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THE MIXTURE OF WATER HYACINTH PLANT AND CHITOSAN-BENTONITE AS A MODIFIED ABSORBENT FOR PB(II) REMOVAL IN LIQUID WASTE

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ABSTRACT

Water hyacinth and chitosan bentonite have potential as an absorbent material of heavy metal by higher stability, cheaper and easier in their synthesis. In this study, we combined use of water hyacinth and chitosan bentonite with a ratio of 1:3, 2:2 and 3:1 as a function of Pb(II) removal. Pb(II) was adsorbed after 5 minutes as 2.45, 2.47 and 2.50 mgg^{-1}, respectively. These adsorption amount were higher than each adsorption of Chitosan-Bentonite and Water Hyacinth. Chitosan-bentonite adsorbed Pb(II) after 10 minutes as 1.87 mgg^{-1} and water hyacinth after 20 minutes contact time as 1.22 mgg^{-1}. Presence of more chitosan-bentonite ratio in mixture adsorbent induce strong interaction of functional groups of chitosan-bentonite with Pb(II) ion. It also supported by BET analysis which chitosan-bentonite have higher BET surface area and micropore volume. Instead, water hyacinth have bigger pore size than chitosan-bentonite. Modification the mixture of chitosan-bentonite and water hyacinth become a new strategy to reduce the usage of chitosan-bentonite as renewable natural resources and increase the usage of water hyacinth which produce higher capability to adsorb Pb(II).

KEY WORDS: Water hyacinth, Chitosan, Bentonite, Adsorption, Heavy metals

INTRODUCTION

Environmental contamination by heavy metals such as Pb^{2+}, Cd^{2+} and Hg^{2+} induced the waters and the environment pollution that may be harmful to society. Some modern methods such as deposition (Anujkumar *et al.*, 2018; Krystyna *et al.*, 2012), electrochemical (Thien *et al.*, 2015; Umran *et al.*, 2015) ion exchange (Umran *et al.*, 2015; Bai *et al.*, 2009), and microorganisms (Fil *et al.*, 2012; Salmah *et al.*, 2015) have been developed to eliminate the heavy metal content in the wastewater. This method has shown satisfactory results but it requires fairly expensive operating costs and time consuming. The adsorption method becomes an alternative choice to remove of heavy metal, because of easy and effective in its application.

Some of the organic ingredients such as mangosteen peel, algae, water hyacinth and oil palm have previously been used as bio-sorbents. They absorbed heavy metals from the environment efficiently in their role as bio-sorbents and heavy metal bio-accumulators. The presence of secondary metabolites such as flavonoids with amino groups, carboxyl, thiol, hydroxyl-carbonyl and phosphate will form complex compounds with heavy metals. (Munaf *et al.*, 2014; Chaidir *et al.*, 2015; Zein *et al.*, 2015; Zein *et al.*, 2015; Zein *et al.*, 2014).

Water hyacinth (*Eichhornia crassipes*) is a plant that has a rapid growth rate, which ranges from 400-700 tons of biomass per hectare in a day so that water hyacinth is known as a pest crop. Water

hyacinth contains 10.76% crude protein, 4.94% fat, 17.9% crude fibers, 44.3% nitrogen free extract, 22.1% ash, 1.42% calcium and 0.58% phosphorus. Water hyacinth can be used to remove pollutants, because of its function as a biological filtration system, removing mineral nutrients, to remove heavy metals such as Cu, Au, Co, Sr, Pb, Sn, Cd, and Ni (Munaf *et al.,* 2014; Chaidir *et al.,* 2015; Zein *et al.,* 2015). The absorption of heavy metals in the presence of Rhizosfera microbes in the roots and supported by adsorption capability and a large accumulation of certain pollutants, can be used as an alternative control of pollution in heavy metal adsorption waters due to the interaction between active functional groups of adsorbents, so that the chemical structure of the adsorbent will affect the adsorption process (Shahabaldin *et al.,* 2015; Uddin *et al.,* 2007; Kiky *et al.,* 2014; Oladipo *et al.,* 2014; Abdel *et al.,* 2016).

