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CORN STALK (ZEA MAYS) MODIFIED BY NITRATE ACIDS (HNO3) TO ADSORB DISSOLVED COPPER IONS (Cu^{+2}) IN ADSORPTION COLUMN

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ABSTRACT

Corn stalk modification was used as an adsorbent to remove metal ions of Cu^{2+} in solutions and have done in the adsorption column with continuous operation. The corn talk was modified with nitrate acid (HNO3). The Adsorption operations were applied with corn stalk variation sizes 50 mesh, and 70 mesh with initial concentrations of metal ions 50 and 150 mg/l. The solution flow was controlled at 5 and 15 ml/min. The adsorption operations have been done in up-flow and down-flow. Each operation collected the flow effluent base on pore volume intervals of 4 to 32 PV. To confirm the changes in surface structure and chemical components after modifying have used SEM and EDX. The results show changes significantly. While, the application of corn stalk was modified shown by the influence of loading time, % removal efficiency, adsorption kinetics, and breakthrough curve. Increased loading time occurs at increased concentration, decreased flow rate, and increased adsorbent size. While the increase in% removal efficiency occurs in the decrease in concentration, decreased flow rate, and increased adsorbent size. On adsorption up, the flow has longer saturation than in downstream adsorption. The shape of the breakthrough curve for adsorption up the flow and down flow follows the shape of the "S" curve. But the up flow breakthrough curve on adsorption is more stable than adsorption with the down flow.

Keywords: corn stalk, down flow, Cu^{2+}, breakthrough curve, up flow.

INTRODUCTION

Agricultural waste can be used as an adsorbent because it contains cellulose and lignin which can bind heavy metals and can be modified so that it has a stronger binding capacity [1]. For example, waste corn stalks, the largest part of the maize crop [2]. So far the use of waste corn stalks is not much, except for comprehensive uses such as animal feed and fertilizer [3] because most of it is disposed of by direct burning [4]. In fact, it is the chemical reactivity of the hydroxyl (-OH) groups in the cellulose on corn stalks that causes a certain adsorption capacity. However, the adsorption capacity of corn stalks is generally lower, due to the -OH group involved in hydrogen bonding between cellulose molecules. Fortunately, chemical modifications can be made to break these hydrogen bonds, so that the C-6, C-2, and C-3 groups become more reactive to other functional groups, and can result in better adsorption properties [5].

The column method is an alternative method in the adsorption process. The column method uses an adsorbent that is introduced into a column and the metal solution is passed through the column at a certain flow rate. The column method is thought to be capable of adsorbing large amounts of metal ions from the solution [6]. The adsorption column (fixed-bed adsorber) is the most common and efficient means of purifying wastewater [7]. In the column system, flow can be carried out in two ways, namely down flow or up-flow [8]. In both liquids, the solution will be adsorbed quickly and effectively on the initial surface layer of the incoming solution, where the layer is in direct contact with the solution at high concentrations, while the adsorbent layer will then absorb the solution with a low concentration, and so on [9].

The research carried out is to use a chemical modification of the adsorbent corn stalk and compare the two flows in the column, namely the flow from top to bottom (downflow) and flow from bottom to top (up-flow) by varying the factors that support the success of the column system, namely flow rate, adsorb size and initial concentration of metal solution [9].

This study used a modification methodology of nitric acid in the manufacture of the adsorbent and applied it to the adsorption column from two flow directions (up flow and downflow). The purpose of a nitric acid modification is to increase the adsorption capacity of corn stalks, while the process of using an up-flow and down-flow adsorption column is to determine the performance and adsorption mechanism carried out.

Corn stalks are the largest part of the corn plant. Corn stalks are upright, internodes wrapped in leaf midrib, easily visible [10] round cylindrical, and filled with bundles of vessels thereby strengthening the stems [11]. According to Dien *et al,* 2012 [12], The chemical components found in corn stalks are as follows:

Table-1. Chemical components of corn stalks.

