

Pellets' pore characteristics on the fly ash-chitosan composite crosslinked to glutaraldehyde

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Abstract: Modification of fly ash into pellets could be conducted by compositing using crosslinked chitosan-glutaraldehyde. Fly ash composite pellets and chitosan could be used as adsorbent of Hg^{2+} in the liquid with variation of fly ash and chitosan mixtures crosslinked to glutaraldehyde. The mass variation of fly ash was 2 g, 3 g and 4 g in 20 mL chitosan solution. Characterization of adsorbent was conducted by FTIR and *Gas Sorption Analyzer* to determine the pore character of fly ash, chitosan and adsorbent composite. The results showed that adsorbent with 3 g fly ash in the 20 mL chitosan solution has the largest surface area and pore total volume for 30.97 m^2/g and 4.54 cc/g , respectively. Whereas the smallest pore average radius is 29.31 Å. Identification of fly ash-chitosan composite functional groups from infrared spectra indicate the presence of functional groups to absorb Hg^{2+} which can be seen at wave numbers 3433 and 2932 $1/cm$.

Key words: pellets, composite, fly ash, chitosan, Hg^{2+} .

1. Introduction

Liquid waste from industry and mining contain heavy metal pollutants. Water containing heavy metals may be harmful to human health if the concentration exceeds the allowable threshold¹. One of the heavy metals that can contaminate the water and acts as a pollutant is mercury (Hg^{2+}). Mercury is a carcinogenic heavy metal that potentially threatens human health even at a very low concentration. Some data have shown that mercury can cause brain damage, disorders on liver, kidneys, digestion tracts and central nervous system, and are toxic to cells by binding to sulfhydryl groups on the intracellular level². The maximum limit levels of mercury ions in drinking water is 2.0 $\mu g/L$ and the total waste mercury ions that allowed is 10.0 $\mu g/L$ ³. Therefore mercury waste treatment methods are needed before the waste discharged into the river water.

Several methods that have been developed and used to treat mercury ions from wastewater are: the reduction⁴, chemical precipitation⁵, separation using membranes⁶, ion exchange⁷, solvent extraction⁸, and coagulation⁹. However, all these methods require large cost and less effective for low concentrations. Therefore

we need a method that cheap, efficient, easy to operate and can be used for a wide range of concentrations, thus comply to the method of adsorption¹⁰.

Adsorption is a process that occurs when a dissolved gas or liquid accumulates on the surface of a solid or liquid adsorbent, that form molecules or atomic layer (adsorbate)¹¹. Adsorption method which has been developed to treat mercury waste including by using active carbon adsorbent¹², carbon aerogel¹³, clay¹⁴, silica surface¹⁵, microporous titanosilicate¹⁶, and aluminosilicate¹⁷. All these adsorbent needed in large amounts, thus the costs are also fairly expensive. Another adsorbent that has been developed is hydrophilic crosslinked hydrogel-polyacrylamide, but this adsorbent still has disadvantage that is easily *swelling*¹⁰. Therefore is needed the adsorbent that cheap and not easily swelling, such as fly ash adsorbent.

Fly ash is the particle with light weight that is produced as side product from coal combustion¹⁸ and particles that come out through the chimney combustion. Fly ash can be used as an adsorbent because it has a major component in the form of silica (SiO₂), alumina (Al₂O₃) and iron oxide (Fe₂O₃), a number of unburnt carbon and these components have an important role in the adsorption process¹⁹. Fly ash was used to adsorb metal ions of Hg and Pb²⁰, and modified fly ash pellets can be used for the adsorption of metal ions of Cu(II) and Cd(II) in the water²¹. However, in this method the adsorption capacity is still low at 34% and 17%²⁰, besides that during the adsorption process the mass loss of fly ash is quite large, although it has been modified into pellets²¹. Then it is necessary to modify the fly ash before it is used as an adsorbent by immobilization of fly ash on chitosan which has been crosslinked with glutaraldehyde.

Chitosan is a biopolymer of D-glucosamine produced from chitin deacetylation process by using strong alkali. The uses of chitosan often utilize crosslinking to modify the chemical structure and texture by bind to the side of amine or hydroxyl²². Chitosan is a membrane that can be crosslinked with glutaraldehyde on the amino group (-NH₂). Crosslinking that occurred could form pores which can improve the adsorption properties. Pores which formed on the chitosan membrane will be the place for immobilization of fly ash²³. Therefore chitosan is often used as a co-polymer.

