Removal of Cu (II) Ions from Aqueous Solution over Calcium-Aluminium/Carbon-derived**
2 **Fish Bones**

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10
11 **ABSTRACT**

12 In this research, removal of Cu(II) ion was investigated using the adsorption process, which is
13 widely known as simple operation, low cost, and high efficiency. Therefore, we have designed
14 an adsorbent with the aim to increase its surface area and adsorptive capability. Calcium and
15 aluminium were impregnated onto fish bones that were carbonized at 500 °C for an hour, which
16 is denoted as Ca-Al/CFB-500. The performance of Ca-Al/CFB-500 adsorbent to adsorb Cu²⁺
17 ion from solution was measured. The chemical and physical properties of Ca-Al/CFB-500
18 adsorbent were investigated by using X-ray diffraction (XRD), Infrared (IR) spectroscopy, N₂
19 adsorption-desorption, scanning electron microscopy (SEM) and Thermogravimetric (TG)
20 analysis. The Ca-Al/CFB-500 adsorbent are effective to act as an adsorbent for removing Cu²⁺
21 ion from solution, whereby the removal efficiency reached 98% after 1440 min. The removal
22 of Cu²⁺ ion from solution by Ca-Al/CFB-500 adsorbent was influenced by pH condition,

23 especially the pH less than 3. It is noticed that the removal of Cu^{2+} ion onto Ca-Al/CFB-500
24 follows the pseudo second order model.

25 Keywords: adsorption, removal Cu^{2+} ion, carbon-derived fish bone support, pseudo second
26 order model

27

28 INTRODUCTION

29 The metal elements, which have density greater than 5 g cm^{-3} and high molecular weight, are
30 well recognized as heavy metals. Numerous heavy metals, especially those highly soluble in water
31 ($\text{pH} < 5$), could cause human health issues when excess use of copper (Cu), ferum (Fe), nickel (Ni),
32 zinc (Zn), and manganese (Mn). Generally, those soluble heavy metals undergo very fast entrance
33 into the blood circulation system and then, they are thoroughly distributed to the whole body. The
34 excess use of the heavy metals in the human body can cause the following unpleasant effects,
35 including vomiting, diarrhea, abdominal cramps, nausea, liver damage, kidneys damage and more
36 seriously, leading to death [1].

37 Since Cu(II) ions are also leading to those adverse effects, thus many attempts have been taken
38 to resolve Cu (II) ions in water resources and wastewater, for examples, membrane filtration,
39 ultrafiltration, ion exchange, solvent extraction, complexation, adsorption, coagulation,
40 phytoextraction, chemical precipitation, chemical oxidation or reduction, evaporation and reverse
41 osmosis. Adsorption method is the most often used by researchers due to it is simple, low cost,
42 easy of handling, and high efficiency. On the contrary, other methods might require a lot of
43 reagents, high energy intensification, incomplete metal release, low selectivity, high operational
44 costs and not being environmentally friendly [2, 3].

45 On that account, elimination of Cu (II) ions from aqueous solution over a variety of adsorbents
46 have been investigated by several researches. Those adopted adsorbents used are comprised of
47 pretreated fish bones [4], Kolubara lignite [5], agricultural by-products sawdust [6], activated
48 carbon, silica, activated carbon composites, and so forth [7]. Despite of the fish bones were
49 pretreated with NaOH, H₂O, H₂O₂, HNO₃ and C₂H₅OH, they are not efficient to act as adsorbents
50 thus far as its long duration during the adsorption process.

51 Prompting by the aforementioned limitation, we have taken a step further to improve the
52 efficiency of fish bone adsorbent by impregnating calcium (Ca) and aluminium (Al) onto carbon-
53 derived fish bones that carbonized at 500 °C. The prepared adsorbent is denoted as Ca-Al/CFB-
54 500 and this abbreviation will be used throughout the manuscript. The encapsulation of Ca and Al
55 onto fish bones aims to increase the surface area and adsorption capacity by forming CaO and
56 Al₂O₃ onto carbon-derived fish bones via the calcinations process. Worth noting that Cu(II)
57 adsorptive equilibrium could be achieved in a shorter time duration over Ca-Al/CFB-500. The
58 characterizations of adsorbent from carbon-derived fish bones impregnated calcium and aluminum
59 were investigated using XRD, IR spectroscopy, SEM, TG analysis and N₂ adsorption-desorption.
60 The removal process was checked by using the kinetic models and adsorption isotherms.

61

62 **EXPERIMENTAL**

63 **Materials**

64 The waste of Belida fish bones were collected from many company around Samarinda, East
65 Kalimantan, Indonesia. The fish bones were washed with boiling water until free of impurities.
66 The fish bones dried in an oven at 110 °C for 24 hours. Furthermore, it was dried in an oven at 110
67 °C for 24 hours and make it powder (100 mesh) by crushing and sieving. The fish bones powder

68 (FB) was impregnated by calcium and aluminium (1000 μmol) and then it was carbonized (500
69 $^{\circ}\text{C}$, 1 h) in a furnace. The results are labeled Ca-Al/CFB-500.

70

71 **Adsorbate**

72 The stock of Cu^{2+} ion (1000 mgL^{-1}) was prepared by using $\text{Cu}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ (Merck)
73 compound which was dissolved in distilled water. The stock solution was use to prepare another
74 concentration of Cu^{2+} ion.

75

76 **Characterizations**

77 The characterization of the sample was determined by using XRD, FTIR, SEM, TGA and N_2
78 adsorption-desorption test. The crystallinity of the sample was investigated base on XRD pattern
79 which recorded with a Bruker AXS Advance D8 diffractometer using $\text{Cu K}\alpha$ radiation
80 ($\lambda = 1.5405 \text{ \AA}$, 40 kV and 40 mA). The Shimadzu IR spectrometer was used to record spectra of
81 the functionalize groups in the samples. The surface morphology of the samples was investigated
82 by using SEM instrument (JEOL JSM-6701F, 15 kV). The amount of carbon in the samples were
83 determined by using TG Analysis (STA Linseis PT1600) with heat rate $10 \text{ }^{\circ}\text{C min}^{-1}$ and target
84 temperature $900 \text{ }^{\circ}\text{C}$. The surface area and pore size distribution of the samples were calculated
85 base on N_2 adsorption-desorption data at 77 K (Quantachrome 11.0).

86

87 **Batch Adsorption Studies**

88 The adsorbent (0.5 g) was contacted with Cu^{2+} ion solution (50 mL , 100 mgL^{-1}) in 250 mL
89 Erlenmeyer flasks at room temperature under stirring for duration time of 5, 10, 15, 30, 60, 120,
90 240, 480, 720 and 1440 min. The solid adsorbent and filtrate was separated by using centrifugation

91 process. The Cu^{2+} ion in filtrate was detected by using Atomic absorption Spectrophotometric
92 analysis (Analysis 200 AA, Perkin Elmer, USA). The range of 1.0 – 6.0 of pH which prepared by
93 mixing 0.1 M HCl and 0.1 M NaOH was used to investigate the effect of pH in metal ion removal
94 process. The amount of metal adsorption in the adsorbent was determined by the equation[8]:

95
$$\text{Metal adsorption (\%)} = \frac{(C_i - C_f)}{C_i} \quad (1)$$

96 where C_i is initial concentration and C_f is final concentration in the solution [9].

