

# Synthesis of Mesoporous Silica-Alumina from Lapindo Mud Using Gelatin from Catfish Bone as a Template: Effect of Extracting Temperature on Yield and Characteristic of Gelatin as well as Mesoporous Silica-Alumina

Wega T.<sup>1\*</sup>, Iip I.F.<sup>1</sup>, Muhammad Fajar M.<sup>1</sup>

<sup>1</sup>Department of Chemistry, Faculty of Mathematics and Natural Sciences, Gadjah Mada University, Yogyakarta, 55281, Indonesia

\*corresponding author: e-mail: wegats@ugm.ac.id

## Abstract

Mesoporous silica-alumina was synthesized from silica and alumina extracted from Lapindo mud with gelatin from catfish bone as a template. The bone was refluxed in demineralized water at 60, 70, 80 and 90 °C to extract the gelatin. Gelatin was analyzed by FTIR and SDS-PAGE. The alumina was separated from the mud by reflux method using HCl solution and the silica was separated form mud by reflux method using NaOH solution. The purity of silica and alumina were determined by XRF. The mesoporous silica-alumina was synthesized using SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> from Lapindo mud and the catfish gelatin as a template under hydrothermal method at 100 °C for 24 h and calcined at 500 °C for 5 h and characterized by TEM and N<sub>2</sub> adsorption-desorption. The yield of extracted gelatin at 60, 70, 80 and 90 °C was 4.79%, 6.09%, 8.13% and 12.24%, respectively. The purity of silica and alumina extracted from Lapindo mud were 100% and 89.69%. The synthesized silica-alumina showed mesoporous characters and had pore diameter of 105.14 Å, pore volume of 0.1974 cc/g and BET surface area of 75.105 m<sup>2</sup>/g.

**Keywords:** Gelatin, Catfish bone, Mesoporous silica-alumina, Lapindo mud

## 1. Introduction

As well known, microporous zeolite has long been used in numerous applications in various fields, for example catalysts, adsorbents and others (Song *et al.*, 2009; Upare *et al.*, 2017; Wijaya *et al.*, 2013; Zang *et al.*, 2016). However, it later emerged the need of porous material with a larger pore size for example materials as catalyst supports in the process of cracking the large hydrocarbon molecules and large molecules adsorbent. This makes the study of mesoporous materials developed rapidly in recent years. One of mesoporous material widely studied is a mesoporous silica alumina. Mesoporous silica alumina was widely studied because it has an optimum pore size, large surface area and the presence of acid sites of Al atoms in its structure (Al-Zeghayer *et al.*, 2005; Cai *et al.*, 2011; Ifah *et al.*, 2016). In the process of synthesis, mesoporous silica alumina usually require a template to direct the formation of mesoporous and limit the size of pores. Template commonly used in the synthesis of mesoporous silica alumina was CTAB or HMI (Meynen *et al.*, 2009). In

previous studies, we managed to use gelatin extracted from bovine bone as a template in the synthesis of mesoporous silica (Trisunaryanti *et al.*, 2016). Gelatin is known to have a lot of NH groups that can bind with silanol groups on the mesoporous silica material (Trisunaryanti *et al.*, 2016). However, the use of bovine bone as gelatin source considered ineffective because bovine bone is often used as food ingredients. Therefore, we try to use gelatin extracted from catfish bone in this study. On May 29, 2006, Indonesia was shocked by the mudflow on natural gas drilling site in the Banjar Panji-1 conducted by Lapindo Brantas Inc. Tragedy mudflow black color was followed by explosions in most homes around. The mud gushed as high as 8 meters from ground level and had a hot enough temperature (60 °C). Hot mudflow was expected to issue a slurry with a volume of 100,000 m<sup>3</sup> per day (Abidin *et al.*, 2009; Jalil *et al.*, 2010). Since the advent of the hot mudflow, more people are getting interested to examine the content of this Lapindo mud. The content of the Lapindo mud was SiO<sub>2</sub> (53.40%), Al<sub>2</sub>O<sub>3</sub> (23.80%), Na<sub>2</sub>O (5.59%), Fe<sub>2</sub>O<sub>3</sub> (5.47%), Cl (2.89%), MgO (2.62%), CaO (2.40%), K<sub>2</sub>O (1.63%), SO<sub>3</sub> (1.24%) and TiO<sub>2</sub> (0.63%) (Jalil *et al.*, 2010). The results indicate that the main content of the Lapindo mud was an element of Si, Al and Fe. The above results indicate the potential Lapindo mud as a source of silica and alumina that can be used in the synthesis of mesoporous silica alumina. This made researchers interested in making mesoporous silica alumina material using Lapindo mud as a source of silica and alumina and the gelatin from catfish bone as template.

