Characterization of Modified Polyurethane Foam Adsorbents for Mercury Adsorption Applications

Darmadi¹, M R Lubis¹, R Saputra¹, M D Alfarabi¹, S Sarah¹ and Adisalamun*¹
Chemical Engineering Department, Syiah Kuala University.
E-mail: adisalamun@che.unsyiah.ac.id

Abstract. The use of modified polyurethane foam adsorbents for mercury adsorption applications can reduce the impact of mercury pollution. This study aims to study the characteristics of adsorbents made from castor oil, MDI (Methylene diphenyl diisocyanate), glycerol, distilled water and modified by the addition of zeolite and bentonite. Polyurethane foam which has optimum performance is further characterized to determine physical and chemical properties, including: functional groups (FTIR), morphology (SEM) and area (BET). The results of FTIR Characterization showed that in polyurethane foams without modification there was a C=O group which is a typical group in the polyurethane group shown in wavenumber (1654-1516 cm⁻¹, 1680-1514 cm⁻¹, and 1593-1516 cm⁻¹) Whereas in zeolite modified polyurethane foam there is a C=CH group with a wavenumber of 3008 cm⁻¹ which is a typical group for zeolite whereas in bentonite there is a C=CH group with a wavenumber of 3007 cm⁻¹ which is a typical group for bentonite. The results of SEM characterization show that zeolite modified polyurethane foam has a smooth and flat structure with small pores and polyurethane foam with bentonite has irregular or irregular particle shape. The average BET area obtained in the PUF modification is 1.3778 m² g⁻¹. Whereas for the smallest BET area obtained at synthetic PUF 19.1 gr + Zeolite 40% for 0.773 m² g⁻¹, the area is influenced by the comparison of composition from polyurethane foam synthesis.

1. Introduction
Polyurethane is a synthetic polymer formed by the reaction between monomers containing at least two functional groups of isocyanates and other monomers containing at least two hydroxy groups in the presence of a catalyst. The basic raw material in producing polyurethanes is polyols and isocyanates. The molecular structure and size of this compound influences the polymerization reaction and polyurethane structure obtained [1].

Polyurethane foam can be stable in acidic and basic solutions and will not change the structure when heated to a temperature of 180°C [2,3]. Thus, polyurethane foam material is very suitable to be used as an adsorbent for the separation process with immersion techniques and column methods.

Polyurethane foam has been widely applied to various separation processes or pre-concretion methods. The ability of polyurethane foam as an adsorbent has been investigated by Vidoti et al. [4] and Yassin [5]. Lately, several researchers have also modified polyurethane foam to expand its application. Moawed et al. [6] modified polyurethane foam with Rhodamin B to separate trivalent metal ions Bi (III), Sb (III) and Fe (III). In addition, Li et al. [7] modified polyurethane foam with oleophilic monomers as absorbent materials for diesel and kerosene and water. In this study, the polyurethane foam that will be

* To whom any correspondence should be addressed.
produced is modified using natural fillers both inorganic and organic. The inorganic fillers that will be used are bentonite and zeolite, while the organic fillers used are chitosan and cellulose. The resulting polyurethane foam is expected to have good mechanical and absorbent properties and to be characterized according to polyurethane foam.

Characterization of polyurethane is a very important part of a polyurethane industry to determine the application of polyurethane. This polyurethane application is determined by the properties possessed by the polyurethane material. To find out the properties of polyurethane that have been synthesized, characterization of physical and chemical properties is carried out including morphology and molecular structure. In this study used several characterization methods, among others: molecular structure analysis with Fourier Transform Infrared Spectroscopy (FTIR), analysis of surface with scanning electrons microscopies (SEM).

