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REMOVAL OF CU2+ USING UTRICULARIA AUREA AS A BIOSORBENT IN SYNTHETIC INDUSTRIAL WASTEWATER

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ABSTRACT

Biosorption of copper ions (Cu^{2+}) using Utricularia Aurea has been investigated as a function of pH, contact time and particle size of the biosorbent. A series of batch equilibrium adsorption study was conducted to determine the effect of varied pH from pH 2, 4, 7, and 9, contact time at 30, 60, 90 and 120 minutes, biosorbent particle size ranging from 150 µm, 300 µm, 450 µm and 600 µm at an agitation speed of 125 rpm using Utricularia aurea (U. Aurea). Based on the optimization study, it was found that the optimum removal of Cu^{2+} (>90%) occurred at pH4, contact time of 40 minutes and particle size of 450µm. Atomic Absorption Spectrometer was used to analyse the concentration of Cu^{2+} in the sample. A kinetic study on Cu^{2+} adsorption onto U.Aurea was analysed using pseudo-first order and pseudo second order kinetic models. Based on the kinetic study analysis, the adsorption of Cu^{2+} followed pseudo- second order kinetic which r^2 was greater than 0.99 rather than pseudo- first order kinetic models. Thus, Utricularia Aurea can be an alternative as a new adsorbent media in treating heavy metals contaminated for industrial wastewater.

Keywords: biosorption; kinetic model; heavy metal; industrial wastewater

1. INTRODUCTION

Malaysia is a country that has a rapid development in various industrial sectors. Industrialized companies are booming all over the country which makes the developments in turn affecting the environment eco-system. The fabulous boost in the use of heavy metals over the past few decades has certainly resulted in an increased flux of metallic substances in water body. Mine drainage, industrial and domestic effluents, agricultural runoff and acid rain have all

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contributed to some extent to the metal loads in the water bodies (Huang et al., 2017). Metals need special concern because they are non-degradable and persistent (Kushwah et al., 2015).

Heavy metals often present in industrial wastewater, are hazardous to the aquatic ecosystem and also a danger to human resulting in health risks. According to Leone and Mercer (1998), Copper deficiency is associated with anaemia, neutropenia and bone abnormalities but clinically evident deficiency is relatively infrequent in humans. Copper in water bodies can also damage a variety of fishes and invertebrates (Wase & Forster, 1997). The concentration of Copper in water bodies should not be more than 0.2 mg/L for industrial and development project located within the catchment area and 1 mg/L for general purposes (EQA, 1974). It is recognized that finding methods for removal of heavy metals from wastewater is of great importance (Gupta et al., 2006).

Chemical precipitation and filtration, chemical oxidation or reduction, electrochemical treatment, evaporation, ion exchange and reverse osmosis are some of the most commonly used procedures for removing metal ions from aqueous streams (Volesky, 2001). However, these processes have significant disadvantages, such as an incomplete metal removal, expensive equipment and monitoring systems, high reagent or energy requirements and generation of toxic sludge or other waste products that require an adequate disposal process.

Adsorption by using activated carbon is the most efficient classical way as its removal rate can be more than 99% for certain metal ions (Aksu, 1997; Doğan, 2000). However, because of its relatively high cost and cannot be regenerated and recycled, in this study the potential of abandoned naturally occurring adsorbent namely *Utricularia aurea* (*U. Aurea*) was explored to remove Copper ions (Cu^{2+}) from wastewater in attempts to utilize its low cost and environmental friendly approach. *U. Aurea* are submerged aquatic weeds and are classified as an algae family based on its physical properties. Algae, bacteria, fungal, and yeast are examples of biosorbent media and potentially can be used to remove heavy metals in water bodies (Terry & Stone 2002). The aim of this paper is to determine the effectiveness of *U. Aurea* as natural biosorbent for Cu^{2+} removal from industrial waste water with respect to varied pH, size and contact time through batch adsorption study. The behaviour of adsorption mechanism was analyzed based on mathematical modelling using pseudo-first order and pseudo-second order kinetic models.

2. METHODOLOGY

2.1 Biosorbent preparation

U. Aurea that was abundantly grown in the paddy field near to UiTM Pulau Pinang was collected. The biosorbent were washed to remove impurities and dried overnight in oven with temperature of 70°C. *U. Aurea* which have been reduced in size were sieved to attain a particle size of 150 μm, 300 μm, 450 μm and 600 μm.

