The Mixing Speed Effect and Mass of Adsorbent On Copper (Cu) Removal from Wastewater by Water Hyacinth Leaves

Mala Oktaviyana Lussa, *Asih* Wijayanti, *Riana* Ayu Kusumadewi*, *Rositayanti* Hadisoebroto

Department of Environmental Engineering, Faculty of Landscape Architecture and Environmental Technology, Universitas Trisakti, Jakarta, Indonesia

Abstract. This study aims to determine the role of water hyacinth leaves powder on wastewater adsorbed from Cu ion, which is one of the metals responsible for environmental pollution and analyzed using AAS. Cu-wastewater was conducted in bathes and used to optimized the sorption at 250 ml, with 10 grams of water hyacinth leaves adsorbents added at speeds of 100, 150, 200 rpm, with contact times arrangement of 30, 60, 90 minutes. A maximum adsorption rate of 10 grams at a maximum speed of 100rpm, led to a removal efficiency of 98.19% and 60 minutes contact time. The equilibrium data utilized was properly represented in the Freundlich adsorption isotherm model to analyze the mechanism using $R^2 \approx 1$. In addition, Cu adsorption kinetic models were analyzed using the pseudo-second-order model at an adsorption rate of $R^2 \approx 1$. The result showed that the Cu-wastewater used to activate the water hyacinth leaves powder was highly effective for the treatment.

1. Introduction

The harmful pollution suffered by the environment is due to the continuous growth in industrialization. The contamination in the aquatic environment are harmful to human health, therefore, various efforts have been utilized to purify water through the removal of metals. Activated carbon was used for the removal of metal ions, thereore, it has the potential to be applied as a wastewater treatment [1]. Copper is considered toxic to plants when the concentration is higher than 0.1 ppm, however, its water content does not exceed 1 ppm, while its concentration toxicity in sheep is above 20 ppm. Furthermore, its presence in wastewater appears as a bivalent ion of Cu (II) or a hydrolytic product. Paint, paper, petroleum and coating industries contain Cu in there wastewater [2], [3].

There various limitations associated with the use of conventional techniques, in the removal of Cu through precipitation, electrochemistry, ion exchange and membrane filtration. These limitations include high installation costs, secondary contamination because the use of chemicals and the production of toxic sludge [2], [3]. Furthermore, the use of these techniques does not possess the capability to meet the existing quality standards [4], [5]. Adsorption is defined as a conventional and efficient technology used to remove the toxic pollutants from wastewater. Therefore, it is essential to produce cheap, and available, active carbon adsorbents for removing heavy metal ions from the aqueous environment. Its benefit include reusability, low operating costs, improved selectivity, ability to remove heavy metals from the effluent regardless of its toxicity and short operating time [6].

The adsorption process is preferred than other because the silt-free action and the complete removal of dyes, including diluted solutions. The industrial process widely used carbons because of its ability to adsorb organic compounds. However, there are many disadvantages associated for bleachings, such as higher operational costs and losses, which leads to temperature combustion, pore blocking and hygroscopicity. Studies have recently been conducted to determine cheaper substitutes for activated carbon. These new strategies tend to use cheap and easily available biological and agricultural waste when replacing activated carbon. However, one of the inexpensive adsorbents tested for the dye sorption process is water hyacinth leaves [17].

To determine its practical applicability, a deep investigation was conducted on the removal of Cu ions by activated carbon from the water hyacinth leaving the biomass in a discontinuous method. Water hyacinth leaf adsorbents were characterized by AAS to determine the adsorption of Cu. The optimum adsorption conditions were analyzed as a function of the mixing speed in agreement with the contact time, and mass adsorbent. Evaluation of mechanisms of Cu adsorption on water hyacinth leaf adsorbents were conducted in terms of removal efficiency, equilibrium isotherm and kinetic constants.

* Corresponding author: rianaayu.kusumadewi @trisakti.ac.id

2. Materials and methods

2.1 Location and Time of Study

Screen printing wastewater samples were obtained from home industries in Krendang village, Tambora Sub-district, West Jakarta. This research was conducted in Environmental Engineering Laboratory, Trisakti University, from February to July 2019.

