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CORN STALK (*Zea mays L.*) ABILITY IN REMOVING DISSOLVE HEAVY METAL CADMIUM ION (II) IN CONTINUOUS ADSORPTION COLUMN (DOWN FLOW)

Bode Haryanto, Rondang Tambun, Siswarni MZ, Anita M Harahap and Puteri Kemala
Department of Chemical Engineering, Universitas Sumatera Utara, Padang Bulan, Medan, Indonesia
E-Mail: bode.haryanto@usu.ac.id

ABSTRACT

Corn stalk was used as an adsorbent to observe removal metal ions (Cd^{2+}), loading time and channeling effect in continuous adsorption column. This study investigated solution in concentration 50 ppm with variation influent flow rates (5, 10, 15 mL/min) and shape/size adsorbent (1/4 round shape, 50 mesh, and 70 mesh). Kinetic adsorption has been observed of influent flow rate 5 mL/min with size 70 mesh. The experiment was used corn stalk adsorbent in the column and down flow direction. The effluent samples were collected in every interval 28 mL. 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. The results showed that % removal efficiency kinetic obtained 100; 100; 71, 3; 45, 34 (%) with sampling volume 112 mL was reach equilibrium. The highest removal efficiency obtained 43, 55 % at flow rate 5 mL/min with adsorbent size 70 mesh.

Keywords: corn stalk, adsorbent, channeling effect, column adsorption, removal efficiency.

1. INTRODUCTION

Most of the heavy metals waste generally comes from industrial activities. Industries such as mining, coating, coloring, electrochemical metal processing, and battery storage are industries that generally produce heavy metal waste from their activities (Sangiumsak and Pongsakorn, 2014). Metal pollution basically does not stand alone, but can be carried by water, soil and air. If all these components have been contaminated by inorganic compounds, then they may contain various heavy metals such as Cr, Zn, Pb, Cd, Fe and so on (Darmayanti, *et al*., 2012). One of the technologies for reducing heavy metals is the adsorption method (Kampalanomwat and Pitt, 2014). Adsorption is an efficient method, the operation is mud free, easy to handle and abundant availability of adsorbents (Song, *et al*., 2015). In general, the factors that influence the adsorption process (Syauqiah, *et al*., 2011**)** are as follows: Surface area, type of adsorbate, molecular structure of adsorbate, adsorbate concentration, temperature, pH, stirring speed, contact time adsorption porosity, equilibrium time.

Adsorption using columns is one of the most common and efficient ways to remove pollutants in water (Gupta, *et al*., 2016). Adsorption using columns can be used at high levels of waste flow in the pollution control process (Karunarathne and Amarasinghe, 2013).

The most important adsorption process is the adsorbent. Today, the adsorption method has been developed using plant biomass known as bioadorbent. Cheap adsorbents can be developed from agricultural wastes, which are used to remove copper ions, including peanut husks, cashew shells, waste cassava bark, tubers, walnuts, hazelnuts, and almond shells, poplar wood, sawdust, walnut husks, rice bran, wheat bran, wheat straw, soybean straw, corn, corn cob, brown skin, biomass waste, shellfish, sugarcane pulp, and rice husk (Kumar, *et al*., 2015).

Corn (Zea mays L.) is one of the most important world food crops, besides wheat and rice. Corn plants are one type of grain food crop from family grasses. Corn has been used as an adsorbent to absorb metals in liquids (B Haryanto, *et al* 2016; B Haryanto, *et al.,* 2017).

The aim of this study was to know the ability of corn stalks adsorbent on Cd^{2+}metal in the adsorption column continuous with variation flow direction down flow and up flow. To confirm of the impact of channelling effect to adsorb the adsorbed dissolve in solution in continuous operation.

2. METHODOLOGY

The corn stalk obtained from corn garden in Padang Bulan Village-Medan Selayang Sub-district Medan, Indonesia. The shape variation of the corn stalk used in this study is ¼rounds with a thickness of ± 0.5 cm, the size of 50 mesh and 70 mesh. The solution used is $CdCl_2$, hydrochloric acid (HCl) was purchased from Mallinckrodt Baker, Inc., Paris. The sodium hydroxide (NaOH) was purchased from MerckKgaA, Darmstadt, Germany, as a pH and water regulator of the Aquadestilator model: SMN BIO, as a solvent. The equipment operation 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. The steps activities in this study is as shown in Figure-1.

