ABSTRACT: Charcoal nanoparticles obtained through pyrolysis of palm kernel and activated by NaOH were prepared for adsorption of copper ions (Cu$^{2+}$) from aqueous solutions. The effect of contact time (30–150 min) and initial adsorbate concentration (30–150 ppm) on adsorption of Cu$^{2+}$ ions was investigated using batch adsorption experiments. Adsorption efficiency, suitability of Langmuir and Freundlich adsorption models, and kinetics of desorption were studied. The results show that efficiency of Cu$^{2+}$ ion removal decreased with increasing initial adsorbate concentration. Higher removal efficiencies (99%) were achieved at initial adsorbate concentration of 30 ppm and contact time of 90 min. The adsorption process was well described by the Freundlich isotherm model with an exponent (n) and equilibrium constant ($K_f$) of 9.59x10$^{-5}$ mg/g and 0.182, respectively.

Keywords: Charcoal nanoparticles, Adsorption, Freundlich isotherm, Copper ions

1. INTRODUCTION

Copper is one of the most toxic metals and a potential threat to human health and the environment even at very low concentrations. However, it is an essential trace element due to its roles in cytochrome c oxidase and respiratory enzymes [1]. The US Environmental Protection Agency (EPA) has set a maximum permissible copper concentration of 1.3 mg/L in drinking water [2]. At higher concentrations, copper intoxication can cause hypotension, pancreas, jaundice, melena, kidney damage, and even coma [3], [4]. Copper often occurs as a by-product in several sectors, including textiles, electroplating, paints and pigments, galvanizing, fertilizer production, the paper industry, and several areas of the chemicals sector [5], [6]. Industrial wastewater containing copper must be processed thoroughly and appropriately since it has highly adverse effects on human health and ecological systems. Liquid waste containing copper can be processed by membrane separation, electrodialysis, ion exchange, reverse osmosis, electrochemistry, and chemical precipitation [7]–[12]. However, these methods have drawbacks, including the production of toxic sludge from chemical precipitation, and difficult recovery of metal ions from the formed sludge. Furthermore, some processes are extremely costly, particularly for processing low concentrations of metal.

The adsorption process provides a good alternative, since the design and operation of the process is more economical, simple, and flexible; and adsorbent regeneration is easier [13], [14], particularly when being used to process waste at large volume and low concentration (<100 mg/L) [15]–[18]. Consequently, there has been much research into alternative materials for affordable adsorbent, such as bagasse and fly ash [19], coir pith carbon [20], sugar beet pulp [21], tea waste [22], chitin and chitosan [23]–[26], grapefruit peel [27], and algal biomass [28]. Another affordable candidate adsorbent is charcoal derived from the pyrolysis residue of oil palm shell. This study examines the efficiency of using this material, activated with NaOH, for use in absorbing Cu$^{2+}$.

2. EXPERIMENT

2.1 Adsorbent Preparation

The charcoal tested for use as an adsorbent was obtained from the pyrolysis of oil palm shell at 380°C. Details of the pyrolysis procedure were explained in previous reports [29]–[31]. Prior to use, the charcoal was first crushed to particles of nanometre scale by processing in a ball mill for 40 hours. The carbon particles were then chemically activated by soaking in NaOH 0.1 N solution for 1 day, then filtered and washed with distilled water until the pH was neutral (±7). The material was then dried in an oven at 105°C until reaching a constant weight. The structure of the activated carbon nanoparticles was characterized by a Fourier-transform infrared (FTIR; Prestige-21, Shimadzu, Japan) and scanning electron microscope (SEM; JSM-6510 LA, JEOL, Ltd., Shimadzu, Japan).