2.2 Determination of Cu Initial Concentration

Prior to this research, the heavy metals contained in screen printing wastewater were analyzed on several colors namely, black, white, red, yellow and blue. These metals include copper (Cu), zinc (Zn), titanium (Ti), total chrome (Cr), cadmium (Cd), mercury (Hg) and lead (Pb), with the color of wastewater containing the highest Cu selected.

2.3 Adsorbent preparation

The leaves and shoot parts of the selected water hyacinth weeds were separated and washed with aqua dest and running water to remove impurities. After cleaning, the next process was to cut the leaves into small pieces. It then dried with the sun (around 2-3 days) to reduce the moisture. This was followed by tanur-drying at a temperature of 400°C for 2 hours to form charcoal. After that, the leaves were mashed in a uniform size and sieved with 100 meshes. The pulverized charcoal was inserted into the desiccator.

2.4 Activation of Adsorbent

Carbonized water hyacinth leaves were activated by using H_2SO_4 solution with a 20% concentration. The amount of activated adsorbate and adsorbent were 2 ml: 1 gram. The adsorbent was activated by soaking the leaves in 20% H_2SO_4 solution for 24 hours. The leaves were then washed by using distilled water. The oven dried at 110 °C for 2 hours

2.5 Mixing Speed Optimization and Contact Time

Cu-wastewater of 250 ml in ranges of 100, 150, and 200 were used to optimize the mixing speed. Furthermore, the powdered form of the leaves was added using a jartest at a contact time of 30 and 60 as well as 90 minutes. ASS was used to examine theremaining Cu metal in the solution.

2.6 Mass Adsorbent Optimization and Contact Time

Mass weight optimization was conducted in a batch system using The Cu-wastewater weighing 250 ml at a mixing speed of 100 rpm, was used to examine the optimize the mass weight. In addition, the mass weight of the adsorbent which was set in ranges of 10, 15, and 20 grams was added using a jartest with a of 30, 60, and 90 minutes contact time. The remaining Cu metal in the solution was analyzed using AAS.

2.7 Adsorption of Cu

2.7.1 Cu Removal Efficiency

Equation (1) and (2) show the calculation of the removal efficiency and adsorption capacity [7]:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

$$Removal\ efficiency\ (\%) = \frac{(C_o - C_e)}{C_o} 100\% \quad (2)$$

q_e = The equilibrium adsorption capacity (mg g^{-1})
C_o = Initial concentrations
C_e = Equilibrium concentrations (mg/L)
V = Volume of the solution (L)
W = The weight of the adsorbent (g).

2.7.2 Adsorption Isotherms

Adsorption isotherm contains information on the adsorption mechanism, between the solid and liquid phases. The interaction between two adsorption phases of Cu were also determined using the Langmuir and Freundlich adsorption isothermal models as illustrated by equations (3) and (4) respectively [8]:

$$C_e/q_e = C_e/q_m + 1/(q_m.K_l) \quad (3)$$

$$ln\ q_e = lnK_f + (1/n).(lnC_e) \quad (4)$$

q_e = The amount of Cu ions adsorbed (mg g^{-1})
Ce = The concentration and equilibrium of Cu ion (mg/L)
q_m = the maximum adsorption capacity of the adsorbent (mg g^{-1})
K_L = The isotherm constants of Langmuir
K_F = The isotherm constants Freundlich (L/mg)
N = The heterogeneity factor that shows the capacity and intensity of the adsorption.

2.7.3 Adsorption Kinetics

The adsorption rates were investigated to characterize the adsorbent speed. The pseudo-first and second-order models were selected to discover the kinetic adsorption behavior, which assumes that the ion is adsorbed at single and double surface locations, respectively. The comparisons for kinetic models are stated below [7]:
Pseudo-first-order:

$$log(q_e - q_t) = logq_e \frac{k_1}{2.303} t \quad (5)$$

Pseudo-second-order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

q_e, q_t = Ssolute adsorbed at equilibrium (mg g^{-1})

* Corresponding author: rianaayu.kusumadewi @trisakti.ac.id

k_1 = Adsorption constant (min^{-1}),
k_2 = The pseudo-second-order adsorption rate constant (g mg^{-1} min^{-1}).
t = Time (minutes)

3. Result and Discussion

3.1 Wastewater Characterization

Samples were obtained from different phases of the screen printing washing process. The wastewater of each color contains different heavy metal contents. In the wash phase, blue was particularly high in Cu (1.67 mg/l). The different color samples of the copper content in each sewer are shown in **Table 1**.