The synthetic industrial wastewater was prepared by adding Cu standard solution with 100ml of deionized water to obtain initial Cu concentration of 2 ppm. An acidic or alkaline buffer solution was added into the synthetic wastewater sample so that the pH of sample was in the

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range of pH 2 to pH 9. Then, 0.4g of biosorbent has been added into 100 mL of Cu solutions and was agitated using orbital shaker at 125 rpm.

2.2 Adsorption equilibrium study

Biosorption capacity of *U. Aurea* in removing Cu^{2+} from the water sample was carried out using batch adsorption study. The effect of contact time ranging from 0 to 120 minutes, pH ranging from pH2 to pH9 and particle size ranging from 150µm to 600 µm were investigated in this study. The concentration of Cu^{2+} was measured using Atomic Absorption Spectrophotometer (Brand: Shimatzu, Model: AA-6800). The removal efficiency of the biosorbent media was presented in the Equation (1).

$$\%removal = \left(\frac{C_i - C_t}{C_i}\right) \times 100 \quad (1)$$

The adsorption capacity of adsorbent media can be expressed in Equation (2).

$$q_e = \frac{(C_i - C_t)V}{m} \quad (2)$$

Where C_i and C_t is the initial and final concentration of heavy metal pollutant sample (mg/L), V is the volume of sample (L) and m is the mass of adsorbent (g).

2.3 Adsorption kinetic study

Adsorption kinetic study is a mathematical model to describe the adsorption behaviour and the mechanism of adsorbent onto adsorbate. In this study, the adsorption mechanism of *U.Aurea* onto Cu^{2+} removal in synthetic industrial wastewater was analysed using pseudo-first order kinetic and pseudo-second order kinetic models. The equation for both kinetic models can be expressed in Equation (3) and (4).

$$Log(q_e - q_t) = Logq_e - \frac{tk_1}{2.303} \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where q_e and q_t represent the Cu^{2+} uptake (mg/g) at equilibrium and any time t. k_1 (min^{-1}) is the pseudo-first order constant rate of adsorption that can be obtained from the gradient of plotting log (q_e- q_t) versus time (t).

Meanwhile, pseudo-second order kinetic equation is presented in Equation (4). In this linear equation, k_2 represents the pseudo-second order constant rate and it can be determined by the interception of plotting t/q_t versus time (t).

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3. RESULT AND DISCUSSION

3.1 Effect of varied pH on biosorption

pH is one important parameter that influences the adsorption of heavy metals and determines the biosorption mechanisms such as surface precipitation of adsorption. Results on the effect of varied pH for Cu^{2+} removal and adsorption capacity using *U. Aurea* as biosorbent are presented in Figure 1 and Figure 2. Based on the results, the optimum pH was at pH 4 which Cu^{2+} removal was greater than 80% for various particle size. Increasing the particle size may increase the removal of Cu^{2+} in synthetic industrial wastewater. The removal of Cu^{2+} was gradually decreased almost 50% of the removal after it achieved an optimum pH 4. As shown in Figure 2, the maximum adsorption capacity of Cu^{2+} was in the range of 0.39 to 0.42 mg/g for various particle size that occured at optimum pH 4. From the result, the optimum biosorption of Cu^{2+} occured at acidic condition. At lower pH values, the cell binding sites would be closely related with the hydrogen ions and restrict access to binding sites by metal cations as a result of repulsive force. As lower pH increased the negative charge density on the cell surface, it also increased the deprotonation of the metal binding sites and hence enhancing the biosorption performance of the biosorbent (Wattanachai, 2011).

For biosorption on algae group, it is found that most of the optimum pH for an effective removal of heavy metals in within the acidic group of aqueous solution (Volesky, 2006). This is because at acidic state, metal ions could be adsorbed by complexing with negatively charged reaction sites on the cell surface (Gupta et al., 2000).