2.2 Adsorption Test

The activated carbon nanoparticles were then used to absorb Cu$^{2+}$ metal ions. Cu$^{2+}$ was obtained
from CuSO$_4$.5H$_2$O solution at several different concentrations: 30, 60, 90, 120, and 150 mg/L. Then 100 ml of a CuSO$_4$.5H$_2$O solution containing Cu$^{2+}$ was placed in an Erlenmeyer flask with 1 g of adsorbent, then stirred at 100 rpm at room temperature with a variation of contact time (30, 60, 90, 120, 150 minutes). The filtrate was then separated from the adsorbent residue by centrifuging. After adsorption, the Cu$^{2+}$ concentration was analyzed with an atomic absorption spectrophotometer (AA-7000, Shimadzu, Japan).

3. RESULTS AND DISCUSSION

3.1 Study of Adsorption Process

3.1.1 Effect of contact time on Cu$^{2+}$ removal efficiency

The relationship between contact time and removal of Cu$^{2+}$ ions is shown in Figure 1.

![Fig.1 Effect of contact time on Cu$^{2+}$ removal efficiency](image)

Figure 1 shows that Cu$^{2+}$ adsorption rate increased until approximately 90 mins, then subsequently declined. The same tendency is observed for all initial adsorbate concentrations. The results show increasing removal of Cu$^{2+}$ from 30–90 minutes.

The results show that the optimum contact time of 90 min can achieve 99% Cu$^{2+}$ removal. After 90 minutes, removal rates showed a significant decline. The adsorbent reached saturation at 150 minutes. Subsequently, the Cu$^{2+}$ adsorption capability continued to decline, likely due to the scarcity of unoccupied adsorption sites since most sites were already bound to Cu molecules. The rate at which adsorbate binds to the adsorbent tends to decline over time as the active centers on the adsorbent surface become saturated [32], [33]. Munandar et al.[34] reported that adsorbent capability increased at the beginning of the time interval and decreased at the next time interval; the optimum contact time was obtained at 4$^{th}$ hour and it decreased at next hour until saturation at 8 hours of treatment.

3.1.2 Effect of initial Cu$^{2+}$ concentration on removal efficiency

The relationship between initial Cu$^{2+}$ concentration and removal of Cu$^{2+}$ ions is shown in Figure 2.

![Fig. 2 The effect of initial Cu$^{2+}$ concentration on removal efficiency](image)

Figure 2 shows that Cu$^{2+}$ removal efficiency differs for each time interval and initial concentration. The highest (99.9%) and lowest (64.5%) removal efficiencies were obtained for Cu solutions of 30 and 150 ppm, respectively. The higher the concentration of Cu$^{2+}$ solution the lower the removal percentage, since the dose of adsorbent remains constant while the amount to absorb increases, so the removal of Cu$^{2+}$ metal ion decreases [33]. Similar results were also obtained by Munandar et al. [34], showing that the higher the concentration, the lower the removal percentage. Their findings showed that at a concentration of 47 mg/l, removal efficiency was 94%, which decreased to 46% at an initial concentration of 482 mg/L. Another study found that for adsorption process, the highest adsorption efficiency occurred within a concentration range of <60 mg/L [35].

3.1.3 Effect of Contact Time on Cu$^{2+}$ Adsorption Capacity

Figure 3 shows the relationship between contact time and capacity for Cu$^{2+}$ adsorption. Figure 3 shows that, at a contact time of 90 minutes, the achieved adsorption capacities are 3.10, 5.6, 8.6, 10.1, and 9.9 mg/g for initial concentrations of 30, 60, 90, 120, and 150 ppm, respectively. However, the highest adsorption capacity is obtained at an initial concentration of 120 ppm. The data show that optimum adsorption capacity occurs at 90 min for every initial concentration of the Cu$^{2+}$ solution. At 30–90 min contact time, the amount of Cu$^{2+}$ adsorbed
increases, since the adsorbent has a certain timeframe for maximum absorption efficiency. After 90 min, the amount of Cu\(^{2+}\) adsorbed decreases, since the bonds between clusters in the adsorbent and the metal adsorbate keep weakening, and the adsorbate is finally released back into the solution \[36\]. The results show that every 1 g dose of adsorbent achieves maximum Cu\(^{2+}\) adsorption at initial adsorbate concentration of 120 ppm. The adsorption of Cu\(^{2+}\) decreases at an initial concentration of 150 ppm, as the constant dose of adsorbent, is unable to hold the increased weight of the adsorbate. Zhan et al.\[37\] reported similar results, in which at an initial concentration of 0.25–8 mmol/L, adsorption capacity increased at a concentration of 0.25–5 mmol/L and subsequently decreased at a concentration of 6–8 mmol/L.