The use of bentonite as an adsorbent has the advantage because bentonite has an inter-layer structure that can be easily modified so that it will improve its absorption properties. The surface of the bentonite is negatively charged, so it is able to adsorb metal ions which are positively charged, but its ability to adsorb anion is very low (Akl *et al.,* 2014; Soheil *et al.,* 2014). Several studies have succeeded in modifying the bentonite and producing an increase in its absorption ability. Increased absorption from bentonite modification with several surfactants is very effective for absorbing inorganic and organic compounds (Narada *et al.,* 2018; Tapan *et al.,* 2010; Doina *et al.,* 2009; Ma *et al.,* 2011).

However, the use of surfactants and polymers can produce pollutants from their residues, which is feared to cause new environmental problems. Alternatives that can be used are with natural organic materials or organic materials that are safe to use such as chitosan (Vedia *et al.,* 2012; Renji *et al.,* 2017). Chitosan-bentonite has a good performance as an adsorbent for heavy metals Fe, Cd and Cu simultaneously with an average adsorption strength above 90%. In addition the use of chitosan is very safely because chitosan is an ordinary anti-oxidant (forming shrimp skin) human consumption and most importantly does not contain toxic compounds (Vesna *et al.,* 2014; Ba *et al.,* 2014; Elsergany *et al.,* 2016).

Application of chitosan bentonite as an adsorbent were showed as a higher absorption of Pb(II), around 2 mgg^{-1} (Elsergany *et al.,* 2016) compared to only 0.4 mgg^{-1} (Kiky F.R., 2014) was absorbed by water hyacinth. Presence of amine and hydroxyl functional group in chitosan-bentonite were gave the high contribution to adsorbed metal ion compare than water hyacinth which contain hydroxyl group only. However, bentonite is one of the renewable natural resources while water hyacinth can be used as an adsorbent with an abundant amount in nature. To reduce the usage of chitosan-bentonite and increase of water hyacinth but still produce as potential adsorbent for heavy metal removal in liquid waste, in this study we prepared modification adsorbents from a mixture of chitosan-bentonite and water hyacinth by comparison; 1: 3, 2: 2 and 3: 1.

MATERIALS AND METHODS

Water hyacinth plats were taken at Pancur Batu, Medan, North Sumatera, Indonesia and Bentonite as commercial grade.

Water hyacinth preparation

20 g of water hyacinth stems that have been cleaned with water were sun dried for 3 days with an ambient temperature of 25 °C to 31 °C. After 3 days (dry material), the sample was weighed to determine the content of the water in the sample, then the ingredients were drilled for 2 minutes at a speed of 18,000-21,000 rpm and then filtered with a size of 60 mesh.

Chitosan-bentonite synthesis

25 g of bentonite were dispersed into 500 mL of NaCl 1M solution. The suspension was stirred with a magnetic stirrer at 70 ° C for 24 hours. The mixture was separated by decantation and the precipitate was washed with distilled water to remove the remaining chloride ions. The filtrate was tested with $AgNO_3$ 1 M solution until no white AgCl precipitate was formed. Precipitated bentonite were dried at 105 ° C for 1 hour. 180 g of Na-bentonite were put into a 1 L beaker and added with 1 L of chitosan 1000 ppm. Then the sample mixture was shaken for 30 minutes at 160 rpm and filtered using Whatman No.1 filter paper. The filtrate obtained was stored for analysis, and the residue obtained as chitosan-bentonite. Chitosan-bentonite obtained was washed with distilled water until it was free of acid (neutral), then dried in an oven at 100 °C. The dried chitosan-bentonite was smoothed for further use.

Adsorbent characterization

The different of chitosan-bentonite and water hyacinth structure properties were measured by X-Ray Diffractometer, XRD Shimadzu 6100 and based on these XRD data, the crystal parameters were measured by using of EXPO 2014 software (Altomare *et al.*, 2013). To investigate the functional groups content, in each adsorbent were analysed by FTIR. The morphology of crystals was analyzed by Scanning Electron Microscopy (SEM) JEOL JSM-6000 F.

Weight variation and activation of chitosan-bentonite and hyacinth mixture

In a separate glass, 2 g of each mixture of bentonite-chitosan and 2 g of water hyacinth with 200 mesh sieve size dispersed into 250 mL of H_2SO_4 1.2 M solution to clean the pore surface and increase lead absorption, then chitosan-mixture and water hyacinth were stirred. Activation was performed for 24 hours, then filtered and dried at 50-60 ^oC, and it released to adsorption. The same procedure was prepared of Bentonite-Chitosan: Water hyacinth as 1 g: 3 g and 3 g: 1 g respectively.

