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Preparation of Natural Ouw Clay-Chitosan Composite and Its Application as Lead and Cadmium Metal Adsorbent

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Abstract

This study aims to obtain the optimum ratio of Ouw Natural Clay (LAO):Chitosan in the manufacture of chitosan-LAO composites. The composite will be used as an adsorbent for heavy metals Lead (Pb) and Cadmium (Cd). LAO-Chitosan composites were made with the ratio of LAO:Chitosan = 1.25:1, 2.5:1, 5:1. XRD and SEM were carried out for each composite. The performance as a Cd metal adsorbent was determined by calculating the adsorption capacity. Composites with a ratio of 1.25:1 have the best adsorption capacity. The performance as adsorbent for Cd metal was determined by calculating the absorbed Cd concentration. Maximum results are achieved by composites with a ratio of 5:1.

Keywords: Adsorbent, adsorption, cadmium, lead chitosan, Ouw Natural Clay

INTRODUCTION

Many researches on the manufacturing of heavy metal adsorbents have been carried out, both using chitosan (Bijang, Sekewael, & Koritelu, 2014; Motshekga, Ray, Onyango, & Momba, 2015; Rahayu, Tanasale, & Bandjar, 2020; Tanasale, Bandjar, & Sewit, 2018) and seaweed (Bijang, Latupeirissa, & Ratuhanrasa, 2018; Bijang, Tehubijuluw, & Kaihatu, 2018). The use of natural resources in the form of clay to modify chitosan as an adsorbent has also been developed. H. Wang et al., (2014) and Futalan, Kan, Dalida, Pascua, & Wan, (2011) were modified montmorillonite with chitosan and applied it to absorb Co^{2+} ions from aqueous solution. The results obtained indicate an increase in the distance between layers in montmorillonite. The comparison of chitosan to montmorillonite affects the absorption ability of the adsorbent.

Lavorgna et al., (2014) were prepared a multifunctional bionanocomposite by loading chitosan matrix with silver-montmorillonite antimicrobial nanoparticles. Rusadi, Mahatmantie, & Sulistyaningsih, (2018) were carried out the preparation of chitosan-bentonite composites as an adsorbent for methyl orange dye. Characterization using XRD indicated the increase in basal spacing of bentonite in the presence of chitosan intercalation. Sobeih, El-Shahat, Osman, Zaid, & Nassar, (2020) used Glauconite clay-functionalized chitosan nanocomposites for remove fluoride ions from polluted aqueous solution.

In this study, Ouw's natural clay (LAO)-chitosan nanocomposite was made with a comparative study of composition and it's application as an adsorbent of lead cadmium heavy metals. Research has never been carried out using natural Ouw clay and Chitosan as materials for the manufacture of adsorbent composites.

METHODOLOGY

Materials and Instrumentals

Ouw natural clay (LAO), Chitosan, H_2SO_4 (Merck), NaOH (Merck), CH_3COOH (Merck), NH_4CH_3COO (Merck), $Pb(NO_3)_2$ (Merck), HCl (Merck), KCl (Merck), H_3BO_3 (Merck), Methyl Red Indicator (Merck), Bromcresol Green Indicator (Merck), Alcohol 90%, Whatman Filter Paper no 42, Universal pH Paper. Hot Plates (Barnstead hemolyne), Ovens (Memmert), Buechner Fisher, Vacuum Pumps, Glassware Kit (Pyrex), Shaker (GFL 3005), Analytical Balance (Ohaus), 100 mesh Sieve, Centrifuge (Labofuge 200-Hereaus), X-ray Diffractometer (Shimadzu Giniometer XD-3A), Atomic Analysis Spectroscopy (Shimadzu AA-630), SEM-EDX (Zeiss Evo ®MA 10).