![Fig. 3 Effect of contact time on the capacity for Cu\(^{2+}\) adsorption](image)

### 3.2 Adsorption Isotherms

The Langmuir and Freundlich models were employed in order to determine the adsorption isotherms.

![Langmuir and Freundlich isotherms for Cu\(^{2+}\) adsorption](image)

The Langmuir and Freundlich equations are shown in Figure 4 a–b. The Langmuir isotherm represents the relationship between \(C_e\) and \(Q_e\), whereas the Freundlich isotherm is obtained through the relationship between \(\log C_e\) and \(\log Q_e\). Figure 4 shows that Cu\(^{2+}\) adsorption by the activated carbon nanoparticles tends to follow the Freundlich isotherm, with higher coefficient of determination \((R^2=0.943)\) than in the Langmuir model \((R^2=0.773)\). Table 1 shows the values of constants and parameters from the Langmuir and Freundlich models for Cu\(^{2+}\) adsorption.

|                | Langmuir | Freundlich |
|----------------|----------|------------|
| \(R^2\)        | 0.773    | 0.943      |
| \(q_m\) (L/mg) | 0.96     | 0.182      |
| \(k_l\) (mg/g) | -0.67    | 9.59x10\(^{-5}\) |

Table 1 Constants and parameters values of Langmuir and Freundlich models for Cu\(^{2+}\) adsorption

### 4. CONCLUSION

Activated carbon nanoparticles obtained through pyrolysis of oil palm shell provide a highly effective adsorbent for removing low concentrations (30 ppm) of Cu\(^{2+}\) from aqueous solution. Following activation of the nanoparticles by NaOH and mixing at 100 rpm, Cu\(^{2+}\) adsorption efficiencies at 90 min were 99.9, 95.04, 89.83, 87.75, and 67.82 % for initial Cu\(^{2+}\) concentrations of 30, 60, 90, 120, and 150 ppm, respectively. The adsorption trend follows the Freundlich isothermal model, with a higher value of the coefficient of determination \((R^2=0.997)\) than the Langmuir model.

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6. REFERENCES

[1] Dai Y., Zhang K., Li J., Jiang Y., Chen Y., and Tanaka S., Adsorption of copper and zinc onto carbon material in an aqueous solution by ammonium peroxysulphate. Separation and Purification Technology, Issue 186, 2017, pp. 255-263.

[2] U.S. Environ Protec. Agency, Aquatic Life Ambient Freshwater Quality Criteria-Copper. www.epa.gov/safewater/mcl.html.

[3] Zhou Y., Zhang L., and Cheng Z., Removal of organic pollutants from aqueous solution using agricultural wastes: a review. Journal of Molecular Liquids, Issue 212, 2015, pp. 739-762.

[4] Jalilzadeh M., and Şenel S., Removal of Cu (II) ions from water by ion-imprinted magnetic and non-magnetic cryogels: A comparison of their selective Cu (II) removal performances. Journal of Water Process Engineering, Issue 13, 2016, pp.143-152.

[5] Xie X., Xiong H., Zhang Y., Tong Z., Liao A., and Qin Z., Preparation magnetic cassava residue microspheres and its application for Cu (II) adsorption. Journal of Environmental Chemical Engineering, Vol. 5, Issue 3, 2017, pp. 2800-2806.

[6] Bansal M., Mudhoo A., Garg V.K., and Singh D., Preparation and characterization of biosorbents and copper sequestration from simulated wastewater. International Journal of Environmental Science and Technology, Vol. 11, Issue 5, 2014, pp.1399-1412.