Component	Size
Fibre Length	0.7 - 1.5
Fiber Diameter	11.6 - 12.1
Cellulose	39.9
Lignin	21.2
Pentosane	21.8
Extract in Acetone	5.2
Ash	4.8

Corn stalks are rich in natural cellulose, mostly produced from corn waste, but most of them are disposed of by direct burning in the field without effective use, which causes serious environmental pollution. The cellulose structure has a number of reactive hydroxyl groups and can be used for the chemical modification of corn stalks [4]. Following is the chemical structure of corn stalks [1]:

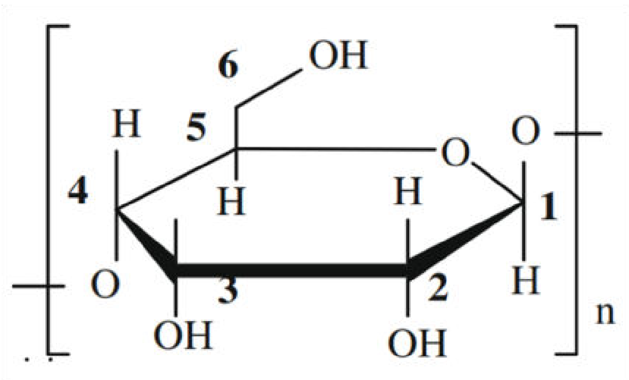

Figure-1. Chemical structure of corn stems.

The chemical reactivity of the hydroxyl groups (-OH) in cellulose is another important function, which causes a certain adsorption capacity in corn stalks. However, the adsorption capacity of the stem is generally lower, due to the –OH group involved in the intermolecular hydrogen bonding of cellulose. Fortunately, chemical modifications can be made to break these hydrogen bonds, so that the C-6, C-2, and C-3 groups become more reactive to other functional groups, and can result in better adsorptive properties [5].

Copper enters the sea through the process of mineral rock and human activities and municipal waste. Elemental Cu is toxic to invertebrates and is synergistic when together with Zn [13]. The presence of copper in small amounts is very useful for living things because it is an essential metal, but in large amounts, it can cause various health problems because of its toxic nature. Copper ions can accumulate in the brain, skin tissue, liver, and pancreas [14].

The presence of Cu metal in the environment needs attention considering that the permissible threshold is so small. Based on the Decree of the Minister of State KLH Kep.02/Men-KLH/1998 concerning the Determination of Environmental Quality Standards, the presence of Cu metal in the environment is expected to be zero, while the maximum allowable limit is 1 ppm [15].

Adsorption is a process that occurs on the surface of a solid that is in contact with a solution where there is an accumulation of solution molecules on the surface of the solid. Organic substances in a solution that have a low solubility in water, the easier it to be adsorbed from the solution. Similarly, the less polar an organic compound is the better it is adsorbed from a polar solution to a non-polar surface [15]. The substance that is absorbed is called an adsorbate while the material that functions as an absorber is called an adsorbent [16].

Adsorption in general is the process of coagulation of dissolved substances in solution, by the surface of the absorbent substance or object, where a chemical-physical bond occurs between the dissolved substance (adsorbate) and the absorbent (adsorbent). The interaction process can occur between liquids and gases, solids, or other liquids. Physical adsorption occurs because of the Van Der Waals bond, and if the attractive bond between the adsorbate molecules and the adsorbent is greater than the bond between the solute molecules and the solvent, the solute will be adsorbed [17]. Meanwhile, chemical adsorption is the result of a chemical reaction between the adsorbate and adsorbent molecules where electron exchange occurs [18].

Adsorption is carried out by adding adsorbent, activated carbon, or the like. The adsorption system consists of two types, namely the batch system and the continuous system (column). Batch adsorption will provide an overview of the ability of the adsorbent by mixing it with a fixed amount of solution and observing changes in quality at certain intervals [26]. Whereas continuous adsorption is practical, this process has a much better approach to application in the field because the operating system is always in contact with the adsorbent with a fresh solution, so the adsorbent can adsorb optimally until saturated conditions [20].

Although batch adsorption studies provide useful data and parameters on the application of adsorbents, the column method is also needed to provide practical operational information with respect to the use of adsorbents. Fixed bed columns can be operated singly, in series, or in parallel whereas the use of small-scale columns is used to stimulate the potential performance of the adsorbent, and the results obtained are extrapolated in a full-scale reactor design [21].