97

98 **RESULT AND DISCUSSION**

99 Fig. 1 shows the XRD pattern of Ca-Al/CFB-500. The peak positions at $2\theta = 25.9, 31.8, 39.8,$
100 $46.8, 49.6, 53.4$ and 64.4 indicated that the crystalline phase of hydroxyapatite dominated onto the
101 sample [10]. The average size of hydroxyapatite crystal is calculated by using the Debye-Scherrer
102 equation[11]:

103
$$T = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \quad (2)$$

104 where T is the average of crystal size, K is the shape factor (0.9), λ is the X-ray wavelength
105 (0.15406 nm), β is the line broadening at full width at half maximum (FWHM = 0.002651) on the
106 $2\theta = 31.224$ scale in radians and θ is the Bragg angle of the peak in degrees. The average crystal
107 size of hydroxyapatite was estimated to be 50.37 nm.

108

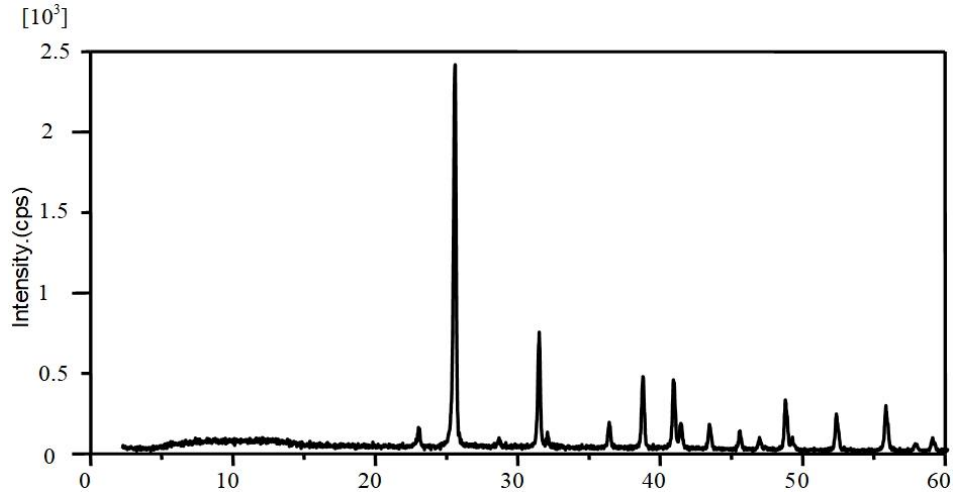


Fig. 1. XRD pattern of Ca-Al/CFB-500

109

110

111

112 The functional groups onto CFB-500 and Ca-Al/CFB-500 surface are shown by IR spectra in

113 Fig. 2. The O–H stretching mode, which correlated adsorbed water in the sample, appeared at both

114 spectra with broad peak at around 3436 cm^{-1} and 1632 cm^{-1} [12]. The peaks at around 2925 and

115 2851 cm^{-1} , which indicated as the absorption of organic material as C–H group symmetric and

116 asymmetric stretching mode, can prove the effect of carbonization process. The carbonate ion

117 substitution in the sample was shown by the absorption peak at around 2129 and 877 cm^{-1} [9]. And

118 the phosphate groups on the sample were showed by the peak at around 679 and 591 cm^{-1} . The

119 carbonate ion and the phosphate groups indicate the hydroxyapatite in the sample.

120

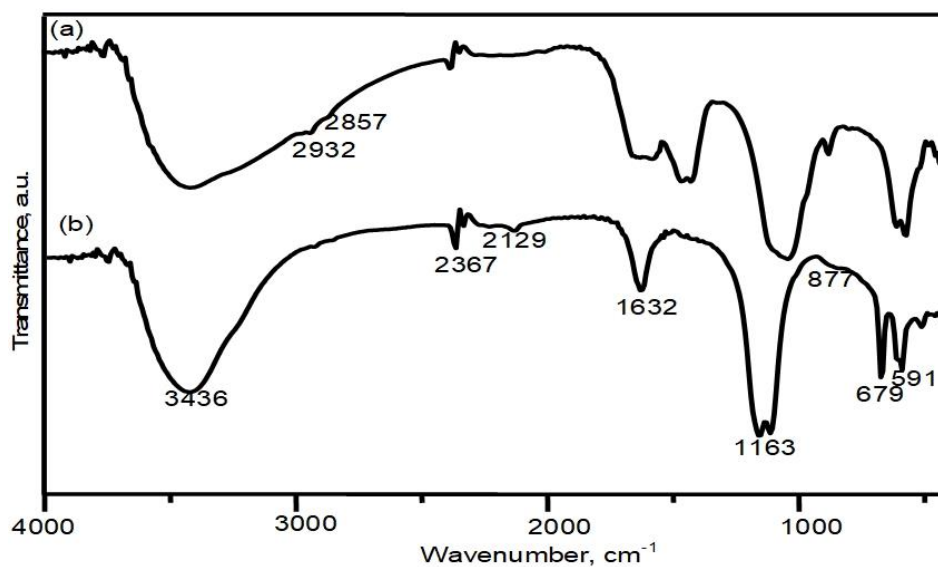
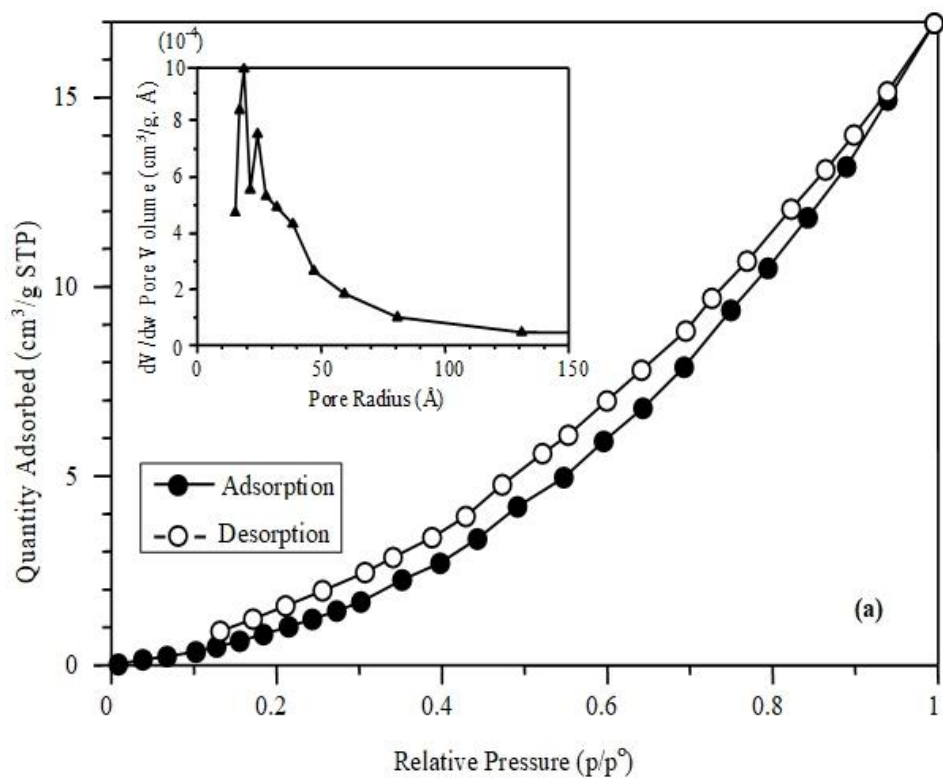


