Corn Stalk (Zea Mays L.) Ability on Copper Removal in Continuous Column (Down Flow)

B. Haryanto[1], D. A. Fithry[1], Anita M. H.[1], Puteri K.[1], Azhari B. G.[1], Ashabi S.[1], Walid A. A.[1] and Michael J. B.[1]
[1]*Department of Chemical Engineering, University of Sumatera Utara, Medan 20155, Indonesia*

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Abstract: Corn stalk was used as an adsorbent to observe removal metal ions (Cu^{2+}). The loading time and channeling effect in continuous adsorption column with down flow direction was investigated in concentration 50 ppm of Cu with variation influent flow rates (5, 10, 15 mL/min) and shape/size adsorbent (1/4 round shape, 50 mesh, and 70 mesh). Kinetic of corn stalk adsorption ability has been observed at influent flow rate 5 mL/min for adsorbent size 70 mesh. The adsorption was applied in the column and down flow direction. The effluent samples were collected in every interval 28 mL. The results showed that the % removal efficiency was obtained 98,30; 62,78; 34,74 (%) for with sampling volume 84 mL was reach equilibrium. The highest removal efficiency obtained 34,74 % at flow rate 5 mL/min with adsorbent size 70 mesh.The shortest loading time obtained at 15 mL/min with corn stalk adsorbent shape at 1/4 round. Phenomenon of channeling effect was clearly exist in adsorbent shape at 1/4 round.

1 INTRODUCTION

Copper (Cu^{2+}) is known as dangerous heavy metals which are usually found in wastewater in industrial activities such as mining, plating, smelting, and on agriculture such as fertilization, pesticides and so on. Source of drinking water contaminated with excess copper can cause various diseases in the body of the organism (Hui, 2015) (Wang, 2016) (Rehab, 2016). Recommendation from WHO (World Health Organization) for safe amount of Cu^{2+} ions is 2 mg/L in drinking water and 3 mg/L in industrial waste disposal (Rifaqat and Umra, 2017).The adsorption method is a commonly used method because it is effective and also economical to remove various metals from waste water. The key to the success of the adsorption method is the selection of adsorbents. Adsorbents used can be derived from agricultural waste and industrial solid waste (Malihe, 2015).

The adsorption process can be operated with two systems: batch system and continuous system (column) (Martin, 2016). The column system is an effective and economical method for large volume capacity, simple design and scale up of system (Shahram, 2016). In the column system can be done with two-way flow of the flow from top to bottom (down flow) and flow from bottom to top (up flow) (Maksudur, 2015).

Corn stalks have good potential to be used as bioadsorbents, due to their presence in abundant and untapped environments. Corn stalk has been investigated to remove copper metal by using batch method in solution with concentration 50 ppm and pH 4,5 (Haryanto, 2017). The utilization of corn stalk as an adsorbent to absorb Cu2+ metal ions has been done by previous researchers (Haryanto, 2017). The study was conducted in a batch system by varying the form of adsorbent, contact time and stirring speed.

This research is a continuation of the above research is to know the ability of corn stalks adsorbent on Cu2+metal in the adsorption column is continuous (down flow). Down flow flow direction is used because it provides ease of operation and also ability as a filter simultaneously. This stream

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can be operated with the help of gravity (Sunil and Jayant, 2015).

2 METHODOLOGY

The material used in this research is corn stalk obtained from corn garden in Padang Bulan Village-Medan Selayang Sub-district Medan, Indonesia. Corn stalk used in this study is ¼ round shape with a thickness of ± 0.5 cm, then the size of 50 mesh and 70 mesh. The solution used is $CuSO_4$. $5H_2O$, hydrochloric acid (HCl) was purchased from Mallinckrodt Baker, Inc., Paris, sodium hydroxide (NaOH) was purchased from Merck KgaA, Darmstadt, Germany, as a pH and water regulator of the Aquadestilator model: SMN BIO, as a solvent. The equipment used in this study includes adsorption columns (diameter 1.5 cm and 7.5 cm high) and peristaltic pumps. Analyzes used AAS, FTIR and SEM.