MATERIALS AND METHODS

The materials used in this study were corn stalks as adsorbent, obtained from corn farming on Jalan Pembangunan I, Padang Bulan Village, Medan Selayang District, Medan City, Indonesia. Corn stalks used in this study were 50 mesh and 70 mesh in size. The solution used is CuSO4. $5H_2O$, hydrochloric acid (HCl) was purchased from Mallinckrodt Baker, Inc., Paris, Nitric acid (HNO_3), sodium hydroxide (NaOH) was purchased from Merck KgaA, Darmstadt, Germany, as a pH regulator, and

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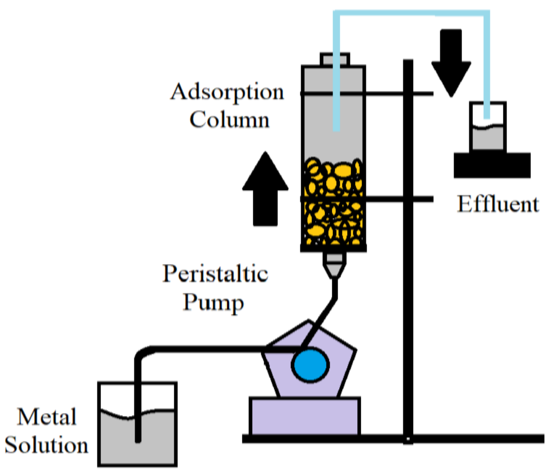
water (H_2O) from the equipment Aqua distillate model: SMN BIO, as a solvent. Then also Whatman 41 filter paper, sample bottles, and label paper.

The tools used in this study are a column (3 cm diameter and 15 cm high), peristaltic pump, 50, 70, and 100 mesh filters, pH meter, hot plate, magnetic stirrer, analytical balance, oven, blender, Atomic Absorption Spectroscopy (AAS) (AA-7000 Series, Shimadzu Corporation, Japan), Scanning Electron Microscope (SEM), and Energy Dispersive X-ray Spectroscopy (EDX) (Phenom ProXDekstop SEM, Thermo Scientific, USA).

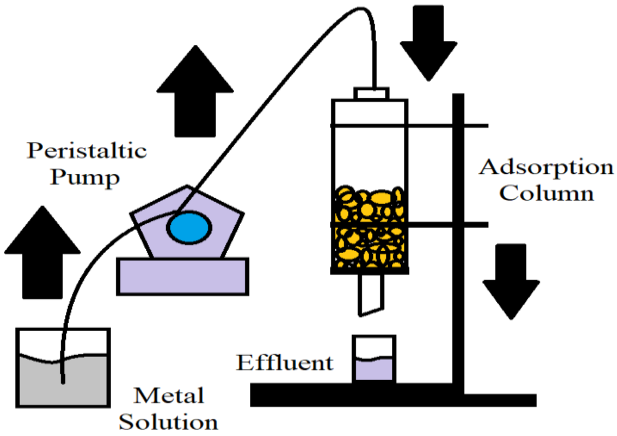
The research procedure included the manufacture of adsorbent corn stalks modified with nitric acid (HNO_3) and the application using up-flow and down-flow adsorption columns. The procedure for making corn stalk adsorbent is the reduction of corn stalks with a size of 70 mesh (through 70 mesh and held in 100 mesh) and 50 mesh (through 50 mesh and stuck in 70 mesh) than weighing 40 grams each and put in a beaker glass. with 200 ml of 1M nitric acid, heated for 2 hours on a hotplate at 50ºC, and stirred with a magnetic stirrer at 200 rpm. After that, it was filtered and washed using aqua dest until the pH of the washing results was the same as the pH of the washing water, and dried at 55ºC for 24 hours.

SEM and EDX were applied to analyze the surface characteristics and chemical compounds of the adsorbent before and after being modified by HNO3. The application procedure of the adsorption column is to make a solution of Cu (II) 50 ppm and 150 ppm by dissolving solid CuSO4.2H2O with aqua dest until the mixture is homogeneous. Then the adsorption column was prepared and 1 gram of adsorption was put in, the Cu (II) metal solution flowed from the bottom of the column and out to the top of the column (Up Flow) and vice versa Cu (II) metal solution flowed into from the top of the column and out to the bottom of the column. (Down Flow). After that, each volume interval is accommodated and analyzed using AAS. The data taken are loading time, adsorption kinetics, and breakthrough curve.