Fig. 2. IR spectra of of: (a) CFB-500 and (b) Ca-Al/CFB-500

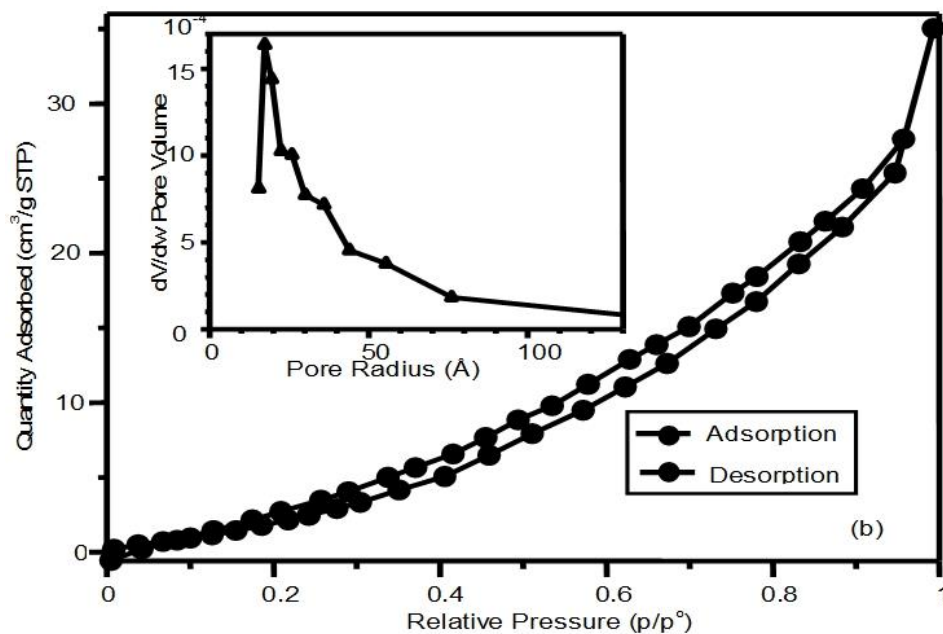
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129

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 of the samples were 17 Å, 0.029 cc/g and 16.0 m²/g for FB and 17.3 Å, 0.061 cc/g and 26.9 m²/g for Ca-Al/CFB-500, respectively.



130

131



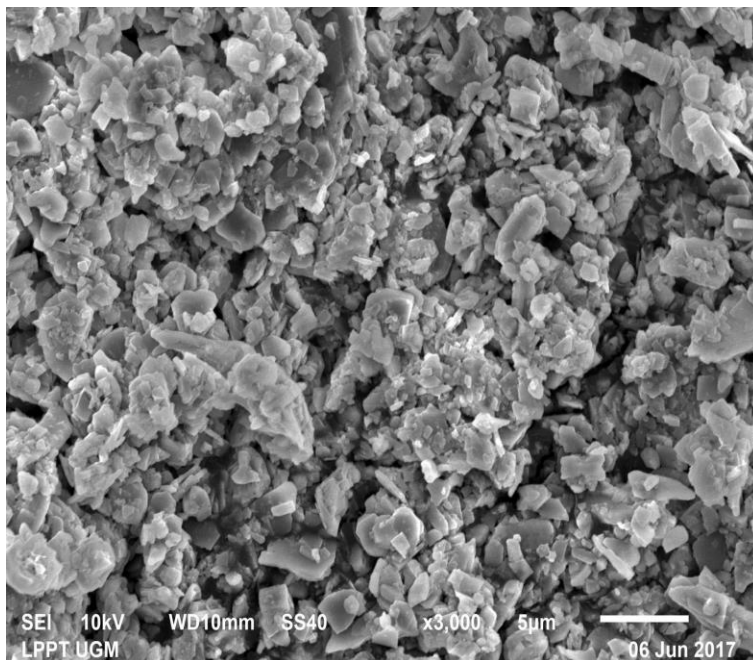
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133 **Fig. 3.** The types of physisorption isotherms and pore size distribution of: (a) FB and (b) Ca-

134

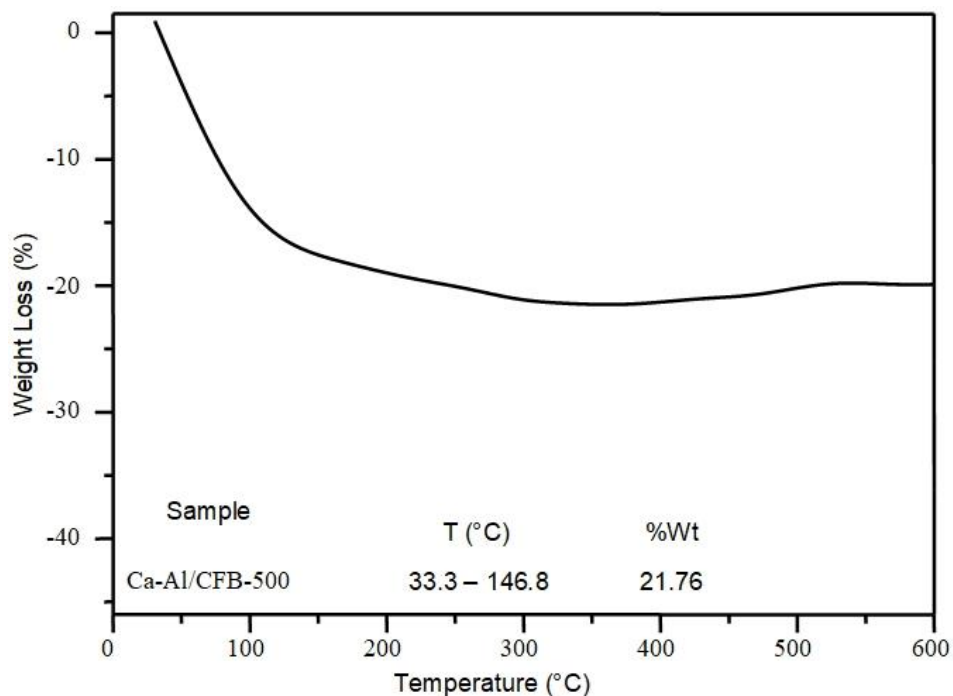
Al/CFB-500

135 The surface morphology of Ca-Al/CFB-500 was investigated based on the SEM image in Fig.
136 4. The surface morphology of Ca-Al/CFB-500 has roughness surfaces and splinters shape.
137



138
139 **Fig. 4.** SEM image of Ca-Al/CFB-500

140
141 The TG analysis curve of Ca-Al/CFB-500 was shown in Fig. 5. The weight losses of the
142 sample were shown in **two-step** temperature ranges. The TG analysis displayed a drastically weight
143 loss ~ 21.76% in the temperature range 33.3 – 146.8 °C (first step) which indicated with the
144 evaporation of the water adsorbed on samples. In the temperature range 200 – 500 °C (second
145 step), the weight loss 2.0% which caused by the decomposition of organic compounds. The carbon
146 contain in the sample also can be determined by the weight loss percentage in the second step.
147



