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BIOSORPTION OF PB(II) AND ZN(II) METAL IONS FROM AQUEOUS SOLUTIONS BY STEM TREE OF SOYBEAN USING CONTINUOUS FLOW METHOD

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ABSTRACT

Biosorption is the process of removal metal ions containing in the solution using agricultural by-product. The research was used stem tree of soybean for Pb(II), and Zn(II) in fixed bed continuous flow column. The experiment was studied for the flow rate of solution and mass of stem tree of soybean. The optimum of sorption capacity for Pb(II), and Zn(II)) metal ion is 12.44, and 6.752 mg/g on flow rate 2 mL/min and 0.1 g mass of stem tree soybean. The simulation of the breakthrough curve was successful with the BDST model. The design of fixed bed column for Pb(II) and Zn(II) removal from wastewater by biosorption onto stem tree of soybean can be done based on the BDST model.

Keywords: biosorption, stem tree of soybean, fixed bed continuous column, breakthrough curve, BDST model.

INTRODUCTION

Rapid industrial development has cause pollution to the environment. As a result of the activities of the mining industry, pulp, and paper industry, textile industry, metal plating, agricultural industries trigger increased levels of heavy metals in the water caused by waste discharged into waters (Metcalf *et al.*, 2003; Tiwari *et al.*, 2015).

Various conventional technology has been widely used to remove heavy metals from liquid waste such as precipitation processes, filtration, ion exchange, coagulation, extraction and reverse osmosis (M. Ashraf, 2011; A. Awaad, 2012). This conventional method was difficult to the processing and costs are relatively more expensive.

Until now developing new technologies in the processing of heavy metal waste in water that biosorption technology. Biosorption technology has been widely used to remove heavy metals from wastewater (Tiwari, 2015). Biosorption is adsorption process which occurs removal of the metal element contained in the fluid by using the adsorbent solids from waste biomaterial called bio sorbent.

Some biomass has been widely used as bio sorbent for heavy metals including wheat straw (Doan *et al.,* 2009), skin peanuts (Caiser *et al.,* 2009), acacia bark (Munagapati *et al.,* 2010), peel bananas (Ashraf *et al.* 2011), solid waste processing olive oil (M. Calero *et al.,* 2011), meranti (Qi *et al.,* 2012), rice husks (Achanai *et al.,* 2012), the leaves of Moringa (Kumar *et al.,* 2012), shell coconut (Cheampong *et al.,* 2011; Cheampong *et al.,* 2013), the skin of almonds (Dionisio *et al.,* 2013), palm kernel shells (Chong *et al.,* 2013), fruit leather palm (Nazaruddin N *et al.,* 2014), the skin olive fruit (Furqoni *et al.,* 2015), the crown of the god (Nasution, AN *et al.,* 2015), Annona muricata (Fauzia S *et al.,* 2013). One of biomass waste that has the potential to be used as bio sorbent absorb heavy metals is a waste stems soybeans. This waste has never been used and had only burned for reducing the waste heap. Thus the waste processing soybean stalks as bio sorbent to remove heavy metals from water is a potential that is promising.

Continuous adsorption

Powder of soybean waste bio sorbent was entered into adsorption column and contacted with the solution containing PbII) and Zn(II) ion. The experiments were conducted by varying bio sorbent mass, and flow rate of Pb(II) and Zn(II) ion metals.

Data analysis

To determination the amount of ion adsorbed by soybean waste in adsorption process, the formula used is:

$$q_{max} = \frac{Q0}{1000\ xm_{ac}} \int_{0}^{t\,max} \left[C0 - C(t)\right] dt$$

where Q_{max} is adsorption capacity (mg/g), C_0 is the initial concentration of metal ion (mg/L), C(t) is the final concentration at equilibrium of process (mg/L), m_{ac} is bio sorbent mass (g) and Q_0 is flow rate (mL/min).

Dynamics models

A mathematical model has been developed for the design of fixed bed column. In this work, the Bed Depth Service Time (BDST) model was used in predicting the behavior of the breakthrough curve because of the model effectiveness. The BDST approach based on the Bohart-Adams model is widely (Cheampong *et al.,* 2013). It assumes that the rate of adsorption is governed by the surface reaction between the adsorbate and the unused capacity of the adsorbent. The BDST model describes the relation between the breakthrough time, often called the service time of the bed and the packed-bed depth of the column. The advantage of the BDST model is that any experimental test can be reliably scaled up to other flow rates and inlet solute concentrations without the further experimental test.