## 2. Experimental

### 2.1 Materials

Catfish bone was collected from Tegalrejo Village, Central Java, Indonesia. Lapindo mud was collected from Sidoarjo Regency, East Java, Indonesia. Sodium hydroxide purchased from VWR Chemicals (USA), asetic acid was purchased from E.Merck (Germany) and hydrochloric acid was purchased from Mallinckrodt (Ireland).

### 2.2 Extraction of gelatin from catfish bone

Extraction of gelatin followed the previous work (Trisunaryanti *et al.*, 2016; Ulfa *et al.*, 2014; Ulfa *et al.*, 2014; Ulfa *et al.*, 2016). The catfish bone was cleaned and washed with demineralized water at 40 °C. The bone was

soaked in 0.1 M NaOH solution (1:5, w/v) for 24 h. After 24 h, the bone was washed with demineralized water until the pH of water become neutral. The bone was then mixed with 1 M HCl solution (1:5, w/v) for 0.5 h. The acid pretreatment was repeated once again. After 1 h, the bone was washed with demineralized water until pH of water become 5. The pretreated catfish bone was refluxed in demineralized water (1:4, w/v) for 5 h at 60, 70, 80 and 90 °C. The mixture was filtered and the filtrate was dried at 50 °C. The gelatin was analyzed by FTIR and SDS-PAGE.

### 2.3 Extraction of alumina from lapindo mud

Extraction of silica and alumina from lapindo mud was carried out according to Dong *et al* (2014) with slight modification. The lapindo mud was dried and sieved to 100 mesh. The mud was refluxed in 6 M HCl solution (1:4, w/v) under stirring at 90 °C for 5 h. The mixture was filtered and the residu was washed with demineralized water and dried at 100 °C for 1 h. The residu was kept for extraction of silica. The filtrate was added with 6 M NaOH solution (2:3, v/v) and the mixture was filtered for separating Fe<sup>3+</sup>. Alumina was precipitated by flowing CO<sub>2</sub> gas into the filtrate. The mixture was then filtered. The solid was washed with demineralized water and dried at 50 °C over a night. The alumina was calcined at 500 °C for 5 h. The purity of alumina was determined by XRF.

### 2.4 Extraction of silica from lapindo mud

The residu of mud from alumina extraction was refluxed in 6 M NaOH solution (1:4, w/v) under stirring at 90 °C for 5 h. The mixture was filtered and the filtrate was added with 2 M HCl solution until the pH of filtrate become 8. The mixture was filtered and the solid was washed with demineralized water. The obtained silica was dried at 100 °C for 24 h. The purity of alumina was determined by XRF.

### 2.5 Synthesis of mesoporous silica-alumina

The synthesis of mesoporous silica-alumina was carried out using hydrothermal method. 5 g gelatin was dissolved in 82 g demineralized water at 40 °C and stirred for 30 min. The gelatin solution was then added with 0.204 g alumina extracted from lapindo mud and stirred for 30 min. On the other glass container, 6 g silica was added with 80 g demineralized water and stirred for 30 min. The mixture of silica was then added with 1 M CH<sub>3</sub>COOH solution until the pH of mixture become 4. The mixture of silica was added into mixture of gelatin and alumina and stirred for 24 h. The formed gel solution was moved into autoclave and hydrothermally treated at 100 °C for 24 h. The final product was filtered, washed with demineralized water, dried at 50 °C over a night and calcined at 500 °C for 5 h for removing of gelatin. The material was analyzed by N<sub>2</sub> adsorption-desorption and TEM.