148

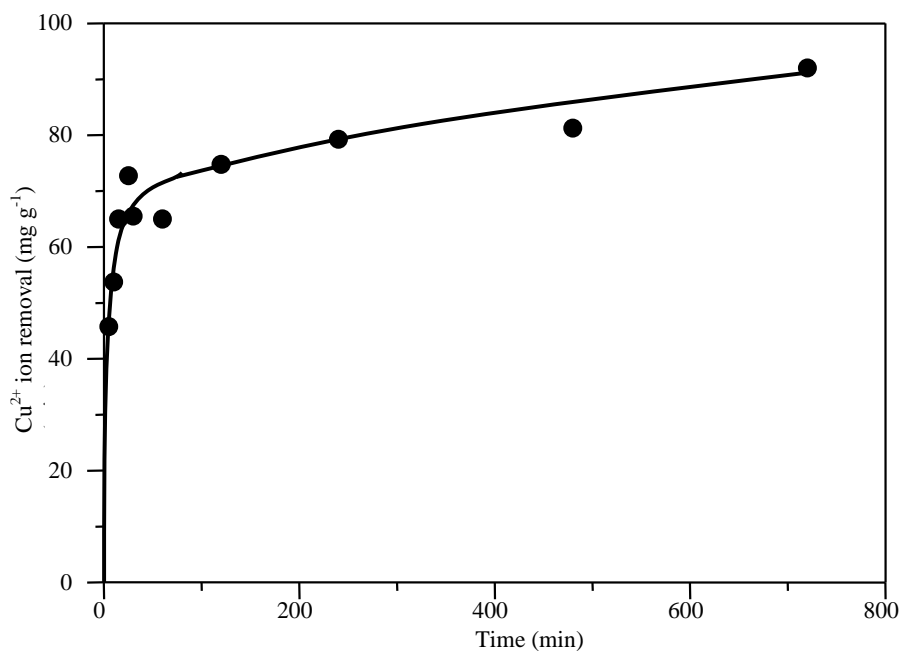
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Fig. 5. Ca-Al/CFB-500 thermogravimetric (TG) curve

150

151 The effect of contact time on the removal of Cu^{2+} ion onto Ca-Al/CFB-500 adsorbent is shown
 152 in Fig. 6. Adsorbents rapidly adsorbed Cu^{2+} ion within the first 5 min of contact time with
 153 adsorption capacity of 45.8 mg g^{-1} . This is because there are plentiful of active sites and empty
 154 pores available on adsorbent surface. Adsorption capacity progressively increased from 53.8 to
 155 79.3 mg g^{-1} within duration contact time 10 to 480 min. The Cu^{2+} ion adsorption achieved 92 mg
 156 g^{-1} when the adsorption process was done for 720 min. The Cu^{2+} ion adsorption capacity achieved
 157 99.3 mg g^{-1} after the adsorption process was carried out around 1440 min. The increasing of Cu^{2+}
 158 ion adsorption capacity was negligible ($\sim 7 \text{ mg g}^{-1}$) within duration of contact time from 720 to
 159 1440 min, indicating that the adsorption process of Cu^{2+} ion reached equilibrium.

160



161

162

Fig. 6. Cu²⁺ ion removal of Ca-Al/CFB-500

163

164 The effect of pH solution on Cu²⁺ ion removal was shown in graph in Fig. 7. The experiments
 165 of the effect pH were carried out in Cu²⁺ ion solution (100 mg/L; 50 mL) with 0.5 g Ca-Al/CFB-
 166 500 adsorbent at room temperature with duration of contact time 1 h at different pH solution (pH
 167 1 ~ 6). The Cu²⁺ ion adsorption process was unaffected in the pH range of 3 – 6. Absorption at pH
 168 less than 3 was not favorable as the excess H⁺ ion may have caused competition in absorption
 169 between the positively charged sites (H⁺) and the Cu²⁺ ion [13]. The effect of solution pH more
 170 than 7 was not done due to Cu²⁺ ion in base solution will be precipitated to be Cu(OH)₂.

171

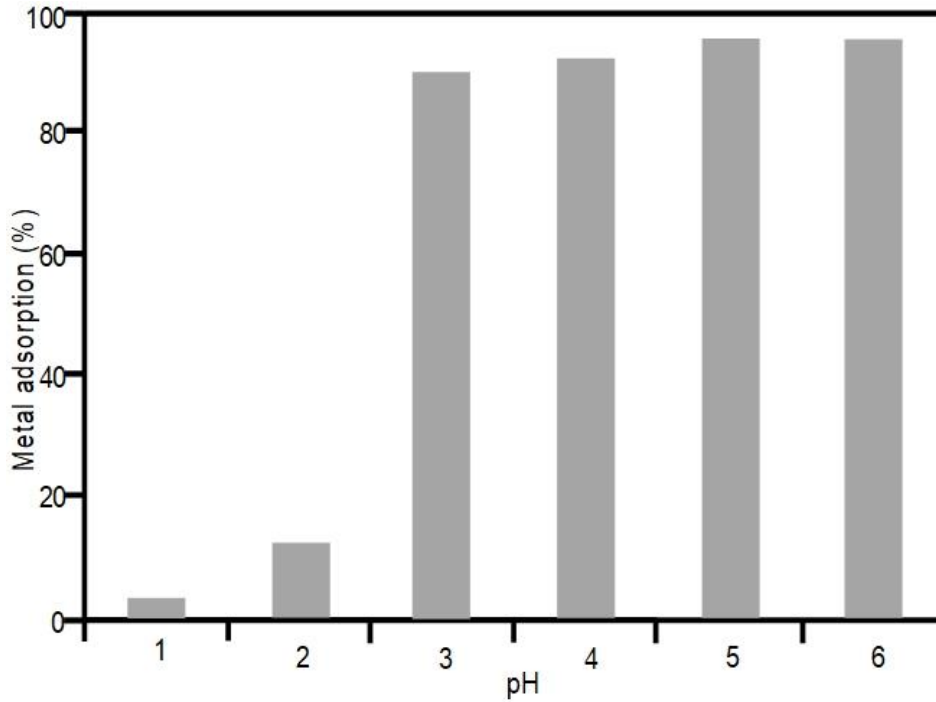


Fig. 7. The effect of pH to Cu^{2+} ion removal

172
173

174

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

$$177 \ln(q_e - q_t) = \ln q_e - k_1 \cdot t \quad (3)$$

178 where q_e and q_t are the amount of Cu^{2+} ion adsorbed (mg g^{-1}) at equilibrium and at time t (min),

179 and k_1 is the rate constant of first order rate Cu^{2+} ion adsorption (min^{-1}). The slope of plot of

180 $\ln(q_e - q_t)$ versus t which shown in Fig. 8(a), was used to calculate the linear relationship (R^2),

181 k_1 , and q_e such as 0.6392, 0.0018 min^{-1} and 37.148 mg g^{-1} . Base on the value of the experimental

182 q_e (90.864 mg g^{-1}) does not agree with the calculated value obtained from linear plot.