Table 1: Copper with different colors

Colors	Parameters	Unit	Result
Yellow	Cu	mg/l	0.0384
Blue			1.6755
White			0.0017
Red			0.205
Black			0.0069

From the analysis, it was obtained that the blue wastewater contained the highest heavy metals with a Cu concentration of 1,6755 mg/l. This amount is below the standard quality of water according to Law number 5 on the regulations of the Minister of Environment, Republic of Indonesia number in the paint industry. The permitted concentration of Cu is less than 0.8 mg/l.

3.2 Removal Efficiency of Cu

3.1.1 Effect of mixing speed and contact time

The mixing speed is determined to obtain the optimum stirring speed in adsorbing copper metal by water hyacinth leaves. This study used a mixing speed of 100, 150, and 200 rpm, respectively with a contact time of 30, 60, and 90 minutes. The effect of mixing speed and contact time on copper adsorption efficiency is shown in **Figure 1**.

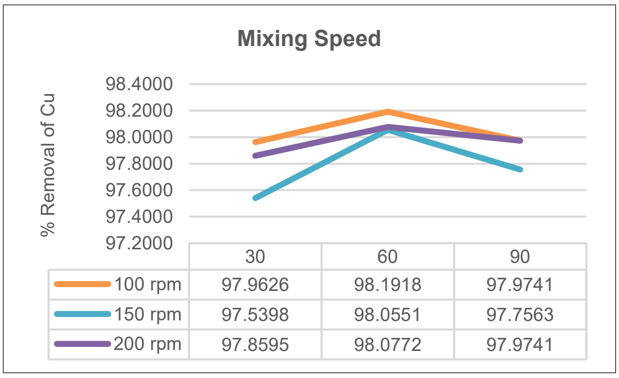

Fig. 1: Effect of Mixing Speed and Contact Time on Cu removal efficiency.

*Corresponding author: rianaayu.kusumadewi @trisakti.ac.id

Fig. 1 shows the maximum Cu removal efficiency of 98.19% was observed at a mixing speed of 100 rpm and a contact time of 60 minutes. The adsorbents and adsorbates were evenly spread to reduce the levels of heavy metal and make Cu more effective. Initially, all active sites in the adsorbent were empty, therefore the adsorption was faster, while the desorption was lower, thereby, leading to a faster increase in the degree of adsorption. Due to the occupied nature of the active sites, the degree of adsorption is lowered and ultimately becomes virtually constant in equilibrium. [21].

3.1.2 Effect of mass adsorbent and contact time

The adsorbent mass of a fixed amount of adsorbate, has the ability to absorb the solution initial concentration. Cu adsorption by water hyacinth leaf powder was studied in ranges of 10, 15 and 20 grams. The effect of initial concentrations of Cu ions is shown ini **Figure 2**.

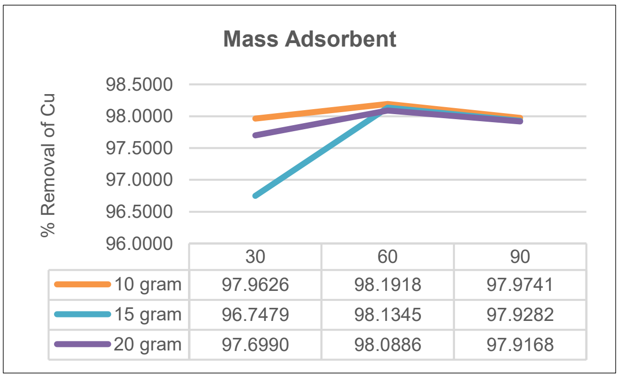

Fig. 2 Effect of Mass Adsorbent and Contact Time on Cu removal efficiency

The experiments were performed at an optimum mixing speed of 100 rpm by adding 10, 15 and 20 grams of adsorbents in the flasks containing 250 ml of Cu solution. The effect of the adsorbent mass on the removal of Cu ions as well as its extraction rise by 98.19% Cu is shown in **Figure 2.** However, there was a decrease in the amount of adsorbed Cu per unit with an increase as the adsorbent. Therefore, for the additional adsorption processes, an adsorbent mass of 10 grams was chosen as the optimum weight. At higher adsorbent doses of 15 and 20 grams, there are limited Cu in the solution, therefore, the adsorption is constant [21].