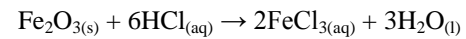
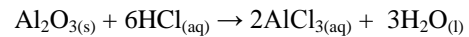
## 3. Result and discussion

### 3.1. Characterization of catfish bone gelatin

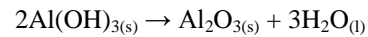
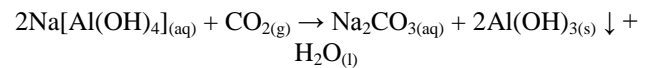
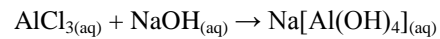
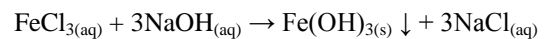
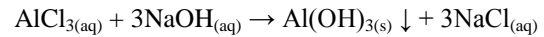
Gelatin extracted from catfish bone was physically the same as the commercial gelatin. Gelatin extracted from catfish bone had a light brown color and easy to absorb water. **Table 1** shows the yield of gelatin extracted from catfish bone at 60, 70, 80 and 90 °C. Amount of gelatin increased as the hydrolysis temperature increased. These results indicate that the increase in temperature could make the collagen hydrolysis reaction into gelatin faster. In addition, the increase in temperature also made the increasing of gelatin solubility in water. Both of these made yield of gelatin at a hydrolysis temperature of 90 °C higher than others.

### 3.2. Extraction of silica and alumina from lapindo mud

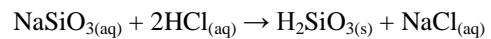
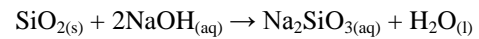
By acid leaching, the Si-Al bond of aluminium silicate in the lapindo mud was split. Al<sub>2</sub>O<sub>3</sub> was dissolved, but SiO<sub>2</sub> could not be dissolved. Because of that, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> could be separated by filtration. Al<sub>2</sub>O<sub>3</sub> was mainly concentrated in the filtrate, while SiO<sub>2</sub> remained in the residue (Dong *et al*, 2014).



The filtrate was mainly consist of AlCl<sub>3</sub> and FeCl<sub>3</sub>. For separating Fe<sup>3+</sup>, the filtrate was added with excess NaOH. In addition of NaOH, AlCl<sub>3</sub> and FeCl<sub>3</sub> changed into Al(OH)<sub>3</sub> and Fe(OH)<sub>3</sub> in solid form. However, Al(OH)<sub>3</sub> would dissolved in excess NaOH and became Na[Al(OH)<sub>4</sub>], while Fe(OH)<sub>3</sub> was still remain. In this case, Fe(OH)<sub>3</sub> could be separated by filtration. Al(OH)<sub>3</sub> was precipitated by flowing CO<sub>2</sub> into Na[Al(OH)<sub>4</sub>] solution.

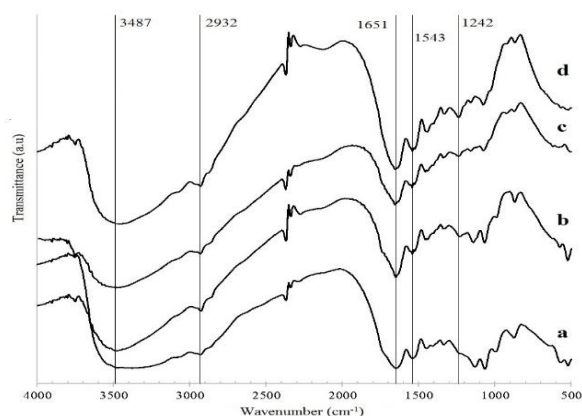


Extraction of SiO<sub>2</sub> used alkaline conditions. SiO<sub>2</sub> reacted with NaOH and produced Na<sub>2</sub>SiO<sub>3</sub>. Adjusting the pH by addition of HCl made SiO<sub>2</sub> precipitated at pH 8 and could be separated by filtration.



