Development of porous structured polyvinyl alcohol/zeolite/carbon composites as adsorbent

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Abstract. Adsorption is a separation process that has higher energy efficiency than others. Analyzing the nature of the adsorbate and the selection of suitable adsorbent are key success in adsorption. The performance of the adsorbent can be modified either physically or chemically to obtain the efficiency and effectiveness of the adsorption, this can be facilitated by using a composite adsorbent. In this study, we have conducted the preparation process of a polyvinyl alcohol (PVA)/zeolite/carbon composites. The resulting adsorbent composites are dedicated for ethanol – water dehydration proposes. The composites were prepared using cross-linked polymerization method followed by supercritical fluid extraction (SFE) to obtain the porous structured upon drying process. The characterization of the functional groups and morphology were performed by using Fourier Transform Infra-Red (FTIR) and Scanning Electron Microscopy (SEM), respectively. The FTIR analysis showed that composite prepared by SFE method formed hydrogen bonding confirmed by the appearance of peaks at 2950 – 3000 cm⁻¹ compared to composite without SFE method, whereas, the results of SEM study showed the formation of three layered structures. On basis of the obtained results, it can be shown that PVA/zeolite/carbon has high potential to be develop further as an adsorbent composite.

Keywords: adsorption, adsorbent, polymerization, composite, polyvinyl alcohol, zeolite, carbon.

1. Introduction

Energy use in the processes, particularly in separation processes i.e distillation, azeotropic distillation, membrane pervaporation, adsorption, extraction, and so on (1, 2) is becoming a major concern of researchers in the past few decades (3-5). However, adsorption process provide higher energy efficiency compared to other techniques (6). Adsorption is a process that occurs when a fluid, liquid or gas as adsorbate, is bound to a solid or a liquid as the adsorbent to finally form a molecular or atomic layer (7). Adsorption term used to describe the presence of a particular substance either liquid or solid with a higher concentration at the surface than in its bulk phase medium. The adsorption process occurs as a result of molecular physical bonds of the adsorbate on the surface of the adsorbent (8). The key factor to the success of the adsorption process is related to the adsorbent performance (9). The bond among the adsorbate and adsorbent will be enhanced whether designing higher surface area of the adsorbent or expanding the contact area among them (10).

In addition, improving interaction among adsorbent and adsorbate can also be done chemically on the adsorbent surfaces (11). Surface modification can be performed by adding the chemical compound...
to the adsorbent (12-14). Polymeric substances are potential as an adsorbent composite in terms of their good mechanical rigidity, adjustable surface chemistry (15), and good selectivity toward organic adsorbate (16). However, their performance is dependent on the type of functional groups used i.e. extent of chemical activation and modification, nature and degree of functionality grafted on the polymeric surfaces.

In this study, PVA is added to the zeolite and activated carbon to form a composite with rich hydroxyl groups. Hydroxyl groups is expected to form hydrogen bonds with water so that the potential adsorbent composite increase the water adsorption capacity of the adsorbent. In this case, certain condition is required in which the PVA polymer can bind to zeolite and activated carbon. The best condition can be achieved by using CO$_2$ at supercritical condition. Under these conditions, the viscosity is lowered so that the polymer can be more reactive and enhance the diffusivity of the polymer to other materials (17). The aim of this study is to develop a PVA/Zeolite/Carbon adsorbent composite with porous structured and possessing good chemical bonding among the three substances forming the composite.

2. Materials and Method

2.1. Materials

In this study, the main materials used are polyvinyl alcohol (MW 140,000 purchased from Emerck), natural zeolite (obtained from Gunung Kidul, Yogyakarta), wood activated carbon (obtained from West Java), glutaraldehyde (purchased from Emerck as crosslinker), CO$_2$ UHP (purchased from Air Liquide), furfural alcohol (purchased from Sigma Aldrich), Toluene (purchased from Emerck) and distilled water.

2.2. Methods

2.2.1. Composite preparation. We have conducted the pretreatment and activation process of natural zeolites by washing using distilled water, acidified and then dried in a furnace at 300°C for 3 hours. Zeolite and activated carbon were crushed using a laboratory ball mill for 72 hours, separated, and then screened to obtain consistent particle size. The activated carbon, furfural alcohol, and solvent toluene were dispersed in a 500 mL glass beaker and stirred using a magnetic stirrer. For the impregnation method, zeolite was inserted slowly into the dispersion mixture and stirred continuously. After 1 hour, the mixture was transferred into an incubator shaker and agitated at 25°C for 24 hours. Afterwards, the solids were filtered and then transferred to a crucible. The next step is carbonization at 150°C to remove moisture, then increased to 800°C with rate 10°C min$^{-1}$ then detained for 8 hours. This treatment produced a zeolite/carbon composite. The amount of PVA was added into a 500 mL glass beaker and dissolved using distilled water at a temperature of 80°C for 3-4 hours and stirred using a magnetic stirrer continuously until the PVA clearly dissolved. The amount of composite zeolite/carbon was added to the PVA mixture slowly and stirred continuously to reach a homogeneous mixture. In order to reach the crosslinking, 4 wt% glutaraldehyde was added to the mixture and stirred overnight. The sample was dried using CO$_2$ Supercritical Fluid Extraction (SFE) units in the pressure 2,000 psi and temperature 50°C for 4 hr.