After the tools and materials are prepared, it is determined first loading time on each variation and observed the channeling effect that is formed. The adsorption ability was obtained from the analysis of metal solutions at 28 mL intervals. Figure 1 shows a series of adsorption equipment.

Process description: A 50 ppm metal solution in beaker glass (1) is pumped with a peristaltic pump (2) with an X mL / min flowrate to a column containing corn stalk (3). Then the effluent of the contamination results is accommodated on a measuring cup (4) and is determined as a sampling point which is then analyzed by AAS to examine how much of the absorbed Cu^{2+}metal and the ability of the corn stalk to absorb Cu^{2+}metals.

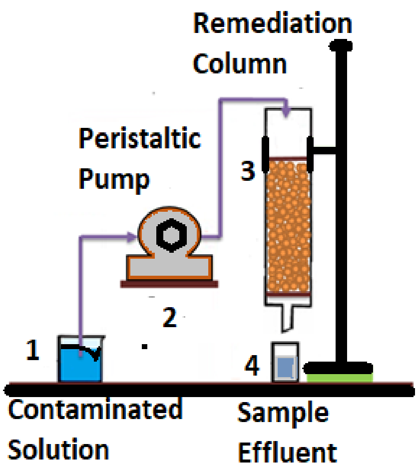

Figure 1: Adsorption equipment set (Dalia, 2015).

3 RESULTS AND DISCUSSION

3.1 Corn Stalk Removal Efficiency Kinetic Adsorption (Size 70 mesh)

The highest corn stalk adsorbent capability in absorbing copper metal ions occurs at the beginning of the adsorption process, but with increasing absorption time decreases until equilibrium conditions are achieved. This condition is caused, the adsorbent active site which absorbs metal ions has saturated (Guyo, 2015).

In Figure 2 shows kinetics removal efficiency based on the accumulation of sampling volume. Removal efficiency increases with the accumulated volume of sampling. From the data obtained it can be concluded that 1 gr of corn bar adsorbent able to absorb Cu2+ metal ions of 92.2634 ppm.

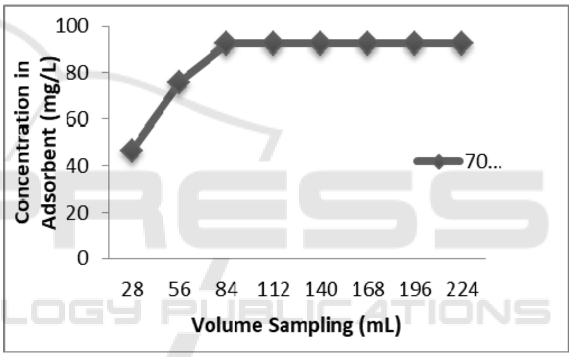

Figure 2: Removal efficiency kinetics on corn stalk adsorption volume accumulation.

3.2 Effect of Flow Rate and Adsorbent Shape/Size on Removal Efficiency

The result data of the influence of the flow rate and the shape/size of the adsorbent on removal efficiency on corn stalk adsorption are presented in Figure 3.

In Figure 3 removal efficiency increases with increasing surface area of corn stalk adorbent. At a flow rate of 5 mL with the shape and size of a 1/4 round; 50 mesh; 70 mesh obtained removal efficiency 9.77; 25,47; 34.74 (%). At a 10 mL flow rate with the shape and size of a 1/4 round; 50 mesh; 70 mesh obtained removal efficiency 2,46; 17,36; 22.50 (%). At a flow rate of 15 mL with the shape and size of a 1/4 round; 50 mesh; 70 mesh obtained 0.84 removal efficiency; 7.40; 9.53 (%). On the adsorbent size of 70 mesh obtained higher removal efficiency when compared with the size of 50 mesh and 1/4 round.

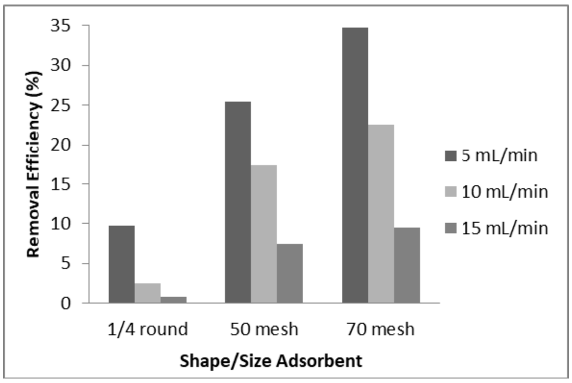

Figure 3: Influence adsorbent shape/size on removal efficiency.

