Preparation of Mesostructure Amorphous AluminumMethionine and Its Potency as Adsorbent

by Ery S. Retnoningtyas

Preparation of Mesostructure Amorphous Aluminum-Methionine and Its Potency as Adsorbent

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Abstract. An amorphous metal-amino acid contains metal based on Aluminium and Methionine as a ligand, was synthesized. The fabricated amorphous Al-Methionine (a-AM) is done in water solvent under moderate thermal conditions. The advantages of using bio ligands, one of which is amino acid, can be used to biologically compatible material. The synthesis was optimized changing chemical (metal and ligand molar ratio) and process (temperature, time) parameters. The a-AM characterization was carried out by XRD, FTIR spectroscopy, FESEM, also gas sorption measurement (BET). From the N_2 adsorption/desorption isotherm, the a-AM is classified as a type IV and has a mesoporous structure. The produced a-AM has a S_{BET} area 287 $m^2\ g^{-1}$, pore size 0.996 $cm^{-3}\ g^{-1}$ and mean pore diameter 13.85 nm. After demonstrated in the dye adsorption, this material has potency as an adsorbent.

INTRODUCTION

Aluminium oxy hydroxide (γ-AlOOH) is one of the metal oxide that has many uses, one of which is as an adsorbent. Aluminum together with the ligand, forms a structure that is able to adsorb other compounds. Aluminum and several types of ligands such as terephthalate, trymethyl 1,3,5 benzenetricarboxylate, and fumarate have proven their ability to absorb compounds such as: o- and p-xylene (compound of petrochemicals), water from seawater and humid air, fatty acid and peroxides (impurities in the vegetable oil) and dye [1-6]. These organic compounds have a molecular size large enough to be very suitable if absorbed by mesoporous adsorbents. One type of ligand that can be used to make mesoporous adsorbents is a natural amino acid.

At present, the use of amino acids as ligands in coordination network construction has been widely carried out including Ni-alanine, Ni-glycine, Mn-phenylalanine, Cu-glutamine, also Cu and Ag-methionine [7-11] In addition to cysteine, methionine is an amino acid that has a metal bonding in the side chain in the form of a thioether sulfur atom, in addition to the two sides of the amine nitrogen metal bond and the carboxylic oxygen atom [11] . Luo et al. (2007) reported that a homochiral amino acid coordination network can be fabricated from metal and methionine via the soft-hard recognition process.

In this study, methionine was used as a performance enhancing agent in aluminum oxide hydroxide with aqueous solutions. The reason for choosing aluminum as a metal in the manufacture of , because of its stable under hydrothermal conditions, inexpensive, abundantly available in nature, and non-toxic metal [12, 13]. The goal of this research is to produce material aluminum-based with amino acid ligand (methionine) which has high adsorption ability.

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METHOD

In this synthesis, methionine (Sigma–Aldrich) and sodium hydroxide (Fisher Scientific) were added to 35 mL of deionized water, according to the desired molar ratio. Furthermore, $Al_2(SO_4)_3.18H_2O$ (J.T. Baker-Avantor) was dissolved in 35 ml of deionized water too. Then the ligand (methionine) that have deprotonated by sodium hydroxide, was added to aluminum sulfate solution drop by drop with agitation for 1 hour and the mixture became into a cloudy–like suspension immediately at mild temperature (60-80 ^oC). The solid product from this process was collected by spin separator and washing with DI water. After that, the solid product was dried in the freeze dryer. The solid product was activated in oven with condition vacuum at 100^{o}C for 10 hours. Furthermore, the material is ready to be used for the methyl orange (Sigma–Aldrich) adsorption experiment as adsorbent.

Furthermore, 10 mg of adsorbent is added with 5 mL of 10 ppm methyl orange solution. After that, the mixture is put into an incubator shaker with 200 rpm and a temperature of 30^{o}C for 24 hours. Calculating of % removal of methyl orange is done by measuring the absorbance of the sample solution after the adsorbent is separated from the solution. Measurements were made using UV-2600 UV-VIS spectrophotometer Shimadzu at a maximum wavelength of 460 nm.