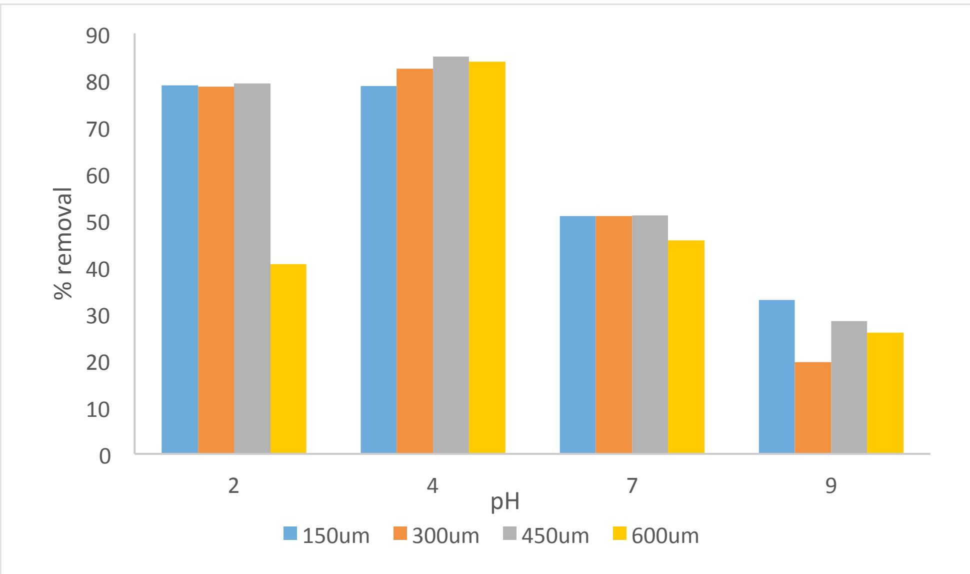

Figure 1: Effect of varied ph on the removal of Cu^{2+}

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3.2 Effect of varied contact time on biosorption

Contact time was one of the factors that influenced the efficiency of Cu2+ adsorption. Figure 3 shows the result of the effect of varied contact time of the Cu2+ adsorption. From the result as shown in Figure 3, it was revealed that the optimum contact time for various particle sizes of adsorbent media occurred at 40 minutes which the removal was greater than 80%. From Figure 3, the maximum removal of Cu2+ was greater than 90% at the adsorbent size of 450 µm. After 40 minutes of contact time, the plot of percentage removal versus contact time had achieved equilibrium and it was found that the adsorption process of U. Aurea was saturated. Thus adsorbent particle size of 45µm was chosen as optimum particle size of adsorbent media in removing of Cu2+ in synthetic industrial wastewater.