The removal efficiency decreases with increasing flow rate. In the Flow rate is an important parameter as a metaphor of contact time of solution with adsorbent in adsorption column. With increasing flow rate then removal efficiency will decrease. At high flow rates the contact time of the inlet solution with the adsorbent is ineffective to exclude the metal ion as the solution leaves the column before the equilibrium is reached, resulting in a high effluent solution concentration (Kumar, 2015). High flow rates cause limited intraction between the pores and the inlet solution resulting in low removal efficiency. In this study the best flow rate is 5 mL/min.

As the particle diameter increases, the stagnant film thickness around the particles increases resulting in the kinetics of the process decreasing as the time for the adsorbent absorbs the short ionic molecule (Ensar and Muhammed, 2014). Increased absorption rate is affected by small particle size, since small particles have large surface of adsorbents. The breaking of large particles becomes smaller aims to open the gaps on the surface of the adsorbent so that the diffusion process is more easily achieved (Kartthikeyan, 2004). In this study the best adsorbent size is 70 mesh.

3.3 Effect of Loading Time and Channeling Effect

Loading time is the time required for the solution to penetrate the pores of the adsorbent until it exits from the adsorption column. Determination of loading time can also be affected by channeling effect (Haryanto, 2018) The effect of loading time and channeling effect is shown in Figure 4.

In Figure 4 with variation of adsorbent size at increasing flow rate obtained loading time decreasing. In the shape of 1/4 round with flow rate 5; 10; 15 (mL / minute) obtained loading time 0,32; 0.11; 0.08 (minutes). At the size of 50 mesh with a flow rate of 5; 10; 15 (mL / min) obtained loading time 2.09; 1.08; 0.50 (minutes). At size 70 mesh with flow rate 5; 10; 15 (mL / min) obtained loading time 2.12; 1.32; 1.20 (minutes).

Increasing the flow rate and down flow flow direction influenced by the force of gravity causes the time required by the solution to exit from the shorter column. Because the time required by the solution to come out short then loading time will decrease. Loading time is the time required for the solution to penetrate the pores of the adsorbent until it exits from the adsorption column (Haryanto, 2018).

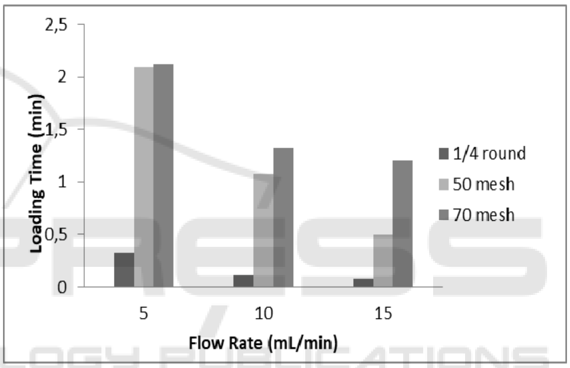

Figure 4: Effect of loading time on shapes variation.

The shape and size of the adsorbent also affects the time required by the solution to exit the column. The larger the shape and size of the adsorbent will result in the formation of a gap that causes the solution to rapidly exit the column.

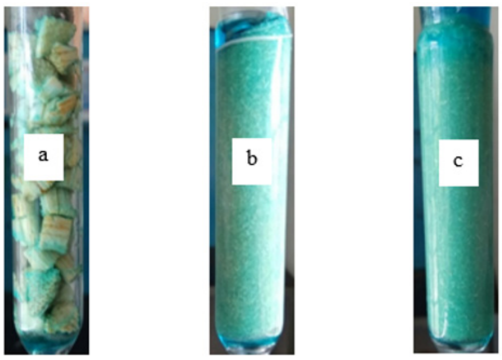

Figure 5: Image of channelling effect on shapes variation.