Methods

Clay Preparation

LAO is cleaned with distilled water until a completely clean clay is obtained. It was then dried in the oven at the temperature of 60 °C for 2 hours. As much as 20 g of LAO is taken and then dispersed into

250 mL of 3 M NaCl solution while stirring for 24 hours. It's filtered and the residue obtained is washed with distilled water to remove the remaining into chloride as shown by a negative test for $AgNO_3$. The washed loam is dried in an oven at 100 °C. After drying, the clay is crushed until smooth and then sieved using a 100 mesh sieve. Furthermore, the clay was soaked with 2 M H_2SO_4 for 24 hours. After soaking, it was then washed with distilled water until it was sulfate-free which was tested with $BaCl_2$. The clay is then dried in an oven at a temperature of 120 °C for 2 hours. After drying the clay is then mashed, sieved with a 100 mesh sieve (Teddy, Bijang, Nurdin, & Kapelle, 2018).

LAO-Chitosan Composite Preparation

The LAO-chitosan composite preparation method used was from S. F. Wang et al., (2005) and L. Wang & Wang, (2007). Each acid activated LAO-chitosan were weighed 1.25, 2.5 and 5 g of and then added to 50 mL of distilled water. Each chitosan is weighed 1 g then dissolved with 50 mL of 2 % (v /v) acetic acid, the pH of chitosan is adjusted to pH 4.9 by adding 20% (w /v) NaOH solution. Furthermore, as much as 50 mL of chitosan was slowly added to 50 mL of LAO solution so that a suspension was formed and stirred at 60 °C for 6 hours. The suspension was then centrifuged for an hour at a speed of 5300 rpm to obtain a composite LAO-chitosan with a ratio of 1.25:1, 2.5:1, 5:1.

Each of the composites formed was washed with distilled water until the pH of the supernatant (liquid) reached 7 and then dried at 60 °C for 12 hours. Furthermore, the composites were sieved to 100 mesh size. The composites are stored in a desiccator and used for further analysis.

Characterization of LAO-Chitosan Composites

Characterization was performed using FT-IR Spectrophotometer, X-Ray Diffractometer, and Scanning Electron Microscopy.

Adsorption Capacity Test

The standard Pb solution with a concentration of 1000 ppm was taken as much as 25 mL and put into three erlenmeyers, each containing 0.1 g of composite with a ratio of 1.25:1, 2.5:1 and 5:1. Each solution is shaken on a shaker at a speed of 120 rpm. This system is maintained at room temperature for 6 hours until it reaches adsorption equilibrium. The solution was then filtered with filter paper and 5 mL of Pb adsorption filtrate was taken each, then the absorption was measured with AAS at a wavelength of 283.3 nm. The same procedure was performed for Cr at a wavelength of 228.8 nm.

RESULTS AND DISCUSSION

LAO-Chitosan Composite Preparation

The preparation process for the LAO-Chitosan composite was made by mixing the LAO suspension with chitosan solution with the LAO: Chitosan ratio = 1.25: 1, 2.5: 1, 5: 1. This process begins by dissolving each chitosan with 50 mL of 2% acetic acid, after which 20% (w/v) NaOH solution is added until the pH is exactly 4.9. Furthermore natural clay is added with distilled water to keep it at 50 mL. According to S. F. Wang et al., (2005) the pH value of the chitosan solution must be maintained at 4.9, namely by adding 20% (w/v) NaOH, because the NH^{3+} group can easily replace cations in clay through a cation exchange reaction.

The mixing stage of the LaO-Kitosan was carried out by mixing chitosan solution slowly into Lao solution while stirring using a stirer for 6 hours at the solution temperature of the 60 °C. The temperature used in the mixing process must not exceed 60 °C because it can damage the chitosan structure which is an organic polymer. In this case it can break the glycosidic bonds on chitosan therefore that the chain becomes short and the molecular weight becomes reduces (L. Wang & Wang, 2007)