Figure 2A of the column adsorption equipment series using Up-Flow [22] and Figure-2 B Down Flow [26]. The flow rates were controlled at 5 and 15 ml/min:



(a)



(b)

Figure-2. Series of up flow (A) and down flow adsorption (B) Column equipment.

RESULTS AND DISCUSSIONS

Morphological characteristics of corn stalks (Zea Mays) using SEM (Scanning Electron Microscope). The SEM observations before nitric acid modification and after nitric acid modification are shown in Figure-3. The SEM results revealed that the surface of the corn stalks changed after experiencing nitric acid modification due to an increase in the negative charge on the surface of the corn stalks which would increase metal absorption [23].

The SEM results reveal the nature of the corn stalk as a porous structure which can be useful in the metal ion adsorption process. The porous structure shows physically on the adsorbent surface that the metal adsorption process plays an important role in the adsorption process [1]. From the figure, there is a change in the pore structure where there is a larger porous channel so that the active side of the surface is greater for binding [24].

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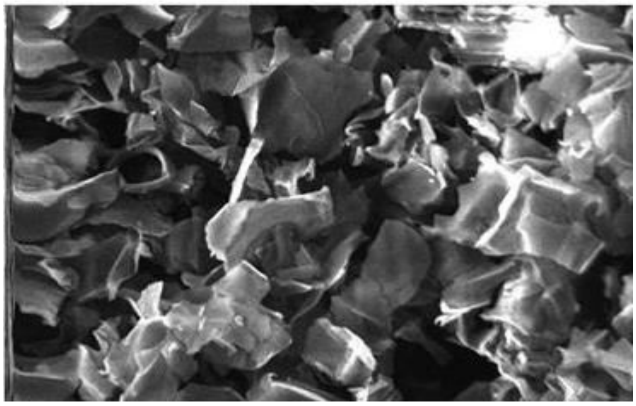
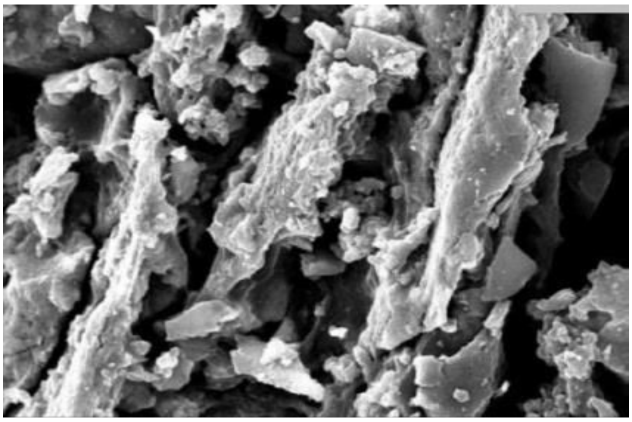


(a)

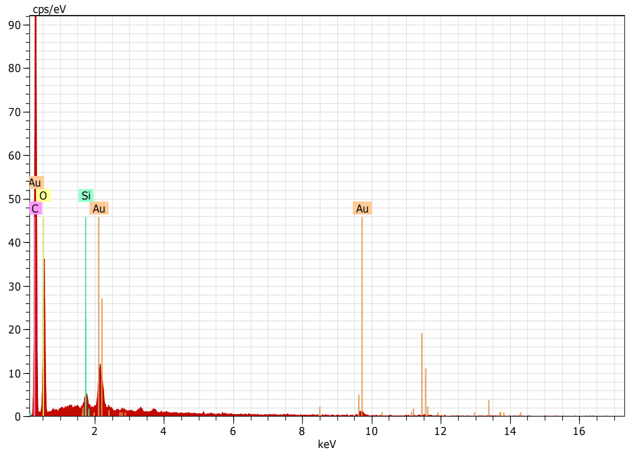


(b)

Figure-3. SEM observations (A) Before nitric acid modification; (B) After modification of nitric acid.