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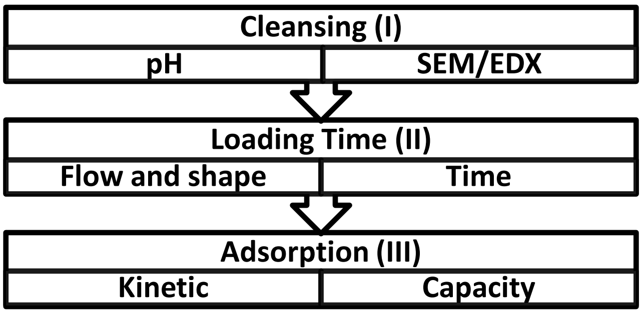

Figure-1. The methodology steps.

The operation tools and materials are prepared; the loading time was determined first on each variation and observed the channeling effect that is formed. The adsorption ability was obtained from the analysis of metal solutions effluent at 28 mL intervals. The Figure-2 shows a series of adsorption equipment.

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

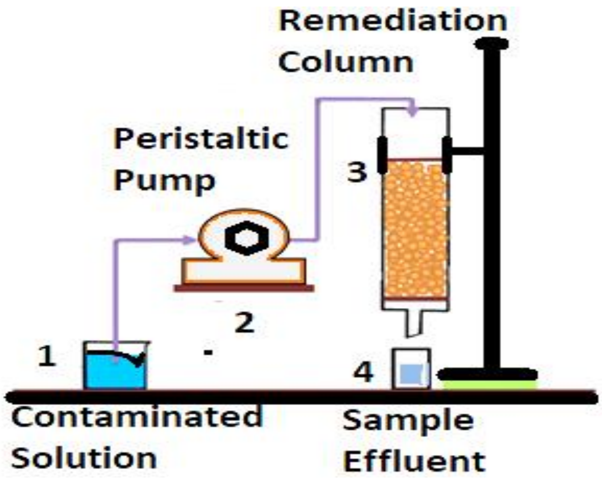

Figure-2. Adsorption equipment set (Dalia *et al*, 2015).

3. RESULTS AND DISCUSSIONS

3.1 Preliminary Treatment on Cornstalk

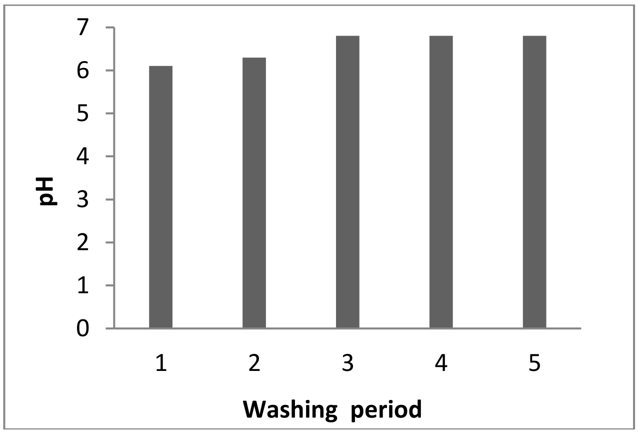

Figure-3. Washing of corn rod adsorbents.

Corn stalks are cleaned from the leaves and the outer shell, and then cut into a quarter circle shape (1/4). To obtain corn stalks free of impurities such as soil and fungicide or insecticide residues, a washing process is carried out on the corn stalks. It was washed by filtrate water near the pH of washing water. The results of the analysis of corn stem washing are presented in Figure-3. As an indicator,the pH of washing water is constant at the 3rd, 4th and 5th washing.

In the corn stalk adsoben the first washing process has a pH of 6.1. The second washing has a pH of 6.3. And in the 3rd, 4th and 5th washing, the washing pH is constant to 6.8. In the 5th washing process shows that the pH of the washing filtrate in the corn stalks is close to a neutral pH. In a neutral pH indicates that the corn stalks are clean of dirt attached to the corn stalks.