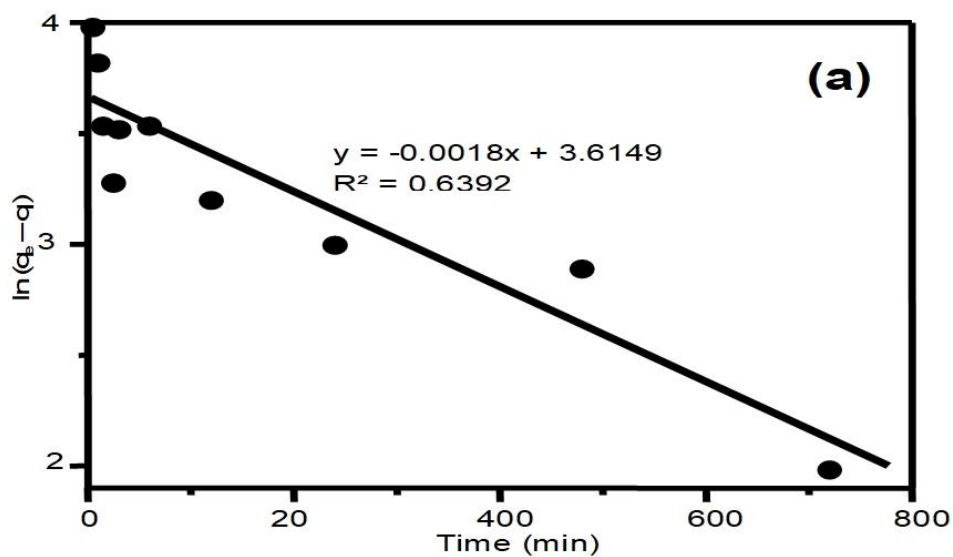
183 The adsorption rate constant of the second order rate also was tested by the Lagergren which

184 the equation was expressed as follows[14]:

$$185 t/q_t = 1/(k_2 \times q_e^2) + t/q_e \quad (4)$$

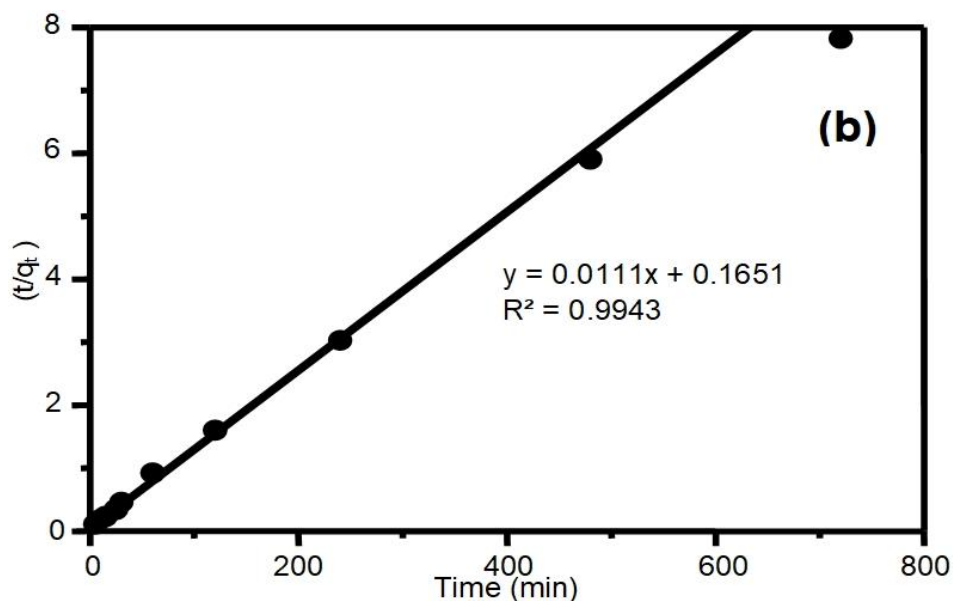
186 where k_2 is the rate constant of second order rate Cu^{2+} ion adsorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$). The plotting
187 t/q_t vs t which shown in Fig. 8(b) was used to calculate the value of the linear relationship ($R^2=$
188 0.9943), k_2 (0.0007) and q_e (90.09 mg g^{-1}) of the second order kinetics. The experimental q_e
189 (90.864 mg g^{-1}) showed good agreement with the calculated value obtained from linear plot. This
190 shows that the adsorption of Cu^{2+} ion onto Ca-Al/CFB-500 adsorbent follow a second order
191 reaction.

192



193

194



195
 196 **Fig. 8.** (a) Pseudo first order of metal adsorption of Ca-Al/CFB-500, (b) Pseudo second order of
 197 metal adsorption of Ca-Al/CFB-500
 198

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

$$201 \log q_e = \log k_f + (1/n) \log C_e \quad (5)$$

202 where k_f is the roughly a measure of adsorption capacity and n is the effectiveness indicator of
 203 adsorption. From Fig. 9 can be determined $1/n$ and k_f which calculated from slope and intercept
 204 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
 205 value $n > 1$, so can be concluded the adsorption Cu^{2+} ion onto Ca-Al/CFB-500 adsorbent was
 206 effective.

207

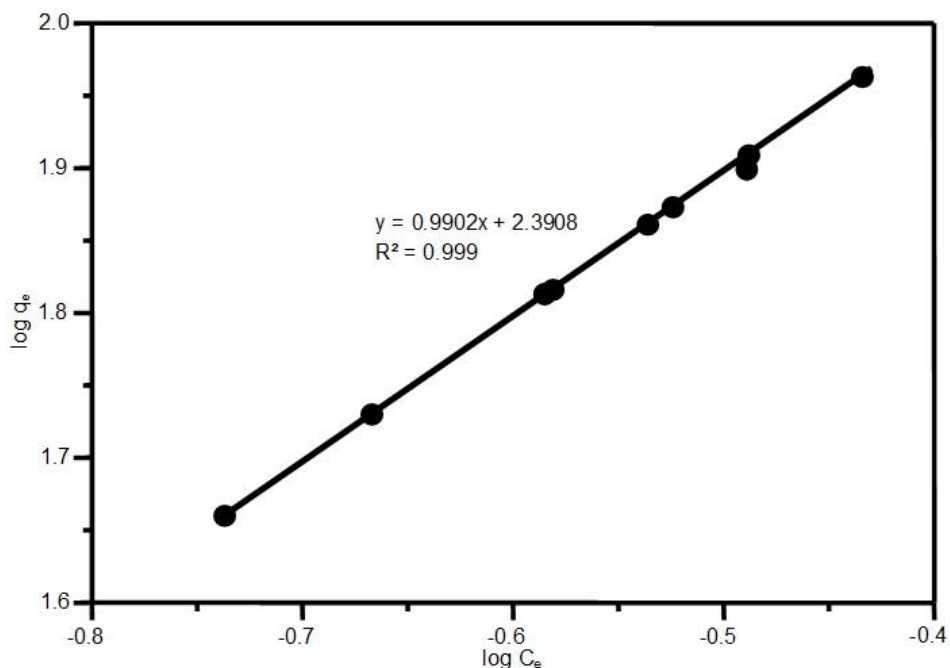


Fig. 9. Fitting adsorption with Freundlich isotherm

208

209

210

211 CONCLUSIONS

212 Fish bones are abundant available as by-product waste from the fish processing industry. In

213 this study, fish bones were **undergone carbonization and impregnated** with calcium and aluminium.