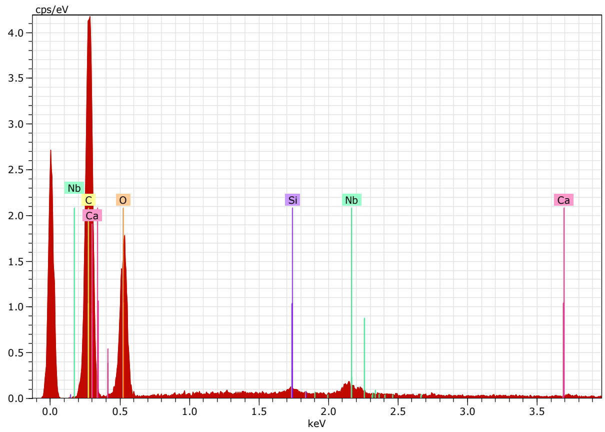
From Figure-4(A), it can be seen that there is more impurity composition in the mixed and bonded corn stalks. Whereas in Figure-4(B) it is seen that it is less in comparison and there is even a missing composition with Figure-4(A). In Figure-4(B) there is an N atom which indicates the acid used as an activator for the surface of corn stalks. So it can be concluded that after modification of the nitric acid, it causes the surface of the corn stalks to become negative which is able to attract metal cations. In addition, the loss and reduction of impurity composition cannot be immediately removed by washing using water [23]. The EDX results also show that the O atom increases its composition after modification of nitric acid due to the oxidation of nitric acid in corn stalks [25].

However, the modifications do have an effect on pH. As stated by Zhang, *et al* (2019) that when the pH increases, the adsorption ability of an absorbent will increase. Absorbent ability also increases as the absorbent surface area increases [26].



(a)

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]	K fact.	Z corr.	A corr.	F corr.
C	6	K-series	57.44	57.44	68.51	7.69	0.872	0.659	1.000	1.000
O	8	K-series	34.14	34.14	30.57	5.30	0.281	1.216	1.000	1.000
Au	79	L-series	7.73	7.73	0.56	0.44	0.034	1.923	1.000	1.185
Si	14	K-series	0.70	0.70	0.35	0.07	0.002	4.350	1.000	1.007
		Total:	100.00	100.00	100.00					



(b)

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]	K fact.	Z corr.	A corr.	F corr.
C	6	K-series	57.19	57.19	65.04	7.35	0.761	0.751	1.000	1.000
O	8	K-series	40.32	40.32	34.42	5.77	0.315	1.280	1.000	1.000
N	17	L-series	1.91	1.91	0.28	0.12	0.010	1.915	1.000	1.008
Si	14	K-series	0.39	0.39	0.19	0.05	0.001	2.783	1.000	1.006
Ca	20	K-series	0.19	0.19	0.07	0.05	0.001	3.352	1.000	1.036
		Total:	100.00	100.00	100.00					

Figure-4. EDX analysis results (A) Before nitric acid modification; (B) After modification of nitric acid.

Loading Time or T loading is the time required for metal contaminants to penetrate the adsorbent pores of corn stalks out of the adsorption column. Figure-5(A) shows that up-flow adsorption has a greater loading time than downflow adsorption. In Figure-5(B) it has a smaller loading time which is influenced by the influence of the channeling effect. The channeling effect is the effect that causes the adsorbent and adsorbate interactions to decrease or not occur at all. Based on the research of Haryanto, *et al.*, 2014 [27] which uses downflow where a solution with a certain concentration tends to flow out directly without interacting with the surface which then produces a channeling effect so that the entire surface of the adsorbent is not wetted and/or comes out without interacting between the adsorbate and the adsorbent.

In the adsorption up-flow and downflow, it shows that the increasing concentration causes the loading time to be greater, while the increase in flow rate and surface area causes the loading time to be smaller.