The following is the observation of EDS on corn stalks before (a) and after washing (b) and SEM image (c) in is shown in Figure-4.

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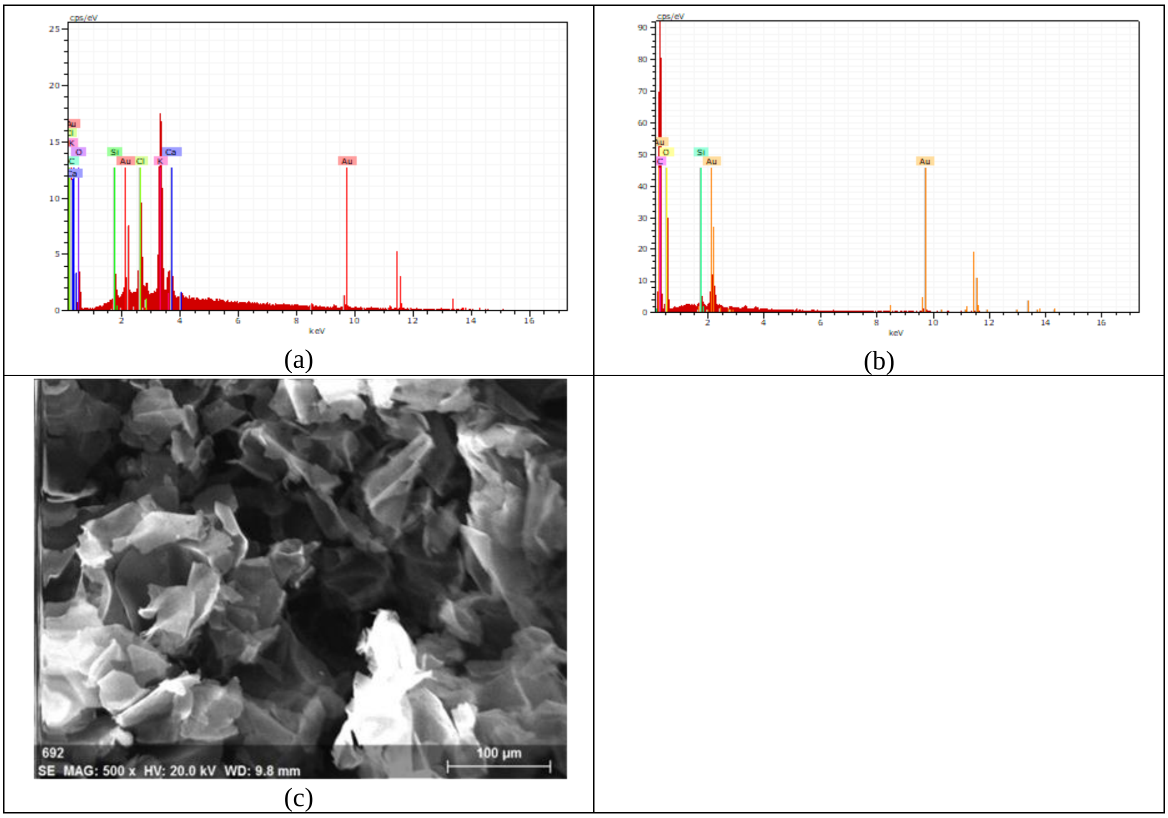

Figure-4. EDS and SEM observation results in (a) Before washing, (b) After washing and surface structure image (c).

This shows that a significant difference occurs after the washing process. From Figure-4(a) shows a lot of compositions other than mixed corn stalks and bound. Where as in Figure-4(b) it looks less compared to Figure-4(a). This shows that the washing of impurities in corn stalks has disappeared so that the corn stalks in this study are sufficiently feasible to be used as natural adsorbents. Washing done on corn stalks aims to obtain a constant pH condition (B Haryanto, *et al* 2016; B Haryanto, *et al.*, 2017) and also to remove impurities found on the surface of the adsorbent (Rahmawati, 2003). After washing the corn stalks with a quarter circle size, then the drying process is carried out at a temperature of 55^0C. Drying is done on the corn stalk so that the water content in the corn stalk is reduced condition (Haryanto and Chang, 2014; B Haryanto, *et al.*, 2016; B Haryanto, *et al* 2017).