Contact time effect on Pb (II) adsorption

The adsorbents of water hyacinth and chitosan-bentonite with particle size of 200 mesh were weighed as 3 variation above. Then add 50 mL of Pb^{2+} metal ion solution with a concentration of 50 ppm into a 100 mL Erlenmeyer and stay with a variation time of 5, 10, 30, and 60 minutes. After the equilibrium reached, the mixture was filtered with Whatman No.42 filter paper and the metal ions left in the filtrate were analyzed by AAS.

RESULTS AND DISCUSSION

Activation adsorbent regeneration was carried out using acid regeneration method using H_2SO_4. The adsorbent regeneration stage was affected by the concentration of the acid solution used and the solubility of the impurities present in the adsorbent. H_2SO_4 as a function of dissolving inorganic minerals in the adsorbent, so that it can reactivate the functional group in adsorbent. The adsorption mechanism is reversible so that the regeneration process can be achieved by increasing the concentration of H^+ ions in the system, where H^+ ions will play a role in acidifying the medium, so that the surface of the adsorbent becomes positively charged and can release the metal in the adsorbent.

FTIR spectra (Figure 1) of chitosan-bentonite and water hyacinth showed the existence of constituent functional groups of each structure. For chitosan-bentonite spectrum shows the presence of hydroxyl group (-OH) at a wavelength of 3610.74 cm^{-1} and the presence of an amine group (-NH) at a wavelength of 3425.56 cm^{-1}. While the presence of hydroxyl group (-OH) in water hyacinth is shown in the wide curve at a wavelength of 3394.72 cm^{-1}. The existence of this functional group that contributes greatly to the absorption of Pb (II) metal due to the attraction of both. Whereas the presence of aromatic rings on the structure of chitosan-bentonite and water hyacinth was shown at a wavelength of 1631.78 cm^{-1} and 1639.49 cm^{-1}

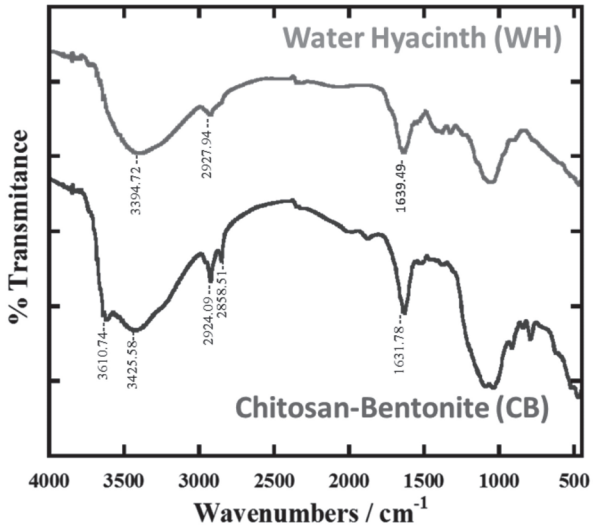

Fig. 1. FTIR spectrum of Water Hyacinth and Chitosan-Bentonite.

Characterization with XRD was carried out to compare the differences in crystallinity structure of water hyacinth and chitosan-bentonite (Figure 2). The results of quantitative analysis using EXPO 2014 Analysis software (Altomare *et al.*, 2013), it observed the adsorbents of chitosan-bentonite and water hyacinth have different structure properties, which is indicated by the values of the lattice parameters, even though chitosan-bentonite and water hyacinth have the same crystal system as triclinic crystal. SEM images in Fig. 3 also observed the different properties of chitosan-bentonite and water hyacinth which a little bite bigger particle size of chitosan-bentonite than water hyacinth at 20 mm images.