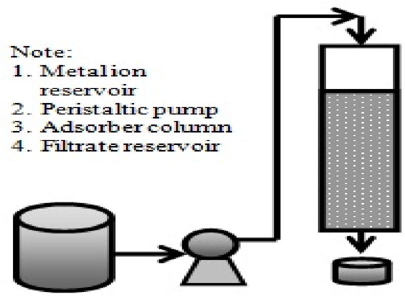

Figure-1. Schematic fixed bed column.

Linearization model of BDST is:

$$t = \frac{N_0}{C_0 F} Z - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_B} - 1\right)$$ (Acheampong, 2013)

In this model, a plot of t versus bed depth, Z in the curve. From the curve, we should yield a straight line where N_0 and K_0 can be evaluated from slope and intercept.

METHODOLOGY

Chemical and equipments

All chemical used in this experiments such as $Pb(NO_3)_2$, $Zn(NO_3)_2$, HNO_3, NaOH, HCl, Buffer solutions are analytical grade from Merck. Distilled water was made from the laboratory. A Crusher, Mortal Grinding, pH meter, analytical balance, oven, adsorber column, AAS, FTIR were used in this experiments.

Preparation of biosorbent

The stem of soybean waste was collected from agriculture waste in Pasaman Barat, West Sumatera, Indonesia. The stem was cut about 5 cm washed with water, dried at room temperature, ground and sieved to obtain the particle size 180 µm. The powder was found soaked with 0.01 M HNO3 for 2 hours. Filtered then rinsed with distilled water until neutral with pH about 7. The bio sorbent was dried and ready to be used.

Figure-2. Soybean (a) native (b) stem tree powder.

RESULTS AND DISCUSSION

The breakthrough curve of biosorption obtained at the variation of flow rate metal ions, and bio sorbent mass. Experiments have done using the variation of the flow rate at 2, 4, and 6 mL/min with initial concentration 500 mg/L at pH 3 for Pb(II) and an initial concentration 250 mg/L for Zn(II) metal ion with bio sorbent mass 0.1 g.

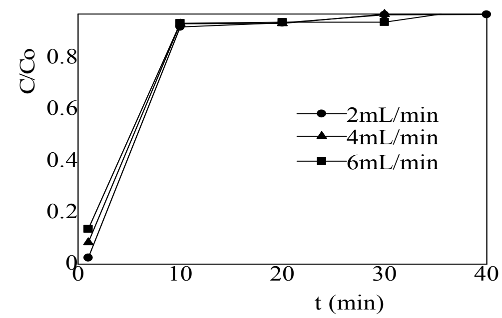

Figure-3. Breakthrough curve for Pb(II) biosorption. Experimental condition: bio sorbent mass 0.1 g, inlet concentration 500 mg/L, and pH 3.

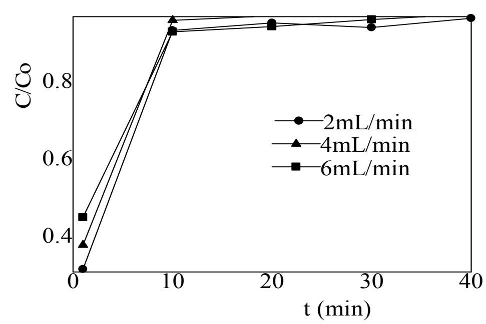

Figure-4. Breakthrough curve for Zn(II) biosorption. Experimental condition: bio sorbent mass 0.1 g, inlet concentration 500 mg/L, and pH 5.

From breakthrough curve in Figure-3. for Pb(II) ion and Figure-4. to Zn(II) ion, can be seen that the increasing flow rate can be service time biosorption decreased so it will be faster to reached saturation condition, but at increasing flow rate adsorption capacity smaller because contact time shorter. Breakthrough curves can be seen in that the flow rate affects the time saturation of biosorption. The higher the flow rate can be seen that the saturation time getting faster, but not great absorption capacity at high flow rates is because of the contact time/mass transfer of metal ions and bio sorbent zone within a shorter column.