Analysis of the data used in this study are: functional group analysis with FTIR. This analysis aims to ensure the formation of polyurethane foams from functional groups displayed by FTIR spectra and also structural analysis of the surface of polyurethane foam with SEM. The analysis aims to characterize the morphology of polyurethane foams [8]. The use of polyurethane foam as an absorbent material is very rare to use because the procedure for making flexible polyurethane foam has not been widely published. With the scarcity of this information, the product form of polyurethane foam produced is often not as expected. According to the information obtained, the economic loss due to the process of making the process of making polyurethane foam is quite large. This is due to the lack of knowledge regarding the nature of the polyurethane flexible foam during its formation reaction.

In the process of making polyurethane foams it can be seen the nature of polyurethane foam during the polymerization reaction takes place. The advantages possessed by polyurethane foam which are modified by zeolite and bentonite are good chemical, mechanical and absorbency properties. As for the consideration in the selection of polyurethane foam making materials are the factors of material characteristics, economic value, and environment. Characteristics of materials are factors that provide special advantages related to the physical-chemical properties of materials, in this case include the properties of absorption to water, thermal conductivity, and so on. These physical chemical properties are generally used as the main reference in determining the selection of materials in the manufacture of polyurethane foams [9].

Based on the description above, in this study the polyurethane foam adsorbent was characterized to see the properties of polyurethane produced as an adsorbent, so as to provide information and benefits in the industrial field for the application of mercury adsorption.

2. Methodology

2.1. Materials and tools

The material used in this study is castor oil as polyol, methylene diphenyl diisocyanate (MDI) (chemically pure, Fuchen LLC China), distilled water as blowing agent, glycerol (Merck, Steinheim, Germany), Hg Standard Solution (Merck, Steinheim, Germany), zeolite, bentonite. The tools used are glassware, Hot Plate, ball mill, digital scales, ovens, furnaces, 100 mesh sieves, Scanning Electron Microscopy With Energy-Dispersive X-Ray (SEM-EDX, Quanta F250, FEI, Oregon, USA), Atomic Absorption Spectroscopy (AAS, Analyst 800, Perkin Elmer Co, Norwalk, CT, USA), Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 6700 FTIR, Thermo, MA, USA).

2.2 Preparation of polyurethane foam adsorbents

Preparation of the modified zeolite is done by one-shot method by trial and error. At first the mixture that will be made in a beaker glass using a hot plate is made by mixing 10 g of castor oil, 1 g of distilled water, with a variation of glycerol mass (0.2 g; 0.4 g; and 0.6 g), with zeolite (4 g; 5 g; and 6 g) and variations in MDI mass (4 g; 5 g; and 60 g). The mixture is stirred with a speed of 250 rpm for 10 minutes and a temperature of 70°C to form a bubble. Then poured into 6 x 6 x 3 cm³ aluminum mold. The foam formed in 6 x 6 x 3 cm³ aluminum mold is placed in an oven with a temperature of 70°C for 2 hours. Each polyurethane foam that has been formed and hardened, then diced 0.5 cm³ [10].
Polyurethane mixture made in beaker glass and using a hot plate, the mixture is made by varying the mass of the material which is castor oil 10 g, 1 g of distilled water, with a composition of glycerol (4 g; 5 g; and 6 g), variation of bentonite (4 g; 5 g; and 6 g) and MDI (4 g; 5 g; and 6 g). The mixture is stirred at a speed of 250 rpm for 10 minutes at a temperature of 70°C until the foam is formed or for about 20 seconds, then poured into 6 × 6 × 3 cm³ aluminum mold. The foam formed is cured at 70°C for 2 hours. After being removed from the oven and cooled, bentonite modified polyurethane foam formed was then cut into 0.5 cm³ cubes.

2.3. Characterization
Modified polyurethane foam adsorbent was characterized using FTIR, SEM, and visual observations. FTIR analysis was carried out to determine the functional groups of absorbent polyurethane foam, while SEM analysis was carried out to see the morphological structure of the polyurethane foam adsorbent.