Determination of the optimum contact time was

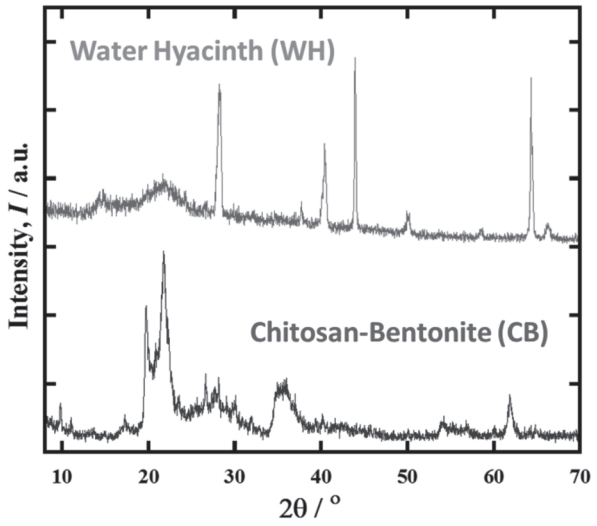

Fig. 2. XRD pattern of Water Hyacinth and Chitosan-Bentonite.

carried out to confirm the minimum time required in absorbing Pb (II) metal ions maximally until saturation was reached. The effect of contact time on Pb (II) metal adsorption in this study was carried out by batch method. All mixture ratio of chitosan-bentonite and water hyacinth were adsorbed as optimum capacity after 5 minutes. All ratio shows higher Pb adsorption amount compared than only use chitosan-bentonite or water hyacinth (Figure 4). Pb^{2+} ion was adsorbed after 5 minutes for all ratio of mixture are 1:3, 2:2 and 3:1 as 2.45 mgg^{-1}, 2.47 mgg^{-1} and 2.5 mgg^{-1}, respectivly. Otherwise, Chitosan bentonite adsorbed Pb^{2+} ion is 1.87 mgg^{-1} and water hyacinth is 1.22 mgg^{-1}. These optimum adsorption of chitosan-bentonite ocuurs after 10 minutes and water hyacinth after 20 minutes. The mixture of chitosan-bentonite and water hyacinth induce the faster optimum adsorption of Pb^{2+} ion. Only need 5 minutes to adsorb with higher capability than only chitosan-bentonite and water hyacinth. It suggest that combination of both adsorbent could enhance the Pb^{2+} ion adsorption capacity due to the interaction of Pb^{2+} ion with fuctional group also were increased because come from both of chitosan-bentonite and water hyacinth functional groups. Adsorption amount of Pb^{2+} of chitosan-bentonite and water hyacinth in this experiment similar with previous report (Kiky F.R., 2014; Elsergany *et al.*, 2016).

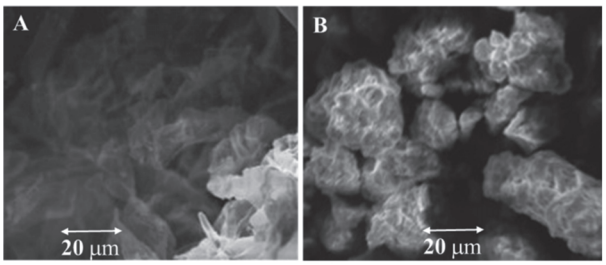

Fig. 3. SEM images of Water Hyacinth (A) and Chitosan-Bentonite (B).

Adsorption capability of all ratio mixture of chitosan-bentonite and water hyacinth are given observe in Figure 4. Modified adsorbent with ratio 3:1 adsorbed the highest of Pb^{2+} as 2.5 mgg^{-1}. Presence of 75 % chitosan-bentonite give a contribution to amine group and hydroxil group in enhance Pb^{2+} ion. Functional group of bentonite-chitosan was stronger than water hyacinth. It support by BET analysis data (Figure 5) which chitosan-bentonite have higher micropore volume as 61 dm^3g^{-1} and BET surface area is 38.22 m^2g^{-1}. Presence of more chitosan-bentonite than water hyacinth which contains more functional group induce bigger volume of pore. Adsorption of mixture adsorbent as ratio of 2:2 and 1:3 were decreased as same as the decrease of chitosan-bentonite ratio (Figure 6.) After 5 minutes contact time, the mixure adsorbent with ratio 2:2 shows higher adsoprtion amount of Pb^{2+} than ratio 3:1. The adsorbent with ratio 3:1 which have high adsorption amount at 5 minutes but gradually deacreased indicate low interaction between Pb^{2+} ion with their fucntional groups. It also supports that due to water hyacinth have bigger pore size than chitosan bentonite. Eventhough the mixture adsorbent 3:1 adsrobed higher Pb^{2+} ion for 5 minute contact time