[7] Mier M.V., Callejas R.L., Gehr, R.B.E., Cisneros J., Alvarez P.J.J., Heavy metal removal with Mexican clinoptilolite: multi-component ionic exchange, Water Research, Vol. 35, Issue 2, 2001, pp. 373–378.

[8] Curković L., Cerjan S., and Filipan T., Metal ion exchange by natural and modified zeolites, Water Research, Vol. 31, Issue 6, 1997, pp.1379–1382.

[9] Strathmann H., Membrane separation processes, Journal of Membrane Science, Vol. 9, Issues 1-2, 1981, pp.121–189.

[10] Ojemaye M.O., Okoh O.O., and Okoh A.I., Adsorption of Cu$^{2+}$ from aqueous solution by a novel material; azomethine functionalized magnetic nanoparticles. Separation and Purification Technology, Vol. 183, 2017, pp. 204-215.

[11] Xue Y., Wu S., and Zhou M., Adsorption characterization of Cu(II) from aqueous solution onto basic oxygen furnace slag. Chemical Engineering Journal, Vol. 231, 2013, pp. 355-364.

[12] Zhu Q., Zehuan W.L., Ye A.H., and Feng X., Hydrothermal synthesis of silico-manganese nanohybrid for Cu(II) adsorption from aqueous solution, Journal of Water Resource. Vol. 12, Issue 1, pp. 332-342.

[13] Salam M.A., Removal of heavy metal ions from aqueous solutions with multi-walled carbon nanotubes: kinetic and thermodynamic studies, International Journal of Environmental Science and Technology, Vol. 10, 2013, pp. 677–688.

[14] Dong Y.B., and Hai L.I.N., Adsorption of Cu$^{2+}$ from aqueous solution by modified biomass material. Transactions of Nonferrous Metals Society of China, Vol. 25, 2015, Issue 3, pp. 991-996.

[15] Xu Q., Wang Y., Jin L., Wang Y., and Qin M., Adsorption of Cu(II), Pb(II) and Cr(VI) from aqueous solutions using black wattle tannin-immobilized nanocellulose. Journal of Hazardous Materials, Vol. 339, 2017. pp. 91-99.

[16] Ali I., and Gupta V.K., Advances in water treatment by adsorption technology, Nature Protocol, Vol. 1, 2006, pp. 2661–2667.

[17] Dabrowski A., Podkoscielny P., Hubicki Z., and Barczak M., Adsorption of phenolic compounds by activated carbon- a critical review, Chemosphere, Vol. 58, 2005, pp. 1049-1070.

[18] Mack C., Wilhelm B., Duncan J.R., and Burgess J.E., Biosorption of precious metals, Biotechnology Advances. Vol. 25, Issue 3, 2007, pp. 264-271.

[19] Rao M., Parwate A.V., and Bhole A.G., Removal of Cr$^{6+}$ and Ni$^{2+}$ from aqueous solution using bagasse and fly ash, Waste Management, Vol. 22, Issue 7, 2002, pp. 821-830.

[20] Namasivayam C., and Kadirvelu K., Agricultural solid wastes for the removal of heavy metals: adsorption of Cu(II) by coirpitch carbon, Chemosphere Vol. 34, Issue 2, 1997, pp. 377-399.

[21] Reddad Z., Gerente C., Andres Y., and Cloirec P.L., Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies, Environmental Science and Technology, Vol. 36, 2002, pp. 2067-2073.

[22] Amarasinghe B.M.W.P.K., and Williams R.A., Tea waste as a low-cost adsorbent for the removal of Cu and Pb from wastewater, Chemical Engineering Journal, Vol. 132 Issues 1-3, 2007, pp. 299-309.

[23] Qi L., Xu Z., Jiang X., Hu C., and Zou X., Preparation and antibacterial activity of chitosan nanoparticles, Carbohydrate Research, Vol. 339, Issue 16, 2004, pp. 2693-2700.