The water hyacinth leaf also known as *E. crassipes*, is a powerful grower, that doubles its population within two weeks. It is cost-efficient and available for the treatment of dyes and effluents. This herb and its various forms, changes have been investigated to increase effectiveness. However, a detailed study of different wastewater and modified forms has the ability to produce simple, better and cheaper water hyacinth with metal effluents in the near future [17].

3.3 Adsorption Isotherms

To analyze the adsorption capacity, the Langmuir and Freundlich methods were graphically represented.

According to the Langmuir isotherm, the monolayer adsorption of a homogeneous surface is used to determine the finite number of sites without interaction between the adsorbed molecules [18]. Adsorption isotherms describe the balance between adsorbent and adsorbate. Figures 3 and 4, shows the mixing speed and mass of Langmuir adsorption isotherm, respectively.

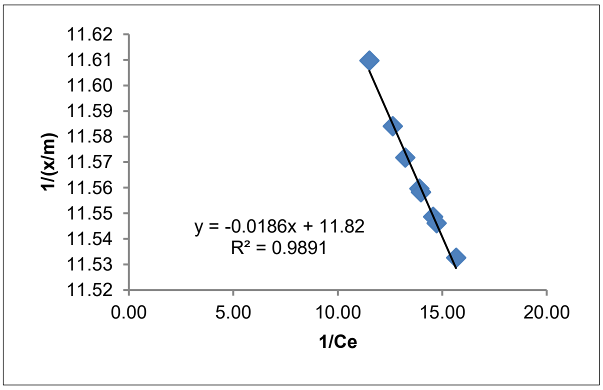

Fig 3: Langmuir adsorption isotherm of water hyacinth leaves adsorbent with mixing speed variations

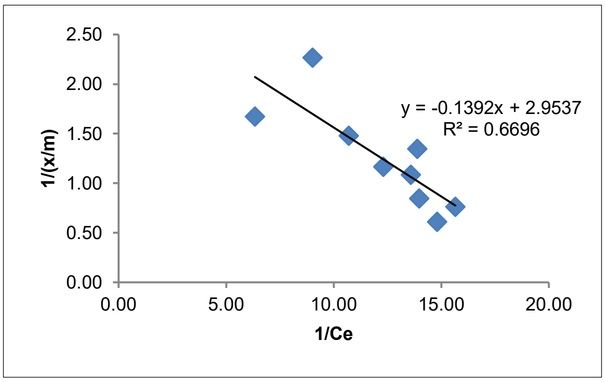

Fig 4: Langmuir adsorption isotherm of water hyacinth leaves adsorbent with a mass of adsorbent variations

The adsorption process was analyzed by using the Freundlich isotherm model which consists of a multilayer distribution process of the adsorbed molecules [18]. Freundlich adsorption isotherm with mixing speed and mass of adsorbent variations is seen in **Figures 5 and 6**, respectively.

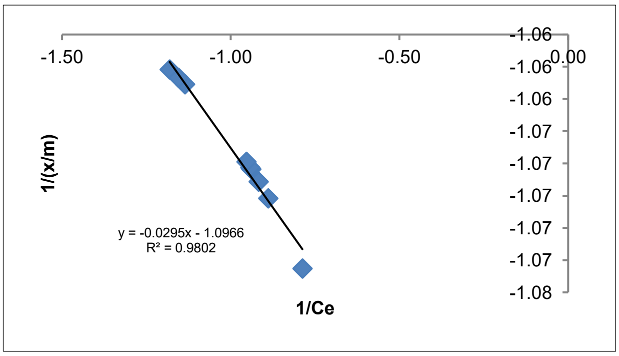

Fig 5: Freundlich adsorption isotherm of water hyacinth leaves adsorbent with mixing speed variations