214 **Carbon-derived fish bones impregnated with calcium and aluminium** (Ca-Al/CFB-500) can be

215 used as sorbent to remove heavy metal. The adsorption capacity was investigated as a function

216 contact time and pH. The results of this research showed that Ca-Al/CFB-500 can be used as a

217 good adsorbent for removing Cu²⁺ ion **due to an increase of surface area from 16.0 m²/g to 26.9**

218 **m²/g. Besides,** the highest removal capacity Cu²⁺ ion was reached, **99.3 mg g⁻¹,** after the adsorption

219 process was carried out around 1440 min. The removal Cu²⁺ ion from solution by Ca-Al/CFB-

220 500 adsorbent can be used with high removal capacity by pH condition more than 3. The

221 adsorption of Cu^{2+} ion onto Ca-Al/CFB-500 was effective and follows the pseudo second order
222 model.

223

224 **ACKNOWLEDGEMENTS**

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227 government by Ristekdikti, Indonesia.

228

229 **REFERENCES**

- 230 1. M. Nurhadi, R. Kusumawardani, I.I. Widiyowati, Wirhanuddin, H. Nur, Utilization of fish
231 bone as adsorbent of Fe^{3+} ion by controllable removal of its carbonaceous component, J.
232 Physics: Conf. Series, 1022, 2018, 012031
- 233 2. H. K. Lima, Hasan, T. T. Tenga, M. H. Ibrahima, A. Ahmad, H. T. Chee, Adsorption and
234 Removal of Zinc (II) from Aqueous Solution Using Powdered Fish Bones, APCBEE
235 Procedia 1, 2012, 96 – 102.
- 236 3. E. M. Zayeda, H.H. Sokkerb, H. M. Albishric, A. M.Faragd, Potential use of novel
237 modified fishbone for anchoring hazardous metal ions from their solutions Ecol. Eng. 61,
238 2013, 390–393.
- 239 4. B. Kizilkaya, A. A. Tekinay, Y. Dilgin, Adsorption and removal of Cu (II) ions from
240 aqueous solution using pretreated fish bones, Desalination, 264, 2000, 37–47.
- 241 5. S. Milicevic, T.B., S. Martinovic, M. Vlahovic, B.B. Vladan Milosevic. Removal of copper
242 from aqueous solutions by low cost adsorbent-Kolubara lignite, Fuel Process. Technol., 95,
243 2012, 1–7.

- 244 6. S. Larous , A-H. Meniai, Removal of Copper (II) from Aqueous Solution by Agricultural
245 By-Products Sawdust, *Energy Procedia* 18, 2012, 915 – 923
- 246 7. A.K. Mona Karnib, H. Holail, Z. Olama, Heavy Metals Removal Using Activated Carbon,
247 Silica and Silica Activated Carbon Composite, *Energy Procedia*, 50, 2014, 113 – 120.
- 248 8. L. Wang, Application of activated carbon derived from ‘waste’ bamboo culms for the
249 adsorption of azo disperse dye: kinetic, equilibrium and thermodynamic studies, *J. Environ.*
250 *Manage.*, 102, 2012, 79 - 87.
- 251 9. R. Donat, A. Akdogan, E. Erdem, H. Cetisli, Thermodynamics of Pb²⁺ and Ni²⁺ adsorption
252 onto natural bentonite from aqueous solutions, *J. Colloid Interface Sci.* 286, 2005, 43–52.
- 253 10. R. Chakraborty, D. Roy Chowdhury, Fish bone derived natural hydroxyapatite-supported
254 copper acid catalyst: Taguchi optimization of semibatch oleic acid esterification. *Chem.*
255 *Eng. J.*, 215–216, 2013, 491–499.
- 256 11. S. Patel, J. Han, W. Qiu, W. Gao, Synthesis and characterisation of mesoporous bone char
257 obtained by pyrolysis of animal bones, for environmental application. *J. Environl. Chem.*
258 *Eng.*, 3, 2015, 2368–2377.
- 259 12. M. Nurhadi, Modification of Coal Char-loaded TiO₂ by Sulfonation and Alkylsilylation to
260 Enhance Catalytic Activity in Styrene Oxidation with Hydrogen Peroxide as Oxidant, *Bull.*
261 *Chem. Reac.Eng. Catal.*, 12(1), 2017, 55-61.
- 262 13. M. Nurhadi, I.I. Widiyowati, Wirhanuddin, S. Chandren, Kinetic of Adsorption Process of
263 Sulfonated Carbon-derived from *Eichhornia crassipes* in the Adsorption of Methylene Blue
264 Dye from Aqueous Solution, *Bull. Chem. Reac.Eng. Catal.*, 14(1), 2019, 17-27.

265 14. W. C. Wanyonyi, J.M. Onyari, P.M. Shiundu, Adsorption of Congo Red Dye from Aqueous
266 Solution Using Roots of Eichhornia Crassipes: Kinetic and Equilibrium Studies Energy
267 Procedia, 50, 2014, 862-869.

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269

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, especially the pH less than 3. 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 exam-

ples, 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 characterizations 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 hours. 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 labeled 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 K_α 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 effect of pH on metal ion removal was studied in the range of 1.0 - 6.0 by using 0.1 M HCl and 0.1 M NaOH. The extent of metal removal was determined by the equation [8]:

$$\text{Metal adsorption (\%)} = \frac{(C_i - C_f)}{C_i} \quad (1)$$

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 size of hydroxyapatite crystal is calculated by using the Debye-Scherrer equation[11]:

$$T = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (2)$$

where T is the average of crystal size, K is the shape factor (0.9), λ is the X-ray wavelength (0.15406 nm), β is the line broadening at full width at half maximum (FWHM = 0.002651) on the 2θ = 31.224 scale in radians and θ is the Bragg angle of the peak in degrees. 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

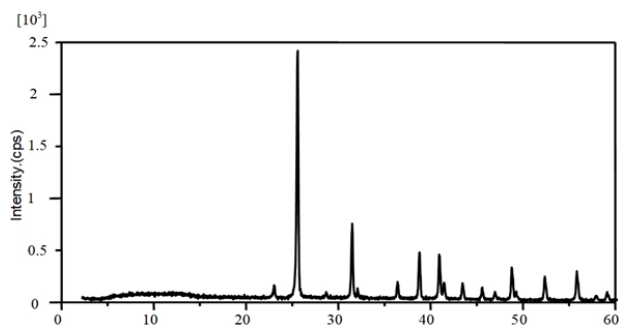


Fig. 1. XRD pattern of Ca-Al/CFB-500.