[24] Liu C. and Bai R., Adsorptive removal of copper ions with highly porous
chitosan/cellulose acetate blend hollow fiber membranes. Journal of Membrane Science, Vol. 284, Issues 1-2, 2006, pp. 313-322.

[25] Meng Y., Chen D., Sun Y., Jiao D., Zeng D. and Liu Z., Adsorption of Cu^{2+} ions using chitosan-modified magnetic Mn ferrite nanoparticles synthesized by the microwave-assisted hydrothermal method. Applied Surface Science, Vol. 324, 2015, pp.745-750.

[26] Wu Z.C., Wang Z.Z., Liu J., Yin J.H. and Kuang S.P., A new porous magnetic chitosan modified with melamine for fast and efficient adsorption of Cu (II) ions. International Journal of Biological Macromolecules, Vol. 81, 2015, pp. 838-846.

[27] Semercioz AS, Gögüş F, Çelekli A, Bozkurt H., Development of carbohydrate material from grapefruit peel with microwave implemented-low temperature hydrothermal carbonization technique for the adsorption of Cu (II). Journal of Cleaner Production, Vol. 165, 2017, pp. 599-610.

[28] Gunasundari, E. and Kumar, S., Adsorption isotherm, kinetics and thermodynamic analysis of Cu (II) ions onto the dried algal biomass (Spirulina platensis). Journal of Industrial and Engineering Chemistry, Vol. 56, 2017, pp.129-144.

[29] Faisal M., Gani A., Husni, and Daimon H., A preliminary study of the utilization of liquid smoke from palm kernel shells for organic mouthwash, International Journal of GEOMATE, Vol. 13 Issue 37, 2017, pp. 116-120.

[30] Faisal M., Chamzurni T., and Daimon H., A study on the effectiveness of liquid smoke produced from palm kernel shells in inhibiting black pod disease in cacao fruit in vitro, International Journal of GEOMATE, Vol. 14 Issue 43, 2018, pp. 36-41.

[31] Faisal M, Gani A, Husni, Baihaqi A, Daimon H., Pyrolysis of oil palm kernel shell into liquid smoke and its application to control anthracnose disease on chili (Capsicum annum L.). Journal of Engineering and Applied Sciences, Vol.11, No. 12, 2016, pp. 2583-2587.

[32] He Q., Jiali D., Liang Z., Kaijun X., and Yurong Y. Synthesis and lead absorption properties of sintered activated carbon supported zero-valent iron nanoparticle. Journal of Alloys and Compounds, Vol. 687, 2016, pp. 326-333.

[33] Taba P., Hala Y., and Nashriah, Mesoporous carbon synthesis, Cmk-1 and their adsorption potential over surfactant in waters. Marina Chimica Acta, Vol. 5, Issue 1, 2004, pp.16-22.

[34] Munandar A., Syaifullah M., and Sri M, Removal of COD from palm oil mill effluent by using nano activated carbon, Jurnal Rekayasa Kimia dan Lingkungan, Vol. 11, 2016, pp.24-31.

[35] Gan M, Sun S, Zheng Z, Tang H, Sheng J, Zhu J, Liu X., Adsorption of Cr (VI) and Cu (II) by AlPO 4 modified biosynthetic Schwertmannite, Applied Surface Science, Vol.356, 2015, pp. 986-97.

[36] Pambayun G.S., Yulianto R.Y.E., Rachimoellah M., and Putri, E.M.M., Electrocoagulation of palm oil mill effluent as wastewater treatment and hydrogen production using electrode aluminum, Journal of Environmental Quality, Vol. 40, Issue 4, pp.1332-1339.

[37] Zhan C.W., Zhao Z.W., Jie L., Jin H.Y., and Shao P.K. 2015. A new porous magnetic chitosan modified with melamine for fast and efficient adsorption of Cu(II) ions, Journal of Biological Macromolecules. Vol. 81, 2013, pp. 838-846.