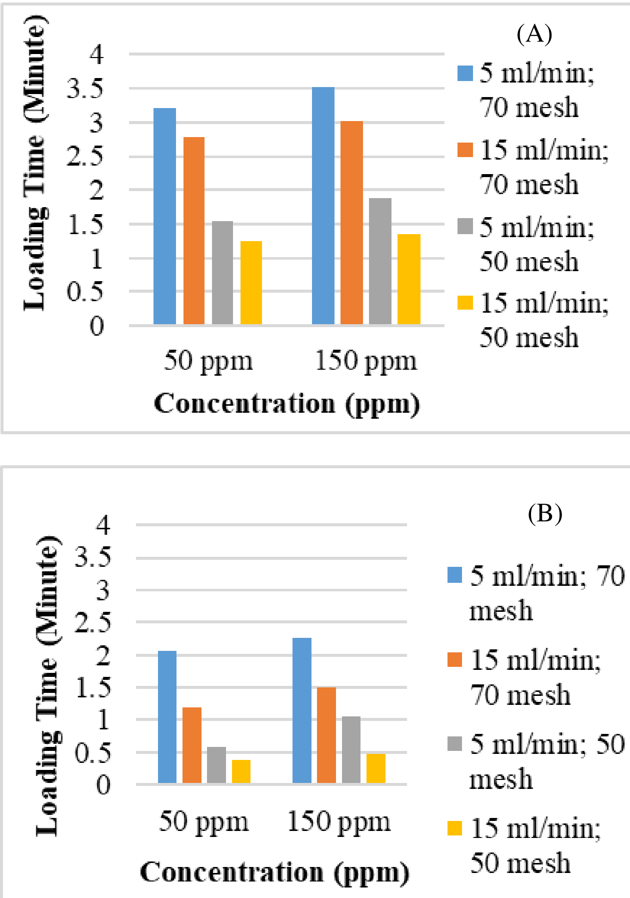


Figure-5. Effect of concentration variation on loading time on adsorption by (A) up flow and (B) downflow.

Adsorption efficiency states the number of metal ion concentrations adsorbed by the adsorbent so that the value is only determined by the change in metal ion concentration after being adsorbed by the adsorbent [27].

$$\% \text{ Re} = \frac{(\text{Co}-\text{Ct})}{\text{Co}} \text{ x } 100\% \quad (1)$$

The picture above shows that up flow adsorption has greater% removal efficiency than downflow adsorption. In Figure-6(B) it has lower% removal efficiency; it is influenced by the contact time that occurs faster so that the interaction between the adsorbent and the adsorbate tends not to be optimal. The greater the contact times between the adsorbent and the adsorbate, the greater the efficiency of the shedding [24].

In up flow and down flow adsorption shows that the increase in influent concentration causes the adsorption efficiency to decrease. This is because the increase in the initial metal concentration causes a lower mass transfer flux of the bulk solution to the particle surface which causes the driving force to become weaker [29]. In the adsorption up flow and downflow, it shows that the increasing flow rate causes the adsorption efficiency to decrease. This is because the contact between the adsorbent surface and the metal for the adsorbent is very small [30].