3.2 The Effect of Flows on Loading Time

Loading time is the time required for the solution to penetrate the pore from the adsorbent until it exits the adsorption column. Determination of loading time can also be influenced by channeling effects (Haryanto and Chien-Hsiang, 2014). The effect of flow rate on loading time is shown in Figure-5.

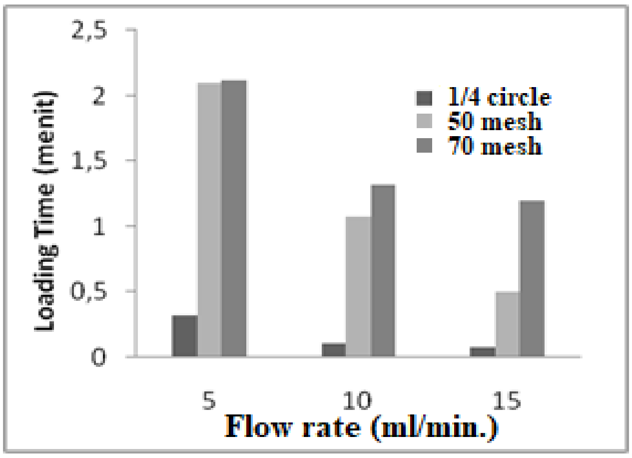

Figure-5. Effect of flow rate against loading time.

Increasing the flow rate and the direction of the down flow flow which is influenced by gravitational forces causes the time needed by the solution to exit the column to be shorter, because the time required for the solution to come out is short. pore from the adsorbent to exit the adsorption column (Haryanto and Chien-Hsiang, 2014). The shape of the adsorbent also affects the time taken by the solution to exit the column. The greater the shape of the adsorbent, the more difficult it is to form a gap that causes the solution to exit the column.The shape and size of different adsorbents can affect the porosity of the adsorbent related to the velocity of the fluid flowing in the column. The varying porosity of the adsorbent can produce a difference in drag on fluid flow which causes the tendency of fluid flow to move freely, giving rise to channeling effects (Vafai, 1986).

3.3 Kinetics of Removal Efficiency of Cd

Data from the results of the removal efficiency kinetics on corn stalk adsorption are presented in Figure-6.

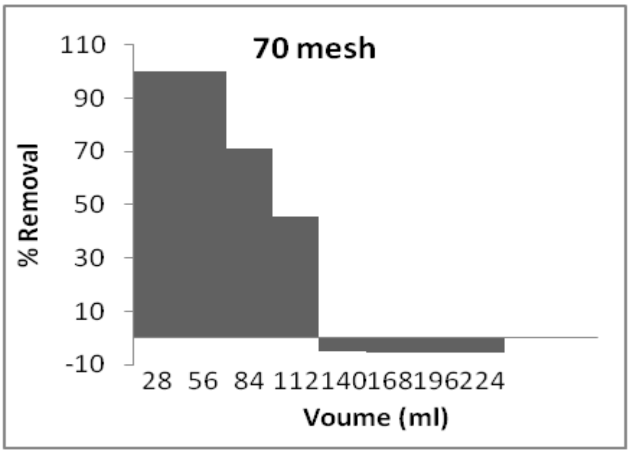

Figure-6. Removal efficiency kinetics of Cd ion by corn stalk.

In Figure-6 removal efficiency decreases with increasing sampling volume. The addition of sampling volume is directly proportional to the increase in time. On the adsorbent with a size of 70 mesh with the 1st sanding; 2; 3 and 4 obtained efficiency100 removal; 100; 71.3 and 45.34 (%). However, at the 5th to 8th distortion, the removal efficiency occurs negatively. At the beginning of the adsorption process, the adsorbent of the corn stem is able to absorb metal ions well, so that the removal efficiency obtained is high. However, with the increase in sampling volume, the removal efficiency decreases. At a sampling volume of 112 mL the corn stem adsorbent has reached its saturation point.