In this research for a high flow rate column filled many metal ions (flooding) so that the metal ion concentration can not be detected according to the data of research that should, causing the metal ion concentration in the filtrate does not track properly. It is different when done research on low flow rate.

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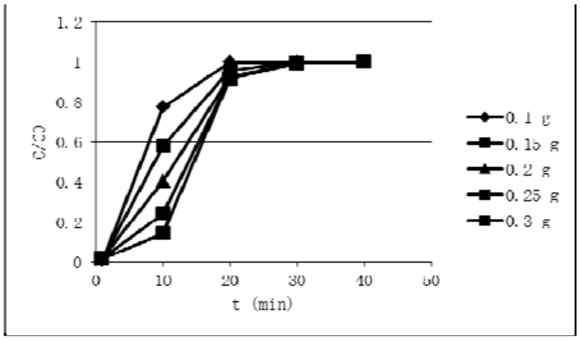


Figure-5. Breakthrough curve for Pb(II) biosorption. Experimental condition: flow rate 2 mL/min, inlet concentration 500 mg/L, and pH 3.

From the calculation results the optimum flow rate to Pb(II) metal ion was 2 mL/min with maximum adsorption capacity (qmax) is 12.44 mg/g. While at Figure-3 obtained optimum flow rate for Zn(II)ion was 6.752 mg/g.

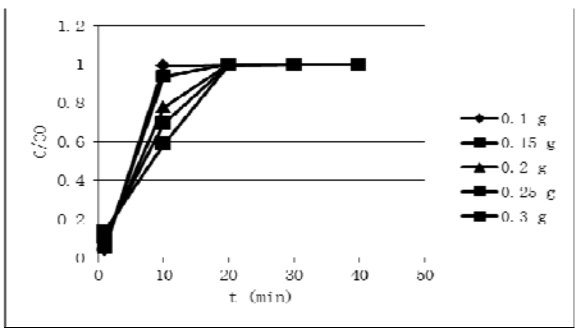


Figure-6. Breakthrough curve for Zn(II) biosorption. Experimental condition: flow rate 2 mL/min, inlet concentration 500 mg/L, and pH 5.

The influence of the bio sorbent mass variation were 0.1, 0.15, 0.2, 0.25 and 0.3 g can be seen in Figure-5 for Pb(II)ion and Figure-6. for Zn(II)ion. Bio sorbent mass variation for Pb(II) was performed on the initial metal concentration of 500 mg/L at pH 3 with the optimum flow rate of 2 mL/min. As for the Zn(II)ion was performed on the metal ion concentration of 250 mg/L at pH 5 with the optimum flow rate which has been obtained previously ie 2 mL/min.

From the breakthrough curves in Figure-5. To Pb(II) and Figure-6. for Zn(II) can be seen that increasing bio sorbent mass can lead to increased service time biosorption process so that with the increasing bio sorbent mass reached the saturation state will take longer. Breakthrough curves can be seen in the mass bio sorbent that affects the timing of saturation of biosorption. The greater the mass it can be seen that the saturation time is getting longer, because the contact time/mass transfer of metal ions and bio sorbent zone in the column to reach saturation longer. The optimum adsorption capacity bio sorbent mass variation is 4,048 mg/g for Pb(II) and 5.76 mg/g for the metals Zn(II) on optimum bio sorbent mass of 0.1 g

Dynamics models

Figure-7 dan Figure-8 shows the plot biosorbent mass versus service time when 50% saturation for Pb(II) and Zn(II) biosorption. Dynamics model used BDST (bed dept service time). The BDST models gave an idea of the efficiency of the column.

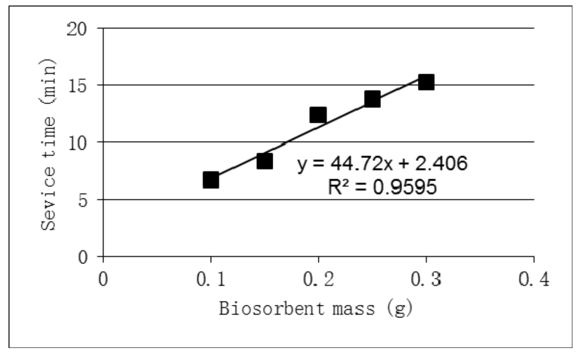


Figure-7. BDST model for Pb(II) biosorption.