2. Research Method

2.1 Tools and Materials

The equipment used in this study include: the 120 mesh sieve, apparatus glass, magnetic stirrer, *Surface Area Analyzer* (SAA), and *Fourier Transform- Infra Red* (FTIR).

Table 1. The composition of fly ash

| Elements | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | etc |
|---------------|------------------|--------------------------------|--------------------------------|------|------|-----------------|------|
| % Composition | 56.76 | 18.14 | 15.35 | 2.80 | 2.62 | 0.17 | 4.16 |

The materials used include: Coal fly ash obtained from the combustion of a power plant (composition of fly ash can be seen in Table 1), chitosan (Industrial Grade) from shrimp shells with a degree of deacetylation (DD) 80-85% obtained from Biotech Surindo, 25% Glutaraldehyde from Merck, Oxalate acid, Sulfuric Acid (H₂SO₄), Chloride Acid (HCl), Natrium Hydroxide (NaOH), mercury sulfate (HgSO₄) and aquadest.

2.2 Research Procedure

Preparation of fly ash

Fly ash crushed using a mortar and then dried for 1 hour at a temperature of 100°C using the oven. Dried fly ash sieved using 120 mesh Sieve and passed fly ash used as the raw material in this study.

The activation of fly ash (Demineralization, Dealumination and Calcination)

Fly ash which passed off 120 meshes sieves soaked with 1 M HCl for 24 hours at room temperature. Then it filtered and washed with aquadest until the solution became neutral. After that, it dried for 2 hours at a temperature of 100°C. Furthermore, fly ash soaked again in H₂SO₄ 1 M for 5 hours. Fly ash which had been soaked then filtered and cleaned using aquadest until neutral. This fly ash is dried for 2 hours at a temperature of 100°C, and then calcined for 2 hours at a temperature of 500°C.

The making of fly ash-chitosan composite pellets

Preparation of adsorbent conducted by dissolving 2 gram of chitosan in 5% oxalate acid for 100 mL and stirred while heated until dissolved. Dissolved Chitosan then cooled at room temperature. Chitosan solution was taken for 20 mL into a glass beaker. Into the solution, we added 2 grams of fly ash which had been activated. A mixture of fly ash and chitosan stirred by magnetic stirrer, then taken using a pasteur pipette and dripped in the solution of 2 M NaOH. Pellets of fly ash-chitosan composite separated from the solution of NaOH and then soaked in a solution of 2% glutaraldehyde for 24 hours until composite pellets of crosslinked fly ash-chitosan were formed. Afterwards fly ash-chitosan composite pellets separated from the solution of glutaraldehyde, then washed with aquadest until the solution become neutral and dried in an oven. These pellets are called adsorbent pellets 2 (FA-2). This treatment was repeated with the addition of fly ash as much as 3 gram to obtain adsorbent pellets 3 (FA-3) and the addition of 4 gram fly ash to obtain adsorbent pellets 4 (FA-4).

3. Result and Discussion

3.1 The activation of Fly Ash (Demineralization, Dealumination and Calcination)

The activation of fly ash is a process to enable the active side of fly ash thus it can accelerate the adsorption process. In this study fly ash that will be used as pellets to adsorb Hg metal ions also activated first, either physical or physico-chemical.

Table 2. Components of fly ash before and after activated

| Mineral components | before activation (mg/kg) | after physical activation (mg/kg) | after physico-chemical activation (mg/kg) |
|--------------------|---------------------------|-----------------------------------|---|
| Pb | 26.98 | 25.05 | 26.40 |
| Zn | 27.50 | 22.58 | 14.58 |
| Cr | 14.25 | 14.50 | 78.38 |
| Cd | 0.78 | 0.63 | 0.58 |
| Mn | 56.80 | 50.60 | 60.80 |

After activation, the content of mineral components in the fly ash increased (Table 2). This shows that the water content and debris in the fly ash was reduced thus it expand the width surface of fly ash, and therefore the mercury metal ions can be adsorbed in greater concentration. The method of chemical activation conducted by immersing the fly ash in acid solution to eliminate unburned carbon that has a characteristic as debris and can interfere the process of adsorption²⁴.