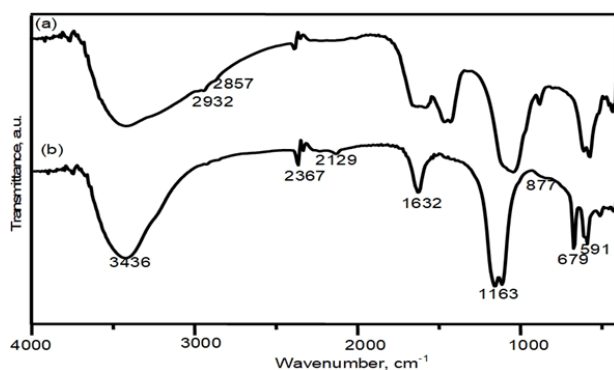


Fig. 2. IR spectra of of: (a) CFB-500; (b) Ca-Al/CFB-500.

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 \AA , 0.029 cc/g and $16.0\text{ m}^2/\text{g}$ for FB and 17.3 \AA , 0.061 cc/g and $26.9\text{ m}^2/\text{g}$ 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 $\sim 21.76\%$ in the temperature range $33.3^\circ\text{C} - 146.8^\circ\text{C}$ (first step) which indicated with the evaporation of the water adsorbed on samples. In

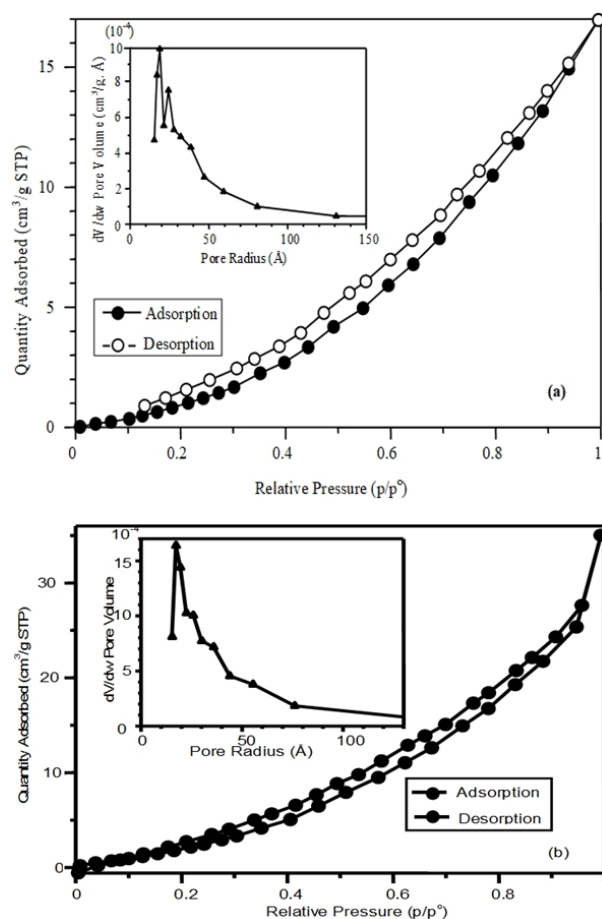


Fig. 3. The types of physisorption isotherms and pore size distribution of: (a) FB; (b) Ca-Al/CFB-500.

the temperature range $200^\circ\text{C} - 500^\circ\text{C}$ (second step), the weight loss of 2.0% is caused by the decomposition of organic compounds. The carbon content in the sample also can be determined by the weight loss percentage in the second step.

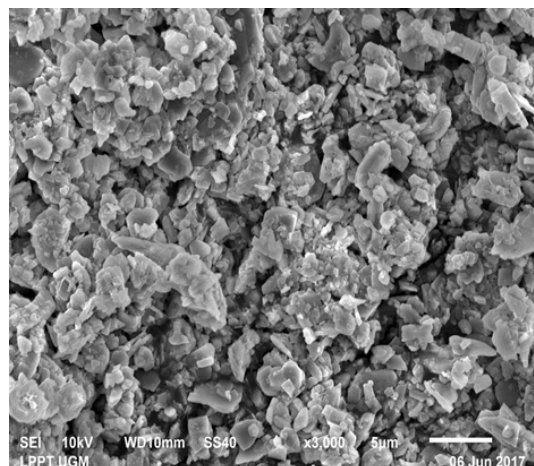


Fig. 4. SEM image of Ca-Al/CFB-500.

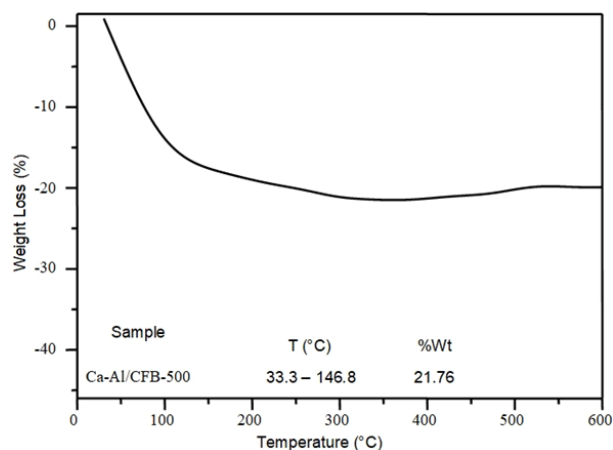


Fig. 5. Ca-Al/CFB-500 thermogravimetric (TG) curve.

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 ($\sim 7 \text{ mg g}^{-1}$) 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

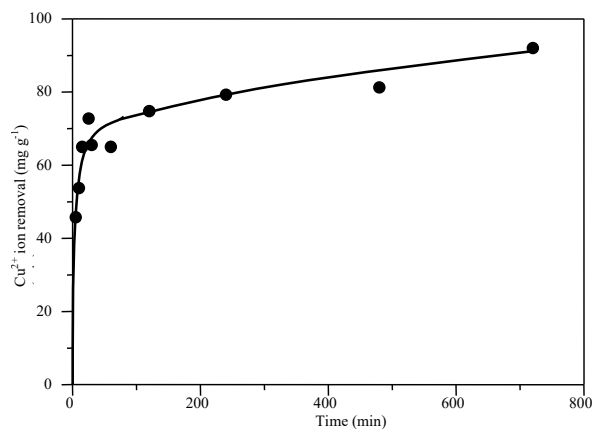


Fig. 6. Cu^{2+} ion removal by Ca-Al/CFB-500.

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. Adsorption at pH less than 3 was not favorable as the excess H^+ ion may cause a competition in adsorption 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]:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \quad (3)$$

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 (90.864 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]:

$$t/q_t = 1/(k_2 \times q_e^2) + t/q_e \quad (4)$$

where k_2 is the rate constant of the second order rate Cu^{2+} ion adsorption ($\text{g mg}^{-1} \text{ min}^{-1}$). 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

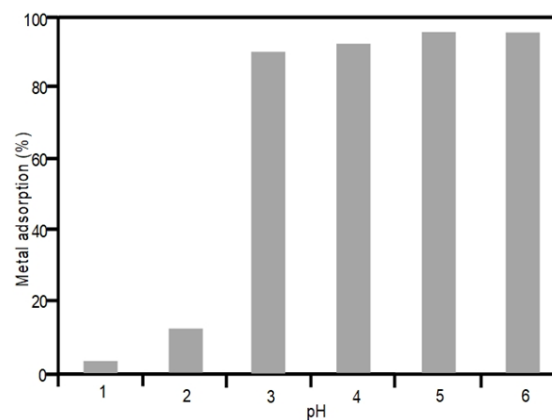


Fig. 7. The effect of pH on Cu^{2+} removal.