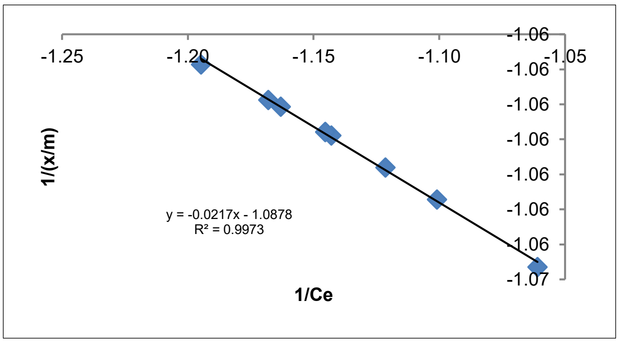

Fig 6: Freundlich adsorption isotherm of water hyacinth leaves adsorbent with a mass of adsorbent variations

The adsorption process used to mix Cu is in close agreement with Freundlich isotherm model (Fig. 3, 4, 5, 6). The coefficient correlation (R^2) values of Freundlich was 0.98 (mixing speed variations) and 0.997 (mass of adsorbent variations), while Langmuir isotherm was 0.989 (mixing speed variations) and 0.669 (mass of adsorbent variations), respectively. The coefficient correlation (R^2) for the Freundlich isotherm curve was closer to 1, and the linear line. The R^2 values for Freundlich adsorption isotherm model were closer to unity (0.98 and 0.997), therefore, the adsorption of Cu onto the adsorbent was heterogeneous and multilayer in nature. The Isotherm Freundlich constant exhibits adsorption capacity at heterogeneous locations with an uneven distribution of the energy level [9]. It assumes that metal ion adsorption occur on a heterogeneous surface with multi-layer adsorption which increases with a rise in concentration [19]. In addition, there is physical adsorption, which means that it occurs on the surface of the absorbent.

The value of n is a constant feature of the adsorption system being studied [20]. When the value of n is above 1, it shows a favorable adsorption, and when it is below 1 it represents poor characteristics. The value of n in this study is -33.9, therefore, the adsorption characteristics with water hyacinth leaves are relatively poor.

The outcome values parameters q_m, b, R^2, and K_f for all experiments using the Freundlich equation, are shown in Table 2.

Table 2: Adsorption equilibrium parameters

The parameters of adsorption	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	q_m (mg g^{-1})	b	R^2	K_f (mg g^{-1} $(l/g)^{1/n}$	1/n	R^2
Mixing speed	635.48	0.08	0.989	3.47	-0.0295	0.980
Mass adsorbent	22.19	0.33	0.669	3.46	-0.0217	0.997

3.4 Adsorption Kinetics

The remaining concentration rates in the wastewater were used to measure the adsorption rate of Cu ions at different time intervals till the equilibrium value was attained. The data were adjusted with different kinetic comparisons, namely, Pseudo first and second orders as shown in **Figures 7** and **8**.