Identification of LAO-Chitosan Based on Their Diffractogram

The diffractogram of LAO-Chitosan can be seen in Figure 1. Figure 1 shows that Montmorillonit is suspended in $2\theta = 20.0063^{o}$, because in this process it uses a temperature of 60 °C. (Wang and Wang, 2007). In chitosan samples, 2θ diffraction patterns were found at 9.2959° and 19.3384°. According to Wang et al. (2005) chitosan diffraction pattern is = 10°, 20°, and 25°. The diffractogram test shows a quite good crystallinity of chitosan. Figure 1 shows composite 1.25:1 Montmorillonite's absorption appear in 2θ= 18.9200° shifted to a smaller number, the distance between fields, D increased from 4.4360 Å to 4.749454 Å. The same circumstances also occur in composite 2.5:1 and 5:1. At the composite 2.5:1, the peak appears in 2θ = 19.3000 Å and D increased from 4.43460 to 4.65940 Å. In composite 5:1, the peak at 2θ becomes 19.8600 Å and D increases to 4.53310 Å.

The shift in 2θ and more dominant peaks shifted to the left showed that Montmorillonite minerals had interacted with chitosan. In addition, the occurrence of a decrease in 2θ and increased distance between fields shows that the interaction between montmorillonite and chitosan minerals is likely to occur in the interlayer area.

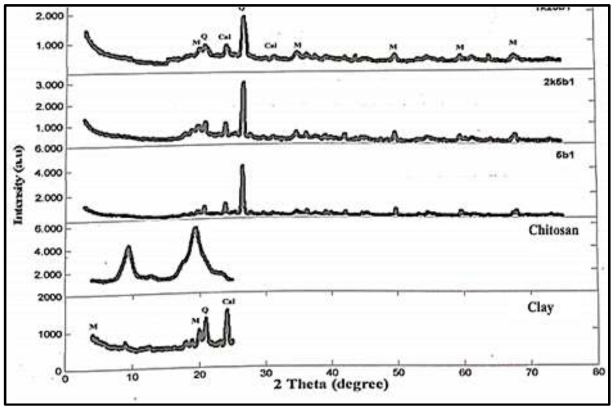
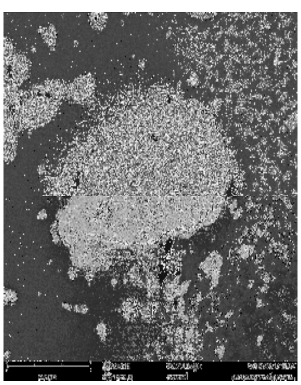


Figure 1. Diffractogramm of LAO, Chitosan and LAO-Chitosan composites

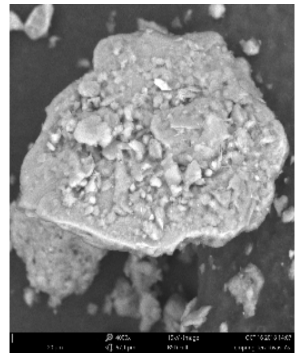
According to Monvisade & Siriphannon, (2009), the event of chitosan entering into the inter-layer space is said to be successful if the new peak appears below the initial peak, therefore it can be said that basal spacing (D) increases. The composite 1.25:1 shows the largest increase in D thus can be said to be the best LAO-chitosan interaction on this composition.

Identification of Acid Activated Clay Based on SEM

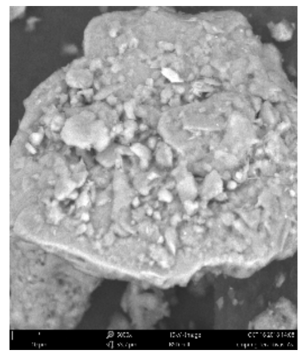
The results of acid activated clay by using SEM with a magnification of 500x, 1000x, and 2000x can be shown in Figure 2.