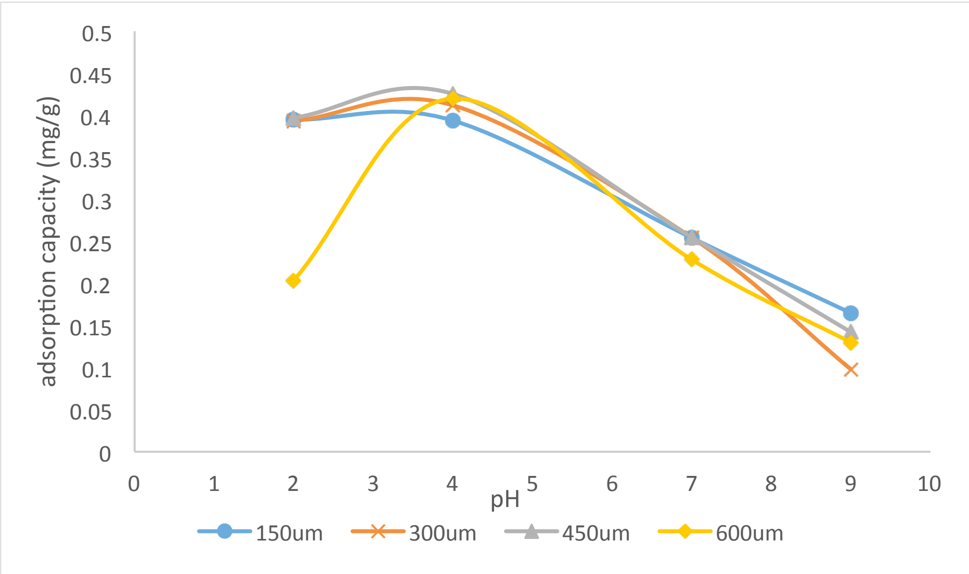

Figure 2: Effect of varied ph on the adsorption capacity of Cu^{2+}

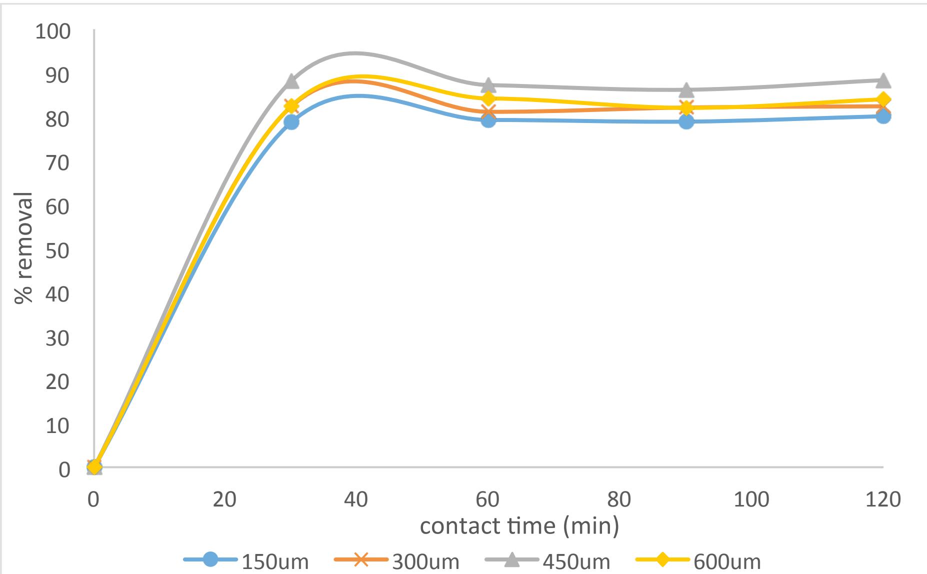

Figure 3: Effect of varied contact time on the Cu^{2+} removal

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3.3 Adsorption kinetic study

The behaviour of adsorption mechanism was analysed using pseudo-first order and pseudo-second order kinetic model. Based on Table 1, it was revealed that the adsorption of Cu^{2+} onto synthetic wastewater followed pseudo-second order kinetic model. The value of regression coefficient, r^2 for various adsorbent particle sizes (ranging from 150μm to 600μm) were greater than 0.99 in the pseudo-second order kinetic model. In the first order kinetic model, the value of r^2 was very low and thus, the model did not follow this model. Therefore, in this study, the adsorption of Cu^{2+} onto synthetic wastewater using *U. Aurea* was followed the second order kinetic model due to higher value of r^2. According to adsorption capacity data as shown in Table 1, the value of q_{cal} was much closed to the q_{exp} for various adsorbent particle sizes in pseudo-second order rather than in pseudo first order kinetic model. In pseudo-second order kinetic model, the value of q_{cal} and q_{exp} were in the range of 0.399 mg/g to 0.438 mg/g while 0.4 mg/g to 0.442 mg/g respectively. Thus, in this study, it was showed that the experimental data was fitted with pseudo- second order kinetic model. Likewise, previous studies have found that adsorption of heavy metals in water and wastewater were fitted with pseudo-second order kinetic and the mechanism of adsorption is chemisorption (Akbar et al., 2016; Ma et al.,2012; Chaudhry et al., 2017).

Table 1: Summary of kinetic study on Cu^{2+} removal

Kinetic model	parameters	Size of bioadsorbent media			
		150um	300um	450um	600um
	q_{exp} (mg/g)	0.4006	0.412	0.442	0.421
1st order	r^2	0.6109	0.1764	0.202	0.1059
	k_1 (min^{-1})	0.0433	0.0405	0.0306	0.0212
	$q_{e\ cal}$ (mg/g)	0.114	0.023	0.048	0.193
2nd order	r^2	0.999	0.999	0.996	0.996
	k_2(min^{-1})	7.432	12.922	12.722	12.548
	$q_{e\ cal}$ (mg/g)	0.399	0.411	0.438	0.417

4. CONCLUSION

As a conclusion, *U. aurea* has a potential as biosorbent in removing Cu^{2+} from synthetic industrial wastewater. The result showed that this biosorbent can remove Cu^{2+} up to 90% at optimum pH4 and contact time of 40 minutes using 45um particle size of *U. Aurea*. Based on kinetic models, the experimental data on the adsorption of Cu^{2+} fitted with pseudo-second order kinetic (r^2 >0.99) were compared to pseudo-first order kinetic model (r^2 < 0.7) for various sizes of adsorbent particles. The result indicated that the adsorption of Cu^{2+} onto synthetic industrial wastewater occurred in chemisorption mechanism. Therefore, the low-cost of bio sorbent with high adsorption capacity might be an alternative in removing heavy metals in industrial wastewater.