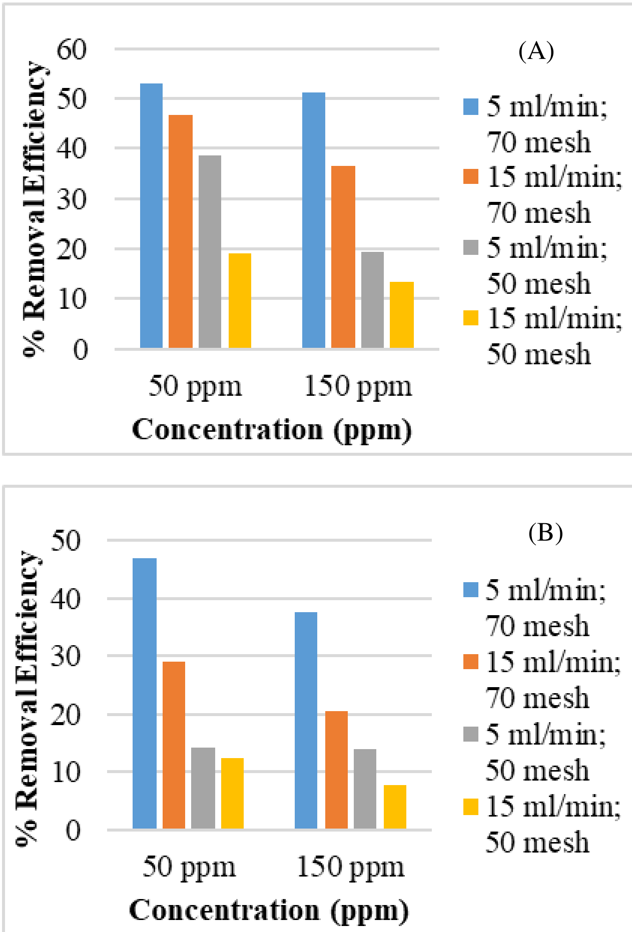


Figure-6. Effect of concentration variation on % removal efficiency on adsorption by (A) up-flow and (B) downflow.

The column system has an operating system that always brings the adsorbent into contact with the solution so that it reaches saturation conditions. The flow model that is carried out is from the bottom up (up-flow) and from the top to the bottom (downflow). In the up-flow

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model, Cu (II) metal solution, solution will be adsorbed quickly and effectively on the lower surface layer. The bottom layer of the adsorbent is the layer where there is direct contact at high concentrations, while the adsorbent layer will then absorb the solution with a lower concentration, and so on. Meanwhile, vice versa for the downflow model [31]. The graph of the results of the research on the kinetics determination of the corn stem adsorbent is as follows in Figure-7. It shows that up flow adsorption has longer saturation than downflow adsorption. Downflow adsorption has a lower % removal efficiency for each effluent volume, it is influenced by the contact time that occurs faster so that the interaction between the adsorbent and the adsorbate tends not to be optimal. The greater the contact times between the adsorbent and the adsorbate, the greater the efficiency of the shedding [26].

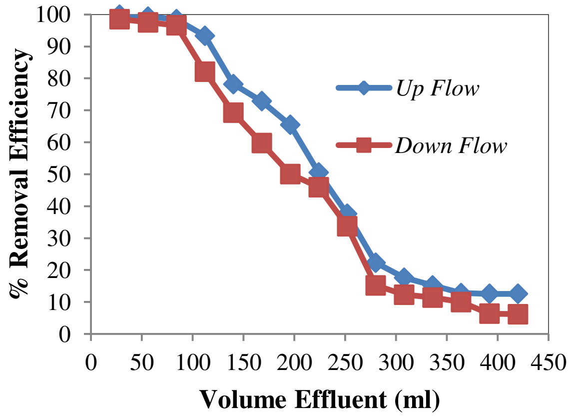

Figure-7. Kinetics determination on corn stalk adsorbent.

This is also due to the reduction in adsorption efficiency that occurs at the low influent contact time of the column. It can be seen that each volume of effluent has a higher adsorption efficiency in up-flow than down-flow adsorption. The adsorption of Cu (II) metal increases rapidly because most of the Cu (II) molecules that can be bonded ionically and covalently are greater than the hydrogen bonds that occur between metal ion molecules in a liquid solution. Meanwhile, corn stalks that have functional pore characteristics in binding to the adsorbate are the most important thing in adsorption so that the adsorption mechanism can occur effectively and efficiently [32].

The volume of effluent carried out in this study was carried out every 4 pore volumes [16, 24]. Pore volume can be said to be the contact time between the adsorbate and the adsorbent in the column every time it enters and contacts out of the column as the contact time at each input and output. Contact time is an important parameter in the amount of molecular adsorption of Cu (II) Metal ions to the active sites of corn stalks. At 4 pore volumes, the adsorption efficiency by up flow and down flow was 99.92% and 98.52% respectively, indicating that corn stalks have a very large ability to adsorb metal ions, and then gradually increasing the pore volume causes the adsorption efficiency to decrease and almost reached saturation, namely the adsorption efficiency of 12.56% and 6.18%. This is because the available active sites are decreasing and almost optimally have been filled by metal molecules [33].

In the adsorption up-flow and downflow, it shows that the initial concentration causes the removal efficiency to decrease towards the increase in the volume of the effluent. This is because the functional groups in the adsorbent may not be sufficient to absorb all adsorbate molecules so the active site is reduced over time as the initial concentration increases into the column [34].