(A)



(B)

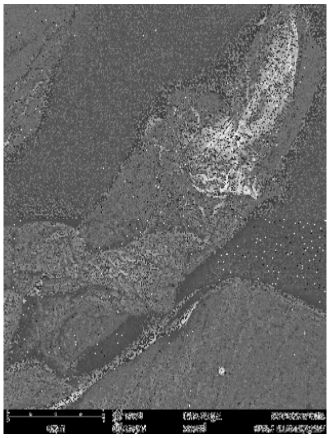


(C)

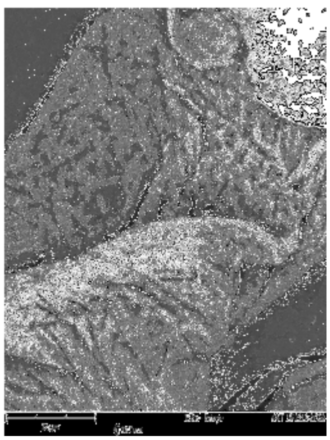
Figure 2. Acid activated clay on 500x magnification (A), acid activated clay in 1000x magnification (B), acid activated clay in 2000x magnification (C).

Figure 2 shows a large number of pores and also more ordered. This is due to acidic activation in clay which will result in increased acidity and a specific surface area of adsorbent.

(A)



(B)

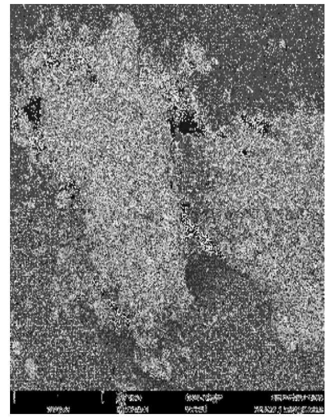


(C)

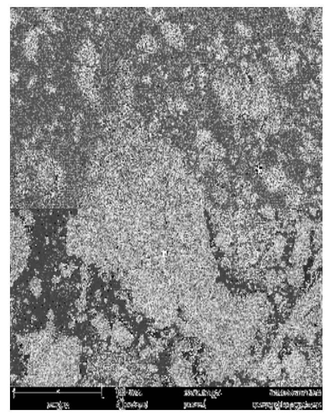
Figure 3. Chitosan on 500x magnification (A), chitosan on the 1000x magnification (B), chitosan on 2000x magnification (C).

Figure 3 shows the results of the identification of chitosan on a different enlargement where chitosan does not have a pore, the EDX of the chitosan spectrum on 500x magnification shows the highest concentration element, which is C element and the lowest is N. While on the 1000x magnification, the element with the highest concentration is C and the lowest is O.

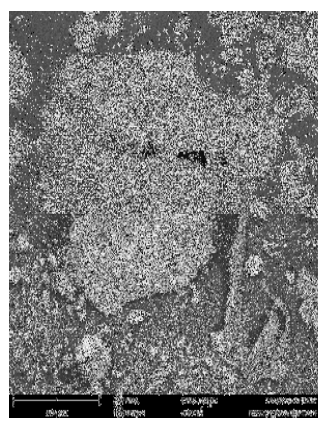
Figure 4 shows the results of the identification of the clay-chitosan with a ratio of 1.25:1 which can be seen the clay covering the surface of the chitosan. The results of identification of clay-chitosan clays with a ratio of 2.5:1 show that chitosan particles are reduced but clay particles also still look like small chunks. While the results of identification of clay-chitosan with a ratio of 5:1 show that there is a particle of clay and chitosan.



(A)



(B)



(C)

Figure 4. Composite LaO:Chitosan with a ratio of 1.25: 1 (A); 2.5: 1 (B); 5: 1 (C)

When compared between clay particles and chitosan, clay particles is more dominat. Therefore the surface area is getting bigger. In addition, in this sample there were particles clay that did not interact with chitosan.

Maximum Lead Adsorption Capacity by LAO-Chitosan Composites

Each composite was added to the standard solution of lead with a concentration of 500 ppm which was then shaked for 6 hours. The resulted filtrate is analyzed by an atomic absorption spectrophotometer to determine the concentration of lead standard solution in solution so that absorbed lead concentration by composite can be calculated as seen in Table 1.