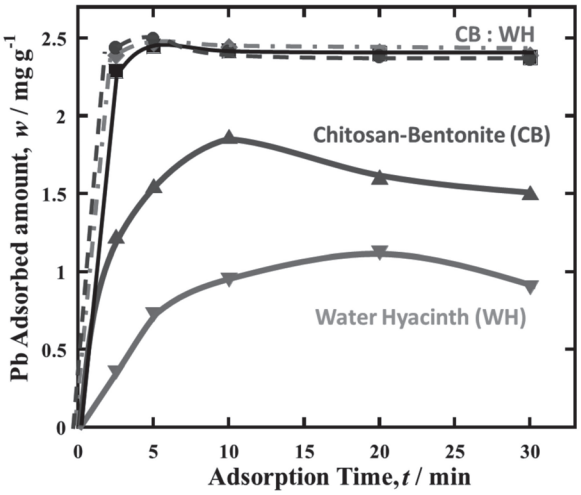

Fig. 4. Pb adsorbed amount of Water Hyacinth and Chitosan-Bentonite and the mixture of Water Hyacinth and Chitosan-Bentonite (3:1, 2:2, 1:3)

but after this optimum condition, the mixture adsrbent which contain more water hyacinth could adsorbed a higher Pb^{2+} ion due to these pore size effect of water hyacinth.

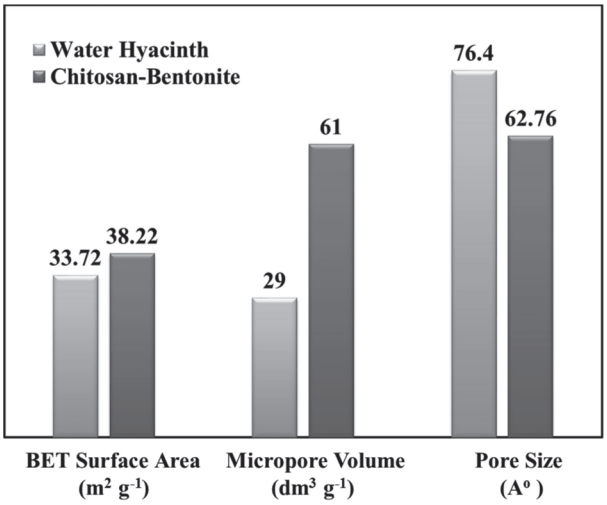

Fig. 5. Pore properties of Water Hyacinth and Chitosan-Bentonite (micro pore volume estimated by DR plot and pore size by t-plot analysis of N_2 adsorption isotherms at 77K)

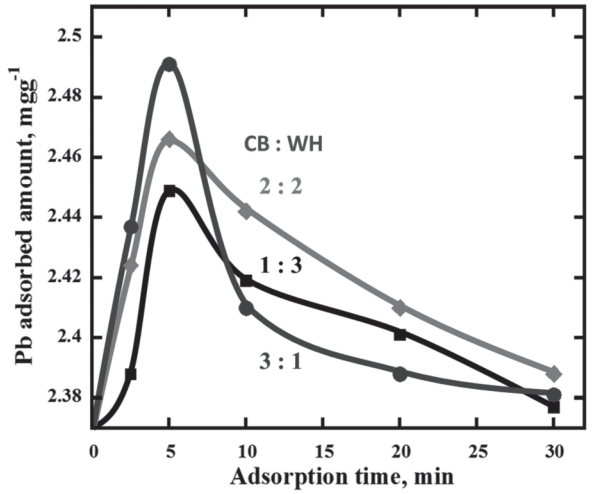

Fig. 6. Pb adsorbed amount of the mixture of Water Hyacinth and Chitosan-Bentonite (3:1, 2:2, 1:3)

CONCLUSION

The new strategy to increase of Pb(II) adsorption amount built by mixture of chitosan bentonite and water hyacinth. All ratio of 1:3, 2:2 and 3:1 of chitosan bentonite and water hyacinth adsorbed Pb(II) ion after 5 minutes are 2.45, 2.47 and 2.50 mgg^{-1}, respectively. These adsorption amounts are much higher than only chitosan-bentonite and water hyacinth adsorption capability. Chitosan-bentonite could adsorbed Pb(II) after 10 minutes as 1.87 mgg^{-1} and water hyacinth after 20 minutes contact time as 1.22 mgg^{-1}. It confirms, we could reduce the usage of chitosan-bentonite as renewable natural resources and increase the usage of water hyacinth but produce the higher capability to adsorb of Pb(II) with faster contact time in adsorption process.

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