The ability to adsorb corn stalks as high as absorb cadmium metal ions occurs at the beginning of the adsorption process, but with increasing time the absorption ability decreases until an equilibrium condition is reached. This condition is caused by the active site of the adsorbent that absorbs metal ions already saturated (Guyo *et al*., 2015). When it reaches saturation, the biomass adsorption power will decrease because the biomass surface is not strong enough to bind the metal cations remaining in solution (Komari and Anjang, 2012).

In the picture there is a decrease in efficiency removal to a negative value. This is because the desorption process also occurs in the adsorption process, this phenomenon occurs because the saturation of the adsorbent surface so that the ion returns from the adsorbent surface to enter the solution (Fajrianti, *et al*., 2016).

The decrease in absorption is due to the weakening of the bond between the active site and the metal ion Cd (II) and also the presence of namesake ion competition in the struggle for active sites. A weak bond makes the bond detachment that occurs between active sites and metal ions Cd (II) (Prastiwi *et al*., 2013).

3.4 Effect of Shape and Flow Rate on Removal Efficiency

Flow rate is an important parameter as a description of the contact time of the solution with the adsorbent in the adsorption column. With increasing flow rate the removal efficiency will decrease (Kumar, *et al*., 2015). Increasing flow rate can cause the absorption rate to decrease, because the adsorbate residence time in the column decreases (Rocha, *et al*., 2015). High flow rates cause the contact between the surface of the adorbent and the metal Cd^{2+} takes place very quickly, so the metal Cd^{2+} to be absorbed by the adsorbent is very little. While at a low flow rate the contact between the surface of the adorbent and metal Cd^{2+} lasts longer, so that the absorption of metal Cd^{2+} is greater (Nur and Danarto, 2007).

In the discussion of the previous section, the relationship between flow rate and loading time has been described. By increasing the flow rate causes the loading times to decrease. The high flow rate causes limited interaction between the pore surface of the adsorbent and the solution so that the removal efficiency is low. In this study the best flow rate was obtained at 5 mL / minute.

In Figure-7 the removal efficiency of the corn stalk adsorbent at the same flow rate can increase by reducing the size of the adsorbent. At a flow rate of 5 mL/minute with the size of the adsorbent 1/4 circle, 50 mesh and 70 mesh obtained removal efficiency 17.46; 29.68 and 43.55 (%). At a flow rate of 10 mL/min with the size of the adsorbent 1/4 circle, 50 mesh and 70 mesh obtained efficiency7, 32 removals; 21.18 and 32.45 (%). At a flow rate of 15 mL/minute with the size of the adsorbent 1/4 circle, 50 mesh and 70 mesh obtained efficiency 0, 79 removal; 11.63 and 16.38 (%).

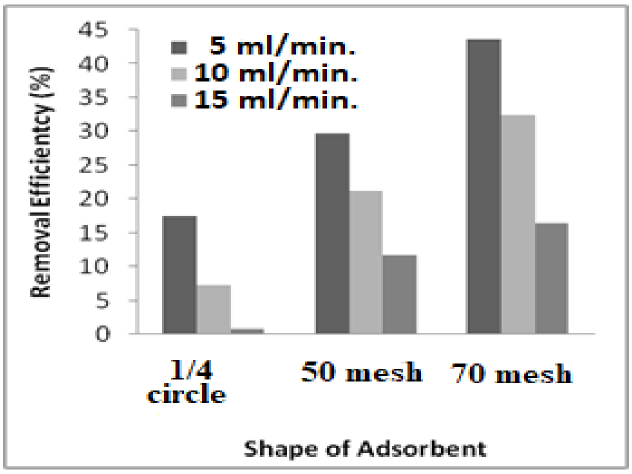

Figure-7. Effect of adsorbent forms on removal efficiency on adsorption of corn stalk.

The results of the above experiments show that in the size of 70 mesh the best removal efficiency is obtained than the size of ¼ circle and 50 mesh. This is because the size of 70 mesh is smaller than the size of the adsorbent ¼ circle and 50 mesh.

Absorption rate is influenced by the size of the adsorbent. Breaking large particles into smaller ones aims to open small cracks and crevices on the surface of the adsorbent so that the diffusion process is more easily achieved. The smaller size of the adsorbent can increase the rate of absorption of a metal. This is because the smaller the size of the adsorbent has a larger surface area of the adsorbent (Karthikeyan, *et al*., 2004).