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REFERENCES

Aksu, Z., Acikel, U., and Kutsal, T.,(1997) Application of multicomponent adsorption isotherms to simultaneous biosorption of iron(iii) and chromium(vi) on *C. Vulga. Journal of Chemical Technology and Biotechnology,* 70, 368–378. doi: http://dx.doi.org/10.1002/(SICI)1097-4660(199712)70:4<368::AID-JCTB772>3.0.CO;2-Z

Doğan, M., Alkan, M., and Onganer, Y. (2000), Adsorption of Methylene Blue from Aqueous Solution onto Perlite. Journal of Water, Air Soil Poll., 120, 229–248. doi: 10.1023/A:1005297724304

Environmental Quality Act (1974) (Act 127). doi: https://www.elaw.org/system/files/MalaysiaEQA1974.pdf

Gupta, V.K., Rastogi, A., Saini, V.K., and Jain, N. (2006) Corrigendum to "Biosorption of copper(II) from aqueous solutions by Spirogyra species. *Journal of Colloid Interface Science*, 296, 59–63. doi: https://doi.org/10.1016/j.jcis.2005.08.033

Huang, J., Yuan, F., Zeng, G., Li, X., Gu, Y., Shi, L., Liu, W., and Shi, Y. (2017). Influence of pH on heavy metal speciation and removal from wastewater using micellar-enhanced ultrafiltration. *Journal of Chemosphere*, 173, 199-206. doi: http://dx.doi.org/10.1016/j.chemosphere.2016.12.137

Kushwah, A., Srivastav,J. K., and Palsania, J. (2015). Biosorption of heavy metal: A review. *European Journal of Biotechnology and Bioscience,* 3, 51-55. doi: www.biosciencejournals.com/download/207/3-12-13.1

Leone A., and Mercer J. F.B. (1998). *Copper transport and its disorder.* Kluwer Academic/ Plenum Publishers. doi: https://books.google.com.my/books?id=npl-YsCPyiAC&printsec=frontcover

Akbar, N.A., Aziz, H.A. and Adlan, M.N (2016). Potential of high quality limestone as adsorbent for iron and manganese removal in groundwater. *Jurnal Teknologi, 78, 9–4* , 77–82.

Ma, X, Li, Liping., Yang, L., Su, C., Wang, K., Yuan, Shibao and Zhou, J. (2012). Adsorption of heavy metal ions using hierarchical $CaCO_3$ – maltose meso/ microporous hybrid materials: Adsorption isotherms and kinetic studies. *Journal of Hazadous Materials*. 209 -210: 467 – 477.

Chaudhry, S.A., Zaidi, Z. and Siddiqui, S.I. (2017). Isotherm, kinetic and thermodynamics of arsenic adsorption onto Iron- Zirconium Binary Oxide- Coated Sand (IZBOCS): Modelling and process optimization. *Journal of Molecular Liquids.* 229: 230 – 240.

Terry, P., A., and Stone, W. (2002) Biosorption of cadmium and copper contaminated water by *Scenedesmus abundans. Journal of Chemosphere,* 47, 249-255. doi: http://dx.doi.org/10.1016/S0045-6535(01)00303-4

p-ISSN 1675-7939; e-ISSN 2289-4934

Volesky, B. (2001) Detoxification of metal-bearing effluents: biosorption for the next century. *Journal of Hydrometallurgy*, 59, 203-216. doi: http://biosorption.mcgill.ca/publication/PDFs/151-HMET'01-59,203-16-NxtCentIBS,BV.pdf

Wase, J., Foster, C. (1997). *Biosorbents for Metal Ions*. Taylor & Francis Publisher doi:https://www.crcpress.com/Biosorbents-for-Metal-Ions/Wase-Wase/p/book/9780203483046#googlePreviewContaine

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