The material which has the highest adsorption ability is further characterized. XRD measurement was analyzed by Bruker D2 Phaser-Xray Powder Diffraction at 30 kV, 10 mA equipped with Cu Kα radiation (k=1.5406 A). FTIR was measured on an FTS-3500 Bio-Rad in KBr method and 4000-400 cm^{-1} of the wavenumber. FESEM was recorded by JSM-6500F Jeol. BET analysis was measured by Quantachrome instrument version 3.0 (Autosorb iQ station 1).

RESULTS AND DISCUSSION

Influence of molar ratio (MR) and reaction temperature on product %yield

Influence of MR and reaction temperature on the synthesis of the aluminium-modifier by methionine was investigated at reaction time 60 h. This synthesis by using methionine ligand and sodium hydroxide as a deprotonation agent consists of three molar ratio variables, 1:1:3, 1:2:6 and 1:3:9, and also three reaction temperature variables 60, 70 and 80^o C is shown in figure 1. Product yield maximum in molar ratio 1:2:6 of metal, ligand, and base respectively is described in Figure 1. This is due to the reaction when the molar ratio of 1:1:3 and 1:3:9 has a low equilibrium constant reaction. Qamar et al.,(2019) reported that the low percentage yield indicates that the reaction has a low equilibrium constant [12] .

Temperature also affects product yield. Figure 1 shows that 60^{o}C produces the highest product yield compared to 70 and 80^{o}C. This relates to the solvent used. The synthesis of this material uses water as a solvent. As a result, at the reaction temperature of 70 and 80^{o}C, there are already a few solvents that begin to evaporate. This condition results in changes in reactant concentration which will also affect the reaction equilibrium. The reaction equilibrium constant becomes low which impacts low product yields as well.

Screened for Adsorption Ability

The a-AM material with various molar ratio and reaction temperature have been produced. Because of the purpose of this material synthesis is for the adsorption process, therefore the selection of the best material is based on the highest adsorption ability. The choice of a-AM material with high adsorption ability is carried out by methyl orange dyes adsorption. % Removal of methyl orange for all material variations can be seen in Fig. 2. According to Fig. 2, materials with a 1:3:9 molar ratio and 70 ^{o}C reaction temperature give the highest % removal result (75.9%). This result indicates that the material produced with this condition has the best performance as adsorbent than the others condition. To investigate the morphology of this material, have analysis with FESEM.

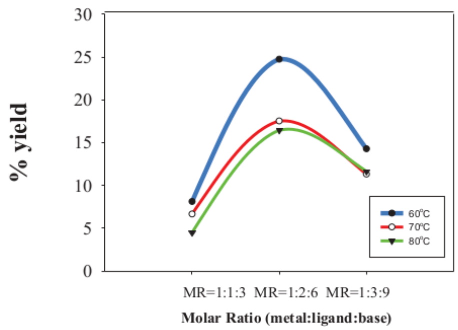

FIGURE 1. % Yield of the a-AM synthesis was influenced by molar ratio (MR) and temperature of reaction.

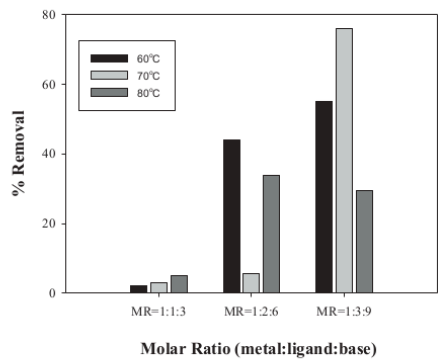

FIGURE 2. Result of the screening by methyl orange adsorption of the system Al^{3+}/methionine/base at two variations of reaction temperature and the molar ratio