3.2 Spectroscopy Measurements (FT-IR)

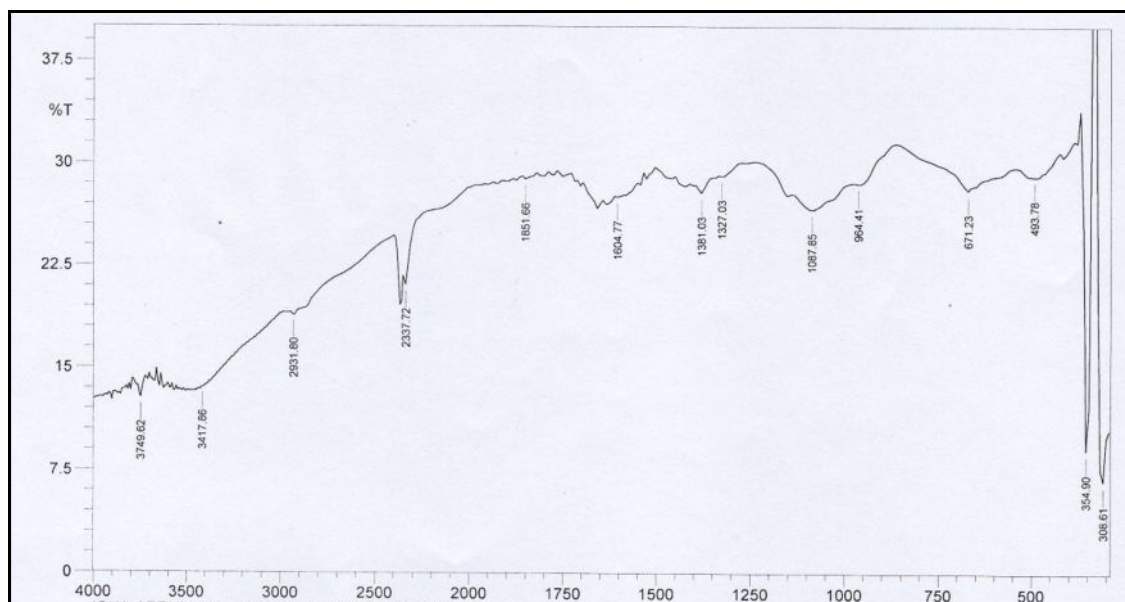


Figure 1. Spectrum of FT-IR chitosan

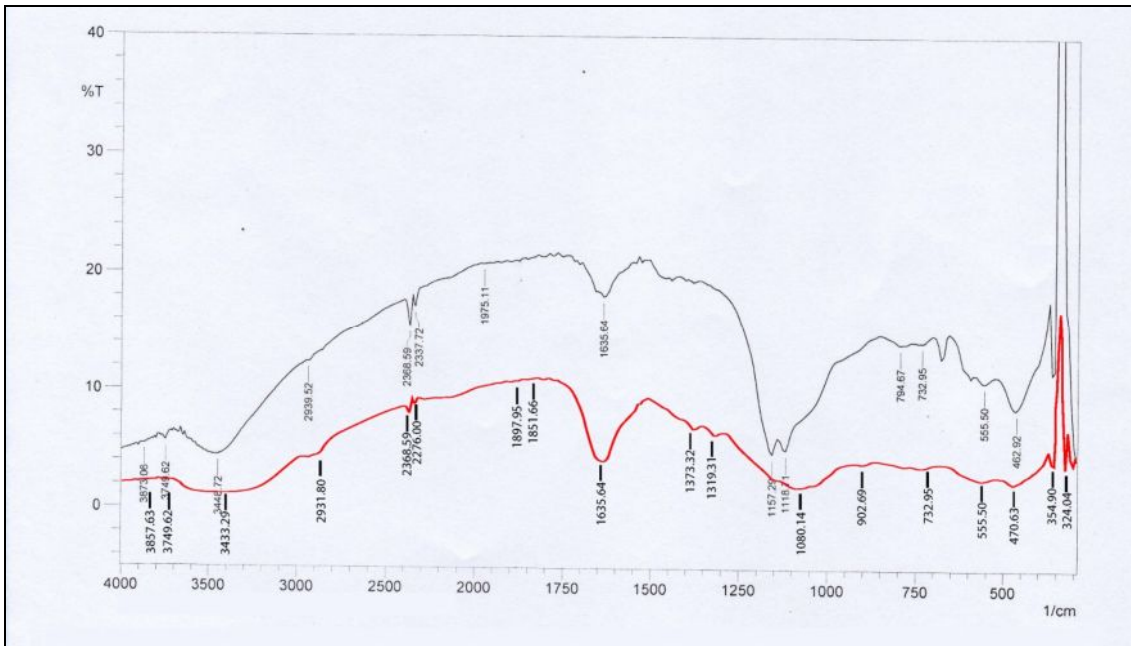


Figure 2. (-) Spectrum of FT-IR of fly ash, (-) Spectrum of FT-IR fly ash composite pellets