The channeling effect phenomenon has been discussed in the previous sub-section, in the larger size of the adsorbent, namely ¼ circle size, it was found that the real phenomenon of channeling effect was compared with the size of 50 and 70 mesh adsorbents. The larger form of the adsorbent results in a large gap between the adsorbent, which forms a channel which can cause the solution to get out of the adsorption column faster. With the presence of a large gap between the adsorbent, it can cause the exit rate of the solution to be faster in the larger size of the adsorbent. Increasing the flow rate of the solution can reduce the contact time between the adsorbent and the adsorbate resulting in reduced absorption capacity (Biswas and Mishra, 2015).

3.5 Characteristics ofResults of Fourier Transform Infrared (FTIR) Analysis

The characteristics of the analysis of Fourier Transform Infra-Red (FT-IR) on 70 mesh corn stalks before and after metal ion contamination Cd^{2+} were carried out to identify the functional groups in each sample. From the analysis of functional groups using FT-IR spectrum results obtained in graph size can be seen in Figure-8.

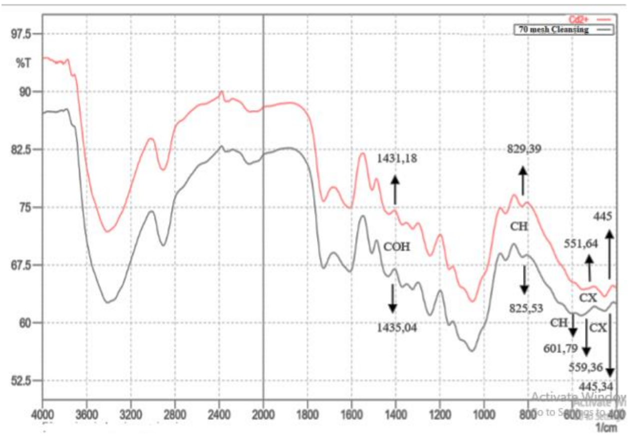

Figure-8. Characteristics of FTIR analysis results.

The increase in wave number occurs at wave number 825.53 $cm^{-1}$to 829.39 $cm^{-1}$and at wave number 451.34 $cm^{-1}$to 455.20 cm^{-1}. The peak at 829.39 cm^{-1} is the wave number of the CH bond. The peak at 455.20 cm^{-1} is the wave number of the C-X bond on the cellulose of the corn stalk. The decrease in wave number occurs at wave number 1435.04 cm^{-1} to 1431.18 $cm^{-1}$and at wave number 599.39 cm^{-1} to 551.64 cm^{-1}. The peak at 1431.18 $cm^{-1}$is the wave number of the C-O-H bond and the peak at 551.64 cm^{-1} is the wave number of the C-X bond.

Wave number removal occurs after Cd^{2+} contamination, is at wave number 601.79 cm^{-1}, that is an N-H bond. Shifts in the spectrum, reduction and removal of frequency peaks indicate there is an interaction of adsorption absorption between functional groups and Cd^{2+} ions (Guyo *et al*., 2015). With increasing frequency of functional groups, it increases the absorption ability of positive ions (Rini, 2014). Corn stalks have good potential to be used as bio-adsorbents, because their presence in the environment is abundant and has not been utilized properly (Haryanto, *et al*., 2016). Corn stalks are rich in cellulose content. The chemical reactivity of the hydroxyl group (-OH) in cellulose is an important functional group in binding metals (Zheng and Peipei, 2015).

In the study it was found that the functional groups involved in the process of absorption of Cd^{2+} ions as shown in wave numbers FT-IR graphs are functional groups COH, CH, NH and CX. The loss of NH functional groups on the adsorbent before contamination and the shift of peak COH functional groups, CH and C-X showed absorption of Cd^{2+} ions.

4. CONCLUSIONS

The down flow column adsorbent shows the kinetics% removal efficiency of 100% until 56 ml then decrease to 70% after 84 ml and 40% at 112 ml. After the volume has reached saturation point and the metal ion tends to desorb from the surface. The highest efficiency removal was obtained 43,74% 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. Corn stalks have good potential to be used as bio-adsorbents, because their presence in the environment is abundant.

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