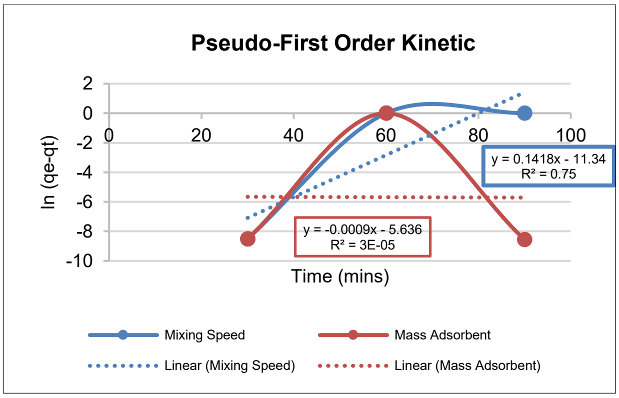

Fig 7: Removal of Cu kinetics according to the pseudo-first-order model

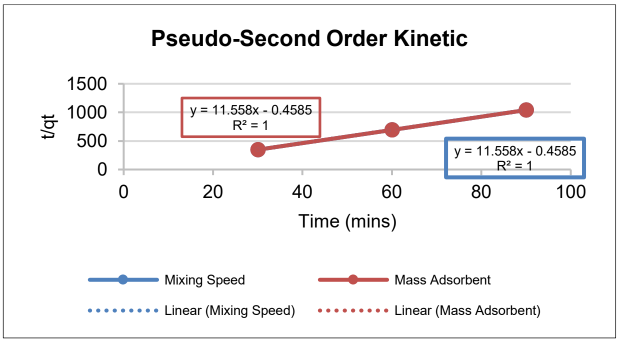

Fig 8: Removal of Cu kinetics according to the pseudo-second-order model

The graphical representations of the kinetic models for the adsorption of Cu compounds shows is **Figures 7, 8, table 3.** The correlation coefficient of the second-order model was high using R^2 with a value of 1. Conversely, the qe value of the second-order model was used in the experimental data and suitable for Cu adsorption in the adsorbent.

Table 3: Adsorption kinetic parameters

The parameters of adsorption	qe, exp (mg g^{-1})	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		k_1(x 10^3) (min^{-1})	qe, cal (mg g^{-1})	R^2	k_2(x10^{-6}) (g mg^{-1} min^{-1})	qe, cal (mg g^{-1})	R^2
Mixing speed	0.087	-0.014	1.19E-05	0.75	-291.36	0.09	1
Mass adsorbent	0.087	0.001	3.57E-03	1	-291.36	0.09	1

3.5 Quality of treated wastewater

Water quality refers to its chemical, physical, biological and radiological properties. In this study, the Cu content of heavy metals after the adsorption process was tested. Water quality after the adsorption process is shown in **Table 4**.

Table 4: Quality of treated wastewater

Hyacinth Leaves Adsorbent					
Mixing Speed Optimum (rpm)	Contact Time (mins)	Untreated wastewater Conc. (mg/l)	Mass of Adsorbent (grams)	Treated wastewater Conc. (mg/l)	Removal Eff. (%)
100	30	1.6755	10	0.0716	97.97
	60			0.0639	98.19
	90			0.0716	97.97
	30		15	0.0813	97.69
	60			0.0675	98.08
	90			0.0736	97.91
	30		20	0.0158	95.53
	60			0.0934	97.35
	90			0.1108	96.86

The quality of untreated wastewater that indicated blue was especially high in Cu (1.67 mg/l) and after treated with wastewater at an optimum mixing speed of 100 rpm, 10 grams mass adsorbent and contact time of 60 minutes it produced a heavy metal with and efficiency of 98.19% and final concentration of 0.0639 mg/l. The quality of the water produced after the adsorption process using the leaves was in accordance with the regulations of the Minister of the Environment on standards for sewage in the paint industry. Therefore, the heavy metal concentration limit Cu is 0.8 mg/l.

4. Conclusion

In conclusion, the mass of water hyacinth leaves contains an adsorbing character that functions as a heavy metal binder, such as Cu. Its adsorbents are promising due to the ability of the Cu to reserve at an optimum mixing speed of 100 rpm with a contact time of 60 minutes. It was therefore found that the bulk adsorbent of the optimum 10-gram water hyacinth leaves increases the sorption process compared to the free adsorbent. The effective parameters of the adsorption processes such as contact time (30, 60, 90 minutes), mixing speed (100, 150, 200 rpm), and mass adsorbent (10, 15, 20 grams) were studied in the batch experiment. Therefore, the optimum removal of Cu ions from the wastewater using 10 grams of adsorbent mass, 60 minutes of contact time, 100 rpm of mixing speed, was obtained for 250 ml with initial concentration solutions of 98.19%. The balance data was properly represented in the Freundlich adsorption isotherm, while the pseudo-second-order model was adapted when the kinetic models for Cu adsorption were analyzed. The quality of water produced after the adsorption process using the leaves met the standard quality regulated by the Minister of Environment.

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*Corresponding author: rianaayu.kusumadewi @trisakti.ac.id