In Fig. 5 with different shapes and sizes of adsorbents showing the presence of an channelling effect. The phenomenon of channeling effect is evident in the shape of 1/4 round. In the figure with the shape of a 1/4 round forming a large gap, so that when the solution comes in there is a portion of the surface of the non-wetted adsorbent as a whole. This can be seen from the color difference in the adsorbent. At the size of 50 mesh and 70 mesh channeling effect also occur, but the phenomenon of channeling effect is not obvious because the gap formed on the size of 50 mesh and 70 mesh is very small.

Different shapes and sizes of adsorbents can affect the porosity of the adsorbent associated with the fluid velocity that flows in the column. The varying porosity of the adsorbent may result in a difference in drag force in the fluid stream which causes the fluid flow tendency to move freely, resulting in channeling effect (Vafai, 1986).

Loading time and channeling effect will affect the ability of adsorption of corn stalk. With the increase in flow rate then loading time will decrease. High flow rates cause limited intraction between the pores and the inlet solution resulting in low removal efficiency. Given the phenomenon of channeling effect resulting in absorption capacity at large adsorbent size is not maximal because the formation of a large gap between the adsorbents on the column resulted in the metal solution out quickly before interacting on the surface of the adsorbent. In this study the best flow rate is 5 mL / min and the best adsorbent size is 70 mesh.

3.4 Results FT-IR and SEM Analyzes

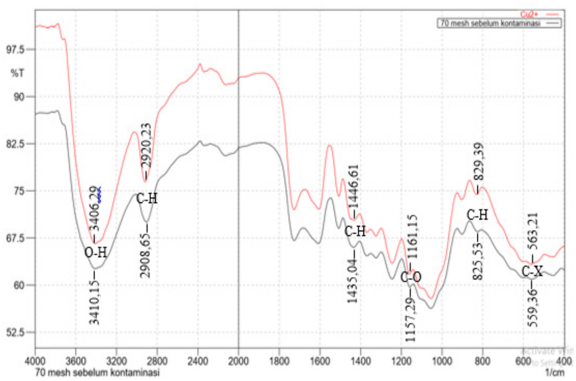

Figure 6: Figure 6 FT-IR Analysis results.

Fourier Transform Infra Red (FT-IR) analyzes of 70 mesh corn stalk adsorbent before and after contamination of Cu^{2+} metal ions were performed to identify the functional groups present in each sample. From the functional group analysis using FT-IR obtained spectrum results are presented in Figure 6.

Figure 6 shows the increase and decrease of wave numbers before and after contamination. Increasing the wave number before and after the contamination occurred at the wave number 2908.65 cm-1 to 2920,23 cm-1 is the C-H bond wave number; the wave number 1435.04 cm-1 to 1446,61 cm-1 is the number of the C-H bond wave; the wave number 1157.29 cm-1 to 1161.15 cm-1 is the number of the bond wave C-O; the wave number 825.53 cm-1 to 829.39 cm-1 is the number of the C-H bond wave; the wave number 559.36 cm-1 to 563.21 cm-1 is the number of the C-X bond wave. The decrease of wave numbers before and after contamination occurred at the wave number 3410.15 cm-1 to 3406.29 cm-1 is the O-H bond wave number (Skoog, 1998). The shift in wavelength indicates there is an interaction of adsorption absorption between functional groups and Cu^{2+} ions. Cu^{2+} ions may bind to carboxyl groups and hydroxyl groups (Rifaqat and Umra, 2017).

The result of Scanning Electron Microscope (SEM) analysis on 70 mesh corn stalk adsorbent before and after contaminated Cu^{2+} metal ion was done to identify morphological structure of corn stalk. From the analysis of the morphological structure using SEM the results obtained are presented in Figure 6.

4 CONCLUSIONS

The conclusion that can be obtained is kinetics% removal efficiency of 98.30; 62,78; 34.74 (%) with 84 mL sampling volume has reached saturation point. The highest efficiency removal was obtained 34,74% at 5 mL/minute flow rate with 70 mesh corn stalk adsorbent. The shortest loading time is obtained at a flow rate of 15 mL/min with a corn stalk 1/4 round adsorbent. The phenomenon of channeling effect is evident in the shape of a 1/4 round corn stalk adsorbent.

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