2.2.2. Material characterization. In accordance with the aim to find the composite functional groups and formation of hydrogen bonding, we have carried out the FTIR (Shimadzu IR Prestige – 21) analyses with ATR as a method of measurement and KBr was used as a carrier. The next step was SEM to analysis morphological and pore structured of the composite. We have conducted SEM (JEOL JSM-6510LA) analysis in 20 kV with a gold coated sample previously in the current 30 mA for 55 sec. Hydroxyl number was used to obtain the amount of hydroxyl groups in the composite. In accordance with ASTM D1957 and E222-10, 30 mL of acetic acid anhydride is dissolved in 350 mL of pyridine. Acetylation of the hydroxyl group involves reacting 2 mL sample into 4 mL of acetic acid anhydride. The reaction was performed at a temperature of 90°C for 2 hours. After 2 hours of reaction, 4 mL of
distilled water was added to the solution at room temperature. Determination of hydroxyl value can be conducted by titrating reaction resulting solution diluted with 1N KOH solution. The hydroxyl value was calculated following the equation:

\[ HV = \left( \frac{(56,1)(N)(V_B - V_{acet})}{W_{acet}} \right) + AV \]

Where HV is hydroxyl value (mg KOH/g sample); MW of KOH is 56.1 g/mole; N is normality of titer; \( V_B \) is amount of potassium hydroxide solution (mL) required to titrate the blank; \( V_{acet} \) is amount of potassium hydroxide solution (mL) required to titrate the acetylated sample; \( W_{acet} \) is amount of sample (g) required for acetylation; AV is acid value of the sample (mg KOH/g sample).

3. Results and Discussion

In this study, the PVA used is in higher hydrolyzed grade. This type of PVA has a high degree of crystallinity (40% to 50%), and can increase the adhesion on a hydrophilic surface. In addition, PVA has higher hydroxyl groups in the molecule structure. Zeolites are aluminosilicate tetrahedral framework structure that provides cavities to be occupied by the cations and water molecules. While the other substance of the composite is activated carbon. It is composed of a random arrangement of microcrystallites and with a strong crosslink among them, then formed a good pore structure. The main characteristics of these three substances plays an important role to undertake the preparation of composite materials. Based on these characteristics, there are several active groups of each substance that can be engineered through chemical bonds, where chemical bond can mix the three substances into a composite.

Analysis of composite formation can be showed from the FTIR study as seen in Fig 1. Several important chemical bonds were formed during the composite preparation process. The IR spectra showed that the wavelength range 400-450 cm\(^{-1}\) appear to form the group C - O - C composite. While in the wavelength range 750-850 cm\(^{-1}\) appear to form the stretching Si - C aliphatic which is the bond within zeolite and carbon. In the wavelength range 1050 - 1100 cm\(^{-1}\) corresponds to the Si - O - C group which is the result of the bond between PVA and zeolite. At a wavelength range of 2900 - 3000 cm\(^{-1}\) corresponds to a hydrogen bond and the OH group stretching. This indicates that the hydrogen from polyvinyl alcohol bounds to zeolite, while the hydroxyl groups on the composite PVA/zeolite/carbon has only in compound polyvinyl alcohol, that is making possibility the occurrence of hydrogen bonds OH groups on poly vinyl alcohol.

According to the hydroxyl value analysis, the amount hydroxyl group of PVA can be determined 1,220.85 mg KOH/g sample. After the composite was formed, the hydroxyl value decreased to 620.94 mg KOH/g sample. From the FTIR analysis, the hydrogen bonds formation on the composite was confirmed. The hydrogen bonding formation in this composite have an important role in changing the properties of the material, particularly on the improvement of the material mechanical strength. Improvement of mechanical properties is very influential to the resistance ability of the adsorbent during the adsorption process takes place. As previously explained, that each initial substance has specific properties. In this case, the PVA is essentially insoluble in water, however it is needed as a OH group donor in the adsorbent. With the change in mechanical properties, it is expected that the glass temperature, Tg, to be increased, thus PVA will be insoluble in water and remain as OH groups donor although the hydroxyl value was decline.
Figure 1. The IR spectra that show the formation of PVA/zeolite/carbon composite and compared with the initial constituent substances. The spectra are (a) activated carbon; (b) PVA/zeolite/carbon; (c) PVA; (d) zeolite.

The morphology of the composite can be analyzed using SEM. In addition, the affinity of the initial substances can be seen as well in order to understand the formation of pore structure and occurring the composite layer specifically as seen in Fig. 2. SEM analysis was performed on two section, first in the interface section to see the morphology and the formation of pores in the top layer, second in the cross section to analyze the composite layer formation and pore structure. SEM analysis indicate that in the interface was formed uniquely pores of the composite material. These pores become a very important characteristic in the adsorption process, while it would improve a higher surface area. In other words, it would be possible that contact among the adsorbate and adsorbent will increase which will impact to the effectiveness and efficiency in the adsorption process.

Figure 2. SEM micrograph analysis of the PVA/zeolite/carbon composite (a) interface section with magnificent 1,500x; (b) cross section with magnificent 430x while in this part consist of three layers (1) PVA; (2) zeolite; (3) carbon.
Furthermore, it appears that the upper layer was smooth that shows the polymer layer. The cross section shows more clearly that the polymer is in the top layer, then zeolites and carbon, respectively. The fact that the first layer is a polymer becomes important considering that PVA is a OH groups donor in the adsorbent, therefore chemisorption process will occur in the first layer adsorption thereafter it will be followed by the process of physisorption on zeolites and carbon layers sequentially. SEM analysis also showed that their regularity and pore structure caused by the formation of hydrogen bonding between PVA with zeolites and zeolite with carbon.

4. Conclusion
In this study, we examined the characteristics of composite materials primarily through supercritical fluid extraction method. We confirmed that the method was instrumental to the unique pore formation and chemical bonding of the three starting substance, in this case hydrogen bonds to form a composite. Composite was expected consisting of three layers namely PVA, zeolites and carbon respectively therefore it has fulfilled characteristics and potential to be used as adsorbent.

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