From Figure-7 the BDST model for Pb(II) biosorption, we can value N_0 is 48.1 and K_0 is 9.543 and from Figure-8 the BDST model for Zn(II) biosorption we can value N_0 is 14.12 and K_0 is 0.02. The BDST model was able to describe performa of fixed bed column with R^2 for Pb(II) biosorption was 0.9154 and for Zn(II) biosorption was 0.8491.

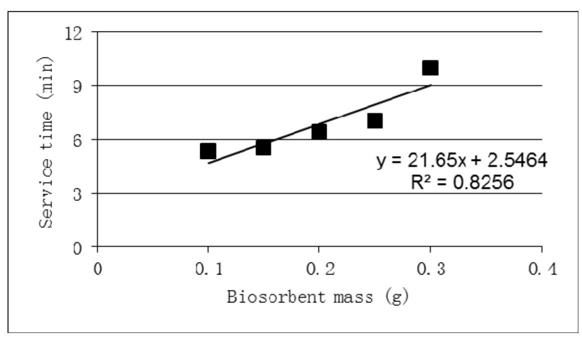
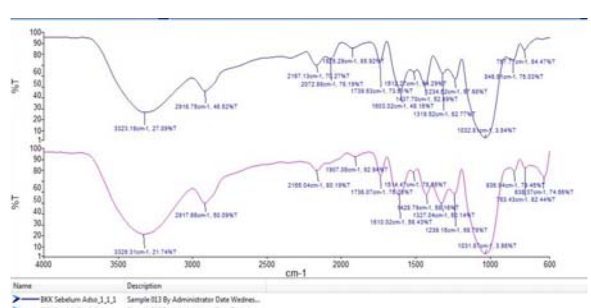
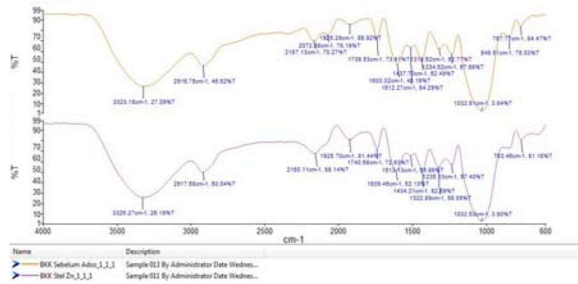


Figure-8. BDST model for Zn(II) biosorption.

FT-IR analysis



(a)



(b)

Figure-9. FT-IR spectrum of soybean waste powder (a) Pb(II) biosorption and (b) Zn(II) biosorption.

The FTIR analysis of soybean waste was shown in Figure-9, this analysis used to determine the functional groups involved in biosorption. The spectrum for soybean waste bio sorbent before and after adsorption for removal Pb(II) (Figure-9a) and before and after adsorption for removal Zn(II) (Figure-9b) demonstrates distinct peak at 3323.8 cm-1 representing N-H bond in amine, peak at 2916.75 cm-1 representing C-H stretching, peak at 2167.13 cm-1 representing C=O in ester. Thus, soybean waste bio sorbent showed an abundance of carboxyl and hydroxyl groups.

After adsorption for removing Pb(II) were observed several difference shifts of the peak. Spectrum 3328 cm-1, 2917.66 cm-1 and 2165.04 cm-1 shows the adsorption band shift and indicates the change of functional groups with Pb(II) metal ion. After adsorption for removing Zn(II) were observed several difference shifts of the peak. Spectrum 3326 cm-1, 2917.58 cm-1 and 2160.11 cm-1 shows the adsorption band shift and indicates the change of functional groups with Zn(II) metal ion.

CONCLUSIONS

Fixed bed biosorption system was found to perform better for Pb(II) and Zn(II) uptake by stem tree of soybean waste at lower feed flow rate and lower bio sorbent mass too. The optimum condition for Pb(II) and Zn(II) biosorption at 2 mL/min and 0.1 g bio sorbent mass with 12.44 mg/g sorption capacity for Pb(II) and 6.752 mg/g sorption capacity for Zn(II) biosorption. Dynamics model in the column was able to describe by BDST models.

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