**Table 1.** Yield of gelatin at various temperature

Hydrolysis temperature of gelatin (°C)	Yield (%)
60	4.79
70	6.09
80	8.13
90	12.24



**Figure 1.** FTIR spectra of gelatin extracted from catfish bone at (a) 60 (b) 70 (c) 80 and (d) 90 °C

XRF analysis results shown in Table 4 proved that the extraction of silica and alumina conducted in this study had been successful. In addition, the purity of silica and alumina were very high. Purity silica and alumina reached 100% and 89.69% respectively. Figure 1 shows five characteristic FTIR adsorption bands for polypeptide called amide A, B and I-III. Amide A band ( $3600\text{--}3400\text{ cm}^{-1}$ ) arises from the stretching vibrations of NH and OH group. Amide B indicate asymmetric stretching vibration of  $\text{CH}_2$ . Amide I ( $1700\text{--}1600\text{ cm}^{-1}$ ) is mainly due to  $\text{C}=\text{O}$  stretching vibration (about 80%) of the amide group coupled with in-plane NH bending (less than 20%). Amide II ( $157\text{--}1480\text{ cm}^{-1}$ ) derives mainly from in-plane NH bending and CN stretching vibration and show less protein conformational sensitivity compared with amide I, while other amide vibrational bands have less practical use in protein conformational studies. Amide III ( $1240\text{--}670\text{ cm}^{-1}$ ) represented the combination peaks between CN stretching vibration and NH deformation from amide linkages as well as absorptions arising from wagging vibrations from  $\text{CH}_2$  groups from the glycine backbone and proline side-chains (Trisunaryanti *et al*, 2016). Figure 1 also shows the five

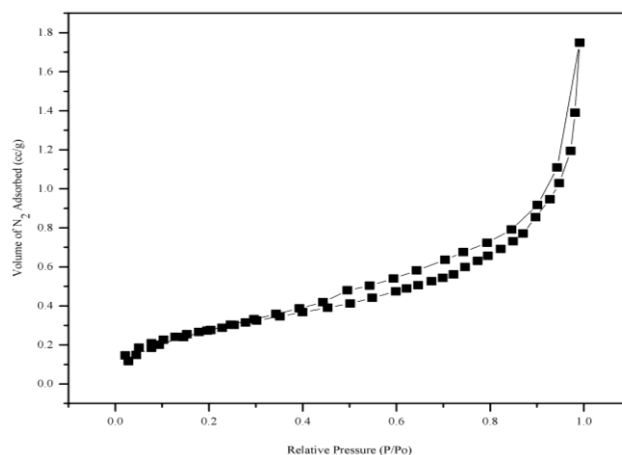
peaks intensity amide functional group of gelatin extracted from catfish bone in this study. The intensity of the absorption peak of the five amide functional groups of gelatin extracted increased as the hydrolysis temperature increased from 60 to 70 and 70 to 80 °C. This result indicated that the number of amide A, B and I-III vibrating increased as the hydrolysis temperature increased. However, the intensity of the five peaks of amide functional groups of gelatin were decreased significantly at 90 °C. This indicated a drastic reduction in the number of vibrating amide so that it could be concluded that the amount of gelatin in the form of a single polypeptide chain also decreased. At a temperature of 90 °C, gelatin shaped single polypeptide chain amide bond can undergo further breakdown into amino acid residues of gelatin (glycine, proline and hydroxyproline). Table 3 shows the molecular weight distribution range gelatin extracted from catfish bone in this study. Gelatin extracted at 60, 70 and 80 °