FT-IR Spectroscopy analysis is a method to characterize and validate the structure of fly ash composite pellets (Figure 1 and 2). Spectrum of FT-IR chitosan shown by absorption at wave numbers 3417 1/cm which indicates the presence of functional groups of NH, -CH at wave number 2931 1/cm, -NH₂ at wave number 1851 and 1604 1/cm, C-O at wave number 1381, 1327 1/cm, and -CN at wave number 1087 1/cm (Figure 1). This spectrum still has not shown the crosslinked between chitosan and glutaraldehyde which will be used for the immobilization of fly ash. Whereas, modified fly ash is shown in Figure 2.

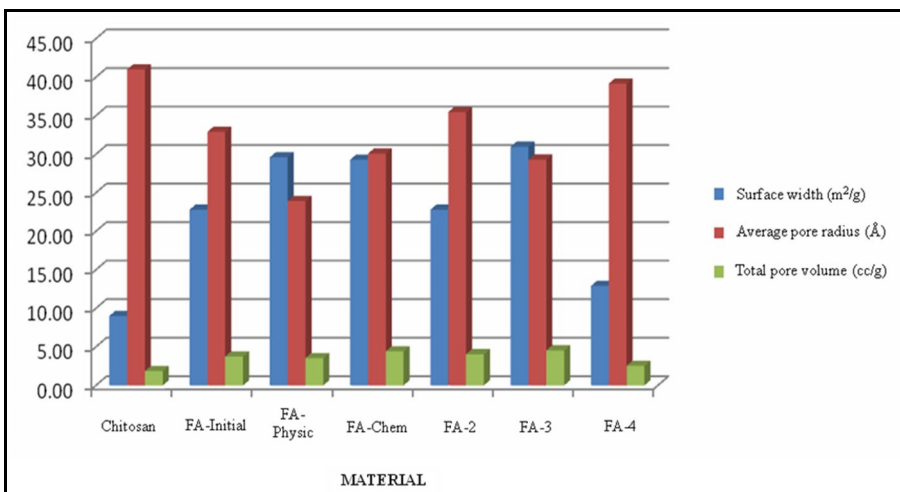


Figure 3. The profile of changes in surface area, pore radius average, and the total pore volume from raw materials and formed composites.

The difference in functional groups between fly ash which has not been modified or immobilized and fly ash which has been modified showed in Figure 2. Clear differences was indicated in the resulting peak particularly at wave number 3433.29 (NH) and 1635.64 (OH). Both wave numbers show widen peaks which indicate that the fly ash has been modified. The spectrum of fly ash on the wave number 1087, 555 and 462 1/cm indicate the presence of asymmetric stretching bound from Si-O-Si which respectively as follows: symmetric stretching bound of Si-O-Si and vibration bond from aluminum oxide. Figure 2 also show a peak of the functional group which capable of absorbing heavy metals such as Si-OH, -NH₃⁺ and Al³⁺; which also seen in fly ash-chitosan composite at wave number 3433 and 2932 1/cm.

3.3 Characterization of Pore Using Gas Sorption Analysis

The results of *Gas Sorption Analyzer* showed that chitosan has average pore radius larger than the fly ash and fly ash-chitosan composite although the total pore volume is smaller and it means that pore size of chitosan is greater than the fly ash and fly ash-chitosan composite. Otherwise, chitosan surface area is smaller than the fly ash and fly ash-chitosan composite. After activated and composited into adsorbent, there is an increase in the surface area and total pore volume from adsorbent composite. Adsorbent composite of FA-3 has the widest surface area and greatest total pore volume, i.e. 30.97 m²/g and 4.54 cc/g respectively and the smallest average pore radius for 29.31 Å.

4. Conclusion

The manufacture of adsorbent fly ash-chitosan composite pellets has been succeeded. Characterization of pores in the adsorbent showed that the adsorbent with the composition of fly ash 3 gram in 20 mL chitosan solution (FA-3) has the widest surface area and greatest total pore volume for 30.97 m²/g and 4.54 cc/g respectively, and the smallest average pore radius for 29.31 Å. Identification of functional groups of fly ash-chitosan composite from infrared spectrophotometer indicate the presence of functional groups that absorb heavy metals such as Si-OH, -NH₃⁺ and Al³⁺ which can be seen at wave number 3433 and 2932 1/cm.

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