3. Results and Discussion
3.1. FTIR analysis
The functional groups found on the surface of polyurethane foam (PU) which are modified by zeolite and bentonite are strongly influenced by the process of making, heating and activating. Castor oil, MDI, glycerol, H₂O, zeolite and bentonite are the main elements in the formation of pore surfaces of polyurethane foam modified by zeolite and bentonite. This element can have a significant influence on the application of the adsorbent, ion surface during the adsorption process and on the surface morphology of polyurethane foam. Figure 1 shows the FTIR spectrum for polyurethane foam and modified polyurethane foam.

Table 1 shows that the N-H group in each foam is shown at 3700 cm⁻¹ absorption number. Addition of zeolite and bentonite in the process of foam synthesis can increase the hydroxyl group, as evidenced by the wave band that extends around the absorption number of 3700 cm⁻¹. The C = C-H group was not readable on polyurethane foam without modification, while the type of foam was read at a wavenumber of 3007-3008 cm⁻¹. In polyurethane foam without modification the C≡N group appears at 2690 cm⁻¹ absorption number, which indicates that there is excess MDI. FTIR spectrum from PU + zeolite foam and bentonite + foam did not show C≡N because MDI had reacted. Cluster C = O is a typical group in the polyurethane group shown in all foams (1654-1516 cm⁻¹, 1680-1514 cm⁻¹, and 1593-1516 cm⁻¹). Shifting the absorption number to the C = O group to the lower direction shows the characteristics of the modified material from zeolite or bentonite. Meanwhile, C = C is a group found in polyurethane,
zeolite and bentonite, indicated by all types of foam at absorption numbers of 1413 cm$^{-1}$. The C-OH group can be seen from the wavenumbers of 1041-1047 cm$^{-1}$ which are general groups in castor oil, zeolite and bentonite.

Table 1. Results of FTIR PU Foam spectrum, PU Foam + Zeolite, PU + Bentonite Foam.

| Functional Group | Wavenumber (cm$^{-1}$) |
|------------------|------------------------|
|                  | PU Foam    | PU Foam + Zeolite | PU Foam + Bentonite |
| N-H              | 3699       | 3799              | 3741                |
| C-C-H            | 2935 - 2856| 2929 - 2854       | 2931 – 2854         |
| C≡C-H            | -          | 3008              | 3007                |
| C≡N              | 2690       | -                 | -                   |
| C=O              | 1654 – 1516| 1680 - 1514       | 1593 – 1516         |
| CH$_2$           | 1448       | 1448              | 1449                |
| CH$_3$           | 1448-1331  | 1456-1311         | 1449-1309           |
| C≡C              | 1413       | 1413              | 1413                |
| C-O-C            | 1219       | -                 | 1221                |
| C-OH             | 1041       | 1141-1043         | 1047                |

Figure 2. The Scanning Electron Microscopy (SEM) result of (a) PU foam, (b) PU foam + 4 g zeolite, (c) PU foam + 5 g zeolite, and (d) PU foam + 6 g zeolite.

3.2. Surface morphology

Scanning electron microscopy (SEM) is used to characterize the morphology of polyurethane foams because mechanical properties are mainly influenced by clear open cell density, thickness, and size. This technique is used to observe the open cell structure, which is typical of flexible polyurethane foam.

The surface morphology of polyurethane foam was analyzed using SEM at 5000 times magnification. The results of observations using SEM are shown in Figure 2 and Figure 3. Figure 2 shows that the
polyurethane foam without modification has a smooth and flat surface structure with small pores. There is empty space between one particle and another particle. Whereas in polyurethane foam modified with zeolite it has a rough surface structure, the presence of empty spaces and the formation of zeolite particles in the form of spherulite. These particles have irregular size and distribution. Zeolite particles dominate the surface structure of polyurethane foams and if the zeolite concentration given is higher, the size of the spherulite structure is greater. Figure 3 shows that polyurethane foam modified with bentonite has irregular or irregular particles. The formed particles also have different sizes and are not distributed throughout the empty spaces. Similar to zeolite, bentonite addition also dominates the structure surface of polyurethane foam, the higher the concentration of bentonite given, the larger particle size will be formed and more evenly distributed to the entire surface of polyurethane foam.