The morphology of the material with porous surfaces can be seen in Fig. 3. With a magnification of 25.000, it appears that the surface of the material is very rough and porous. This situation allows the methyl orange dye adsorption process to occur properly

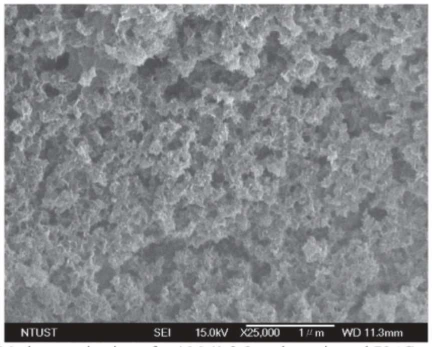

FIGURE 3. FESEM characterization of a-AM (1:3:9 molar ratio and 70 ^oC reaction temperature)

Characterization

To know the internal structure of this material (1:3:9 molar ratio and 70^{o}C reaction temperature), have done quantification of the surface area by the BET method (S_{BET}). Regarding BET information, the S_{BET} of this material is 287 m^2/g while pore size of this material is 0.996 cm^3/g. The average pore diameter of the material is measured by N_2 adsorption–desorption is 13.85 nm. This size showed that this material is mesoporous (type IV).

The XRD pattern of material with 1:3:9 the molar ratio at reaction temperatures of 60, 70 and 80^{o}C (XRD image pattern not presented) indicates that the materials are amorphous. A comparison of the percentage of crystallinity and amorphous can be seen in Table 1.

TABLE 1. The results of the crystallinity composition of material with 1:3:9 molar ratio by XRD analysis

Temperature (^{o}C)	Composition (%)	
	Crystallinity	Amorphous
60	49.8	50.2
70	49.6	50.4
80	39.1	60.9

Table 1 exhibited that material synthesis at reaction temperatures of 60 and 70^{o}C have almost the same composition of crystallinity (49.8 and 49.6 % respectively) but the ability to adsorb methyl orange dyes is very different 55.2% and 75.9% respectively (Fig. 2). This result is the same as Reinsch and Stock (2013) noticed that low crystallinity but it has the large-pore form so can have high adsorption capacity. This phenomena can be happened cause the pattern was not recorded if it has minor of resolved reflections[14]. Qamar et al., (2019) also reported that all synthetic complexes with methionine as ligand have amorphous forms.

Then the next characterization of material with 1:3:9 molar ratio at 70^{o}C reaction temperatures was been an analysis by FTIR. The FTIR spectra of a-AM before activation is shown in Fig. 4. The peak around 3307 cm^{-1} was O-H stretching vibrations and the peak around 3068 cm^{-1} is stretching vibrations of C-H aromatic. The wavelength of 3307 cm^{-1} indicates that the material adsorbed water. The peak 2893 and 2835 cm^{-1} are C-H alkanes stretching vibrations. The peak 1739, 1631-1570 and 1500 are the C=O- carbonyl vibration of free –COOH- groups, N-H bend of amine groups, and the C=C vibrations of the aromatic ring respectively. S-O stretching vibrations from thioether is confirmed at 1068 cm^{-1}.

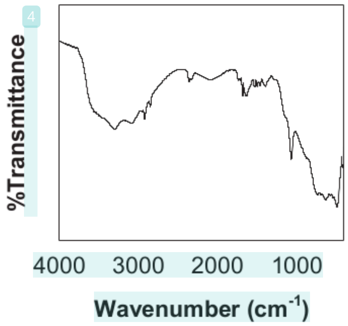

FIGURE 4. FTIR analysis of a-AM (1:3:9: molar ratio at 70°C reaction temperature)

CONCLUSION

An amorphous Al-based material with methionine ligands and have high adsorption ability (75.9% removal), have been successfully synthesized. With a S_{BET}, pore size, and mean pore diameter are 287 m^2/g, 0.996 cm^3/g and 13.85 nm respectively, indicate mesoporous material. This material also has potency as an adsorbent.

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