Table 1.Data of lead metal absorbance

C_k (gram)	C_0 (ppm)	A	f_d	C_e (ppm)	C_{ads} (ppm)	Q
1.25:1	500	0.1178	50	355.339	144.660	28.9320
2.5:1	500	0.1268	50	385.326	114.673	22.9274
5:1	500	0.1270	50	385.993	114.006	22.8013

Note:

C_k = Composite comparison Lao:chitosan
C_o = lead concentration before adsorption
A = absorbance
f_d = dilution factor
C_e = free lead concentration in solution
Cads = lead concentration that is adsorbed by the LAO-Chitosan composite
Q = Adsorption Percentage (%)

Based on Table 1 it can be seen that on the LAO-Chitosan composite with a ratio of 1.25:1 absorb more lead, and composite with a ratio of 5:1 shows the smallest capability. This result is in accordance with XRD and SEM data, that composite 1.25:1 has the best interaction.

Cadmium Maximum Absorption Capacity by Composite Clay-Chitosan

The data on the absorbance of the cadmium standard solution is presented in Figure 5. In the cadmium adsorption process, each composite is added to the standard cadmium solution with a concentration of 500 ppm which is then shaked for 6 hours. The resulting filtrate was then analyzed by SSA to determine the concentration of cadmium in solution, so that the concentration of cadmium absorbed by the absorben can be calculated.

The data of cadmium metal absorbance shown in Table 3. Table 3 shows the LAO surface area is greater than the LAO-Chitosan composite with a ratio of 1.25: 1, 2.5: 1, and 5:1. This is influenced by the active side of chitosan and the pores of clay. The LAO that has not been modified with chitosan has a pores functioning. When clay is mixed with chitosan 1.25:1 the active side plays the role, because in the ratio of 1.25:1 the measured surface area is 0 m^2/g, in SEM photos (Figure 4) it can be seen that chitosan cover the clay surface. The cadmium that enters is bound to the active side of chitosan, namely N. The clay-chitosan ratio of 5:1 is the best result because Cd can enter the LAO-Chitosan pore.

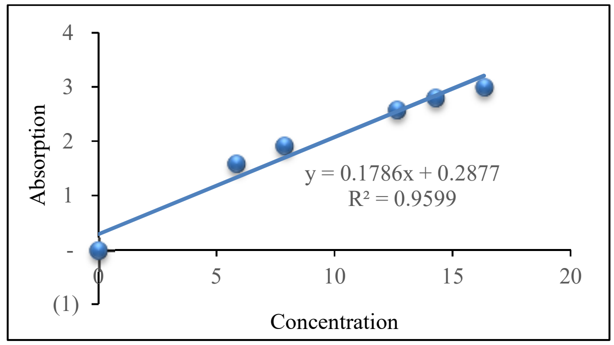


Figure 5. Standard curve of cadmium standard solution

Table 3. Data of Cadmium metal absorbance

C_k (%)	C_o (ppm)	*A*	f_d	C_e	C_o - C_e
1.25:1	500	1.63	50	8.88	491.12
2.5:1	500	1.65	50	10.08	498.91
5:1	500	1.63	50	8.35	491.65

Note:

C_K: Comparison of natural-chitose clay composites
C_0: Concentrate standard solution before absorption
A: Absorbance
fd: Dilution factor
C_E: Free cadmium concentration in solution

The LAO-Chitosan composite with a ratio of 5:1 is able to absorb more cadmium metals, because the greater the concentration the smaller the absorption and so is the opposite, the smaller concentration then the greater absorption. Next in line is composite with a ratio of 1.25:1 and the smallest adsorption ability is shown in the composite with a ratio of 2.5:1.

CONCLUSION

Based on the research results, it has been found that the biggest lead adsorption is shown by the LaO composite:Chitosan with a ratio of 1.25:1 and the largest cadmium adsorption is shown by the LaO Composite:Chitosan with a ratio of 5:1.

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