Figure 3. The Scanning Electron Microscopy (SEM) result of (a) PU foam, (b) PU foam + 4 g bentonite, (c) PU foam + 5 g bentonite, and (d) PU Foam + bentonite 6 g.

Figure 4. BET analysis results Polyurethane foam (PU), synthesis PUF 19.1 g and Zeolite 40%.
3.3. Surface Area
The characterization of the area of polyurethane foam with the BET method (Brunauer-Emmett-Teller) aims to determine the material surface area, pore distribution of material and isotherm adsorption of a gas in the material. The BET method is used for flat material surfaces and does not have plates on each layer that can be used to explain the area of the sample. Table 2 shows the result of BET testing taken based on the characteristics of zeolite and bentonite polyurethane (PUF) foam.

The area of BET for synthetic PUF modified with zeolite obtained a varied pore surface area for each sample code. The average BET area obtained in the PUF modification is \(1.3778 \text{ m}^2 \text{ g}^{-1}\). This small surface area is caused by a comparison of the composition of synthetic PUF when making synthetic PUF. So that it will lead to the ability of synthetic PUF modified with zeolite to absorb Hg metal contained in water.

Table 2. Result of BET analysis.

| Sample Code          | Sample Mass (g) | BET Surface Area A / (m² g⁻¹) |
|---------------------|-----------------|------------------------------|
| PUF                 | 0.2868          | 1.7596                       |
| PUF 18.6 g Zeolite 50% | 0.2991          | 1.3733                       |
| PUF 19.5 g Zeolite 60% | 0.2787          | 0.8561                       |
| PUF 16.9 g Zeolite 40% | 0.2867          | 1.0221                       |
| PUF 20 g.5 g Zeolite 50% | 0.2828          | 1.0349                       |
| PUF 19.1 g Zeolite 40% | 0.2624          | 0.773                        |
| PUF 18.7 g Zeolite 50% | 0.2614          | 2.8257                       |

4. Conclusion
The conclusions that can be drawn from this study are as follows:
1. The results of FTIR characterization show that there are several chemical groups present in the polyurethane foam without modification and also on polyurethane foams modified by zeolite and bentonite.
2. The results of SEM characterization prove that polyurethane foam without modification has a smooth and flat surface with small nodule and no empty space, whereas in zeolite modified polyurethane foam the particles are spherulite, zeolite dominates the surface structure whereas in polyurethane foam modified bentonite is the same with zeolite, bentonite also dominates the structure of the surface of polyurethane foam.
3. The largest BET surface area obtained in PUF modification of 18.7 g + 50% Zeolite is 2.8257 m² g⁻¹. Whereas the smallest BET area was obtained at synthetic PUF 19.1 g + Zeolite 40% at 0.773 m² g⁻¹.

Reference
[1] Triwulandari E, Prihastuti H, Haryono A and Susilo E 2008 *J. Sains Mat. Indo.* ed. December 31
[2] El-Shahat M F, Moawed E A and Burham N 2008 *J. Hazard Mater.* 160 629
[3] Moawed E A 2006 *Ana. Chim. Acta.* 580 263
[4] Vidotti E C, Cancino J C, Olibeira C C, Rollemberg M and do Carmo E 2005 *Ana. Sci.* 21 149
[5] Yassin S A 2012 *J. Sci.* 23 5
[6] Moawed E A, Farag A B and El-Shahat M F 2011 *J. Saudi Chem. Soc.* **17** 47
[7] Li H, Liu L and Yang F 2013 *Procedia Environ. Sci.* **18** 528
[8] Rohaeti E 2005 *Prosiding Seminar Nasional Penelitian, Pendidikan, dan Penerapan MIPA* K-1
[9] Yeon K H, Lee J W, Lee J S, and Moon S H 2002 *J. Apl. Polym. Sci.* **86**(7) 173
[10] Kumari S, Chauhan G S and Ahn J H 2016 *Chem. Eng.* **304** 728