The breakthrough curve is defined as the ratio of the effluent concentration (Ct) to the influent concentration (Co) with respect to time or volume. The shape of this curve is determined by the shape of the equilibrium isotherm and is influenced by the conveying process in the column and the adsorbent. The most efficient adsorption performance will be obtained if the shape of the breakthrough curve is as sharp as possible [35].

The relationship between the properties of the breakthrough curve and bed adsorption is still adequately expressed using the mass transfer zone (MTZ) or primary sorption zone (PSZ). In most cases of absorption by column method operation with wastewater, the breakdown curve shows the characteristic 'S' shape but with varying degrees of steepness [36].

From Figure-8 it can be seen that the form of the breakthrough curve for adsorption by up and downflow follows the shape of the "S" curve. However, the breakthrough curve in the up-flow adsorption is more stable than the downflow adsorption. The instability of downflow adsorption is due to ineffective contact time which causes the absorption to be non-uniform. The breakthrough curve will follow an ideal "S" shape profile which is characteristic of the adsorbate from the small molecular size of the adsorbent which consists of small particles [37].

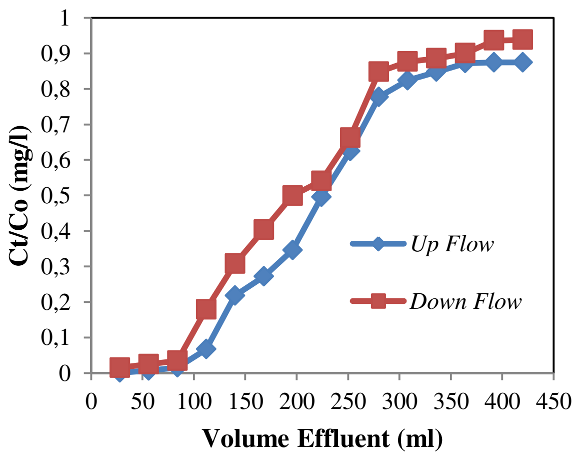

Figure-8. Determination of breakthrough curve on corn stalk adsorbent.

From the research results, it is found that the downflow adsorption has points that are under the up-flow adsorption. The increase in concentration causes a large slope of the breakthrough curve or a shortening of the mass transfer zone. This is due to the high concentration gradient leading to faster transport and more effective intraparticle diffusion. This corroborated the batch results for the intraparticle diffusion model which confirmed the increased pore diffusion effect for more concentrated solutions [37].

In the downflow, adsorption will reach a constant state under the up-flow adsorption. This is because the downflow adsorption has a shorter breakthrough time and bed service time which results in a faster saturation state [36]. The breakthrough curve is sharper as the Cu (II) concentration increases indicating a relatively small mass transfer zone and intraparticle diffusion controlling the absorption process. A higher initial influent concentration causes a higher locomotive force for mass transfer, so the adsorbent reaches saturation faster [38].

The adsorption mechanism that was explored showed that the adsorption rate of the modified raw material had a greater ability. Even so, it is still affected by the feed flow rate or it can be expressed as the loading time and method of feeding [27, 29, 39].

CONCLUSIONS

SEM results show that the adsorbent modified with nitric acid changes its porous structure so that the adsorbent can adsorb large metals. Meanwhile, the EDX results confirm the chemical component which indicates that the adsorbent of corn stalks modified with nitric acid can absorb the metal in a large way. This application is demonstrated by the effect of loading time, removal efficiency, kinetics, and breakthrough curve. Loading time shows that the up-flow is greater than the downflow direction. The loading time and % removal efficiency of corn stalks showed that the best results were at a concentration of 50 ppm, a flow rate of 5 ml/min, and a size of 70 mesh. Up-flow adsorption has a higher % Removal Efficiency than downflow adsorption. The increase in loading time occurs at an increase in concentration, a decrease in flow rate, and an increase in the size of the adsorbent. Meanwhile, the increase in % removal efficiency occurs at a decrease in concentration, a decrease in flow rate, and an increase in the size of the adsorbent. Up-flow adsorption has longer saturation than downflow adsorption. The shape of the breakthrough curve for up-flow and downflow adsorption follows the shape of the "S" curve. But the breakthrough curve in the up-flow adsorption is more stable than the downflow adsorption.

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