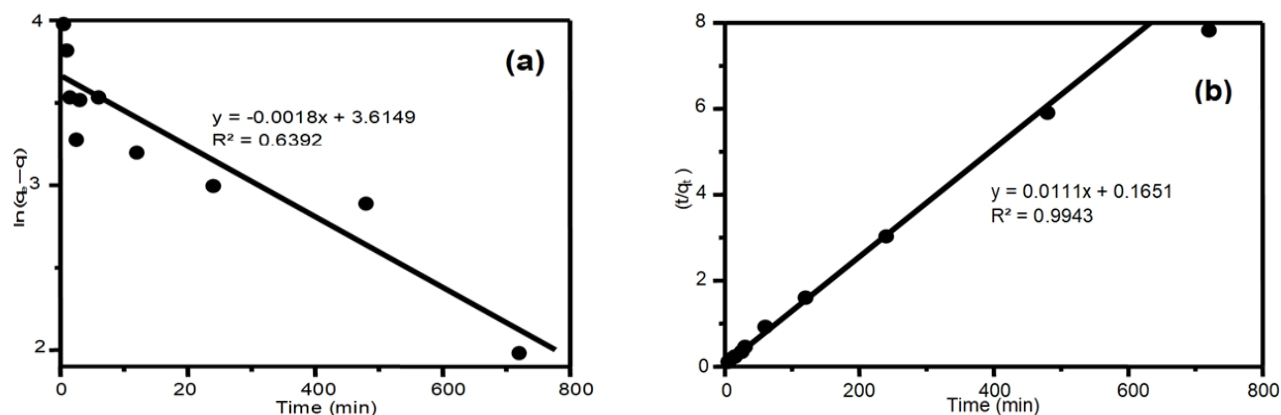


Fig. 8. (a) Pseudo-first order of metal adsorption on Ca-Al/CFB-500, (b) Pseudo-second order of metal adsorption on Ca-Al/CFB-500.

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]:

$$\log q_e = \log k_f + (1/n) \log C_e \quad (5)$$

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.

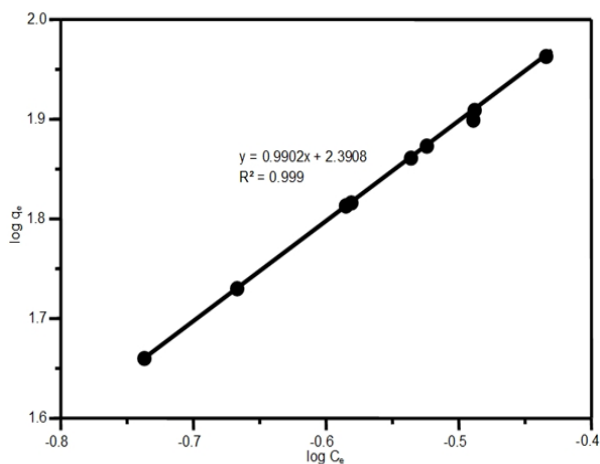


Fig. 9. Fitting adsorption with Freundlich isotherm.

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) can 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 can be used as a good adsorbent for removing Cu^{2+} ion due to an increase of surface area from $16.0 \text{ m}^2/\text{g}$ to $26.9 \text{ m}^2/\text{g}$. 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 adsorption of Cu^{2+} ion onto Ca-Al/CFB-500 was effective and follows the pseudo-second order model.

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REFERENCES

1. M. Nurhadi, R. Kusumawardani, I.I. Widiyowati, Wirhanuddin, H. Nur, Utilization of fish bone as adsorbent of Fe^{3+} ion by controllable removal of its carbonaceous component, J. Physics: Conf. Series, 1022, 2018, 012031.
2. H.K. Lima, Hasan, T.T. Tenga, M.H. Ibrahim, A.

- Ahmad, H.T. Chee, Adsorption and Removal of Zinc (II) from Aqueous Solution Using Powdered Fish Bones, *APCBEE Procedia*, 1, 2012, 96-102.
3. E.M. Zayeda, H.H. Sokkerb, H.M. Albishric, A.M. Faragd, Potential use of novel modified fishbone for anchoring hazardous metal ions from their solutions, *Ecol. Eng.*, 61, 2013, 390-393.
 4. B. Kizilkaya, A.A. Tekinay, Y. Dilgin, Adsorption and removal of Cu (II) ions from aqueous solution using pretreated fish bones, *Desalination*, 264, 2000, 37-47.
 5. S. Milicevic, T.B., S. Martinovic, M. Vlahovic, B.B. Vladan Milosevic, Removal of copper from aqueous solutions by low cost adsorbent-Kolubara lignite, *Fuel Process. Technol.*, 95, 2012, 1-7.
 6. S. Larous, A-H. Meniai, Removal of Copper (II) from Aqueous Solution by Agricultural By-Products Sawdust, *Energy Procedia*, 18, 2012, 915-923.
 7. A.K. Mona Karnib, H. Holail, Z. Olama, Heavy Metals Removal Using Activated Carbon, Silica and Silica Activated Carbon Composite, *Energy Procedia*, 50, 2014, 113-120.
 8. L. Wang, Application of activated carbon derived from 'waste' bamboo culms for the adsorption of azo disperse dye: kinetic, equilibrium and thermodynamic studies, *J. Environ. Manag.*, 102, 2012, 79-87.
 9. R. Donat, A. Akdogan, E. Erdem, H. Cetisli, Thermodynamics of Pb^{2+} and Ni^{2+} adsorption onto natural bentonite from aqueous solutions, *J. Colloid Interface Sci.*, 286, 2005, 43-52.
 10. R. Chakraborty, D. Roy Chowdhury, Fish bone derived natural hydroxyapatite-supported copper acid catalyst: Taguchi optimization of semibatch oleic acid esterification, *Chem. Eng. J.*, 215-216, 2013, 491-499.
 11. S. Patel, J. Han, W. Qiu, W. Gao, Synthesis and characterisation of mesoporous bone char obtained by pyrolysis of animal bones, for environmental application, *J. Environl. Chem. Eng.*, 3, 2015, 2368-2377.
 12. M. Nurhadi, Modification of Coal Char-loaded TiO_2 by Sulfonation and Alkylsilylation to Enhance Catalytic Activity in Styrene Oxidation with Hydrogen Peroxide as Oxidant, *Bull. Chem. React.Eng. Catal.*, 12, 1, 2017, 55-61.
 13. M. Nurhadi, I.I. Widiyowati, Wirhanuddin, S. Chandren, Kinetic of Adsorption Process of Sulfonated Carbon-derived from *Eichhornia crassipes* in the Adsorption of Methylene Blue Dye from Aqueous Solution, *Bull. Chem. React. Eng. Catal.*, 14, 1, 2019, 17-27.
 14. W.C. Wanyonyi, J.M. Onyari, P.M. Shiundu, Adsorption of Congo Red Dye from Aqueous Solution Using Roots of *Eichhornia Crassipes*: Kinetic and Equilibrium Studies *Energy Procedia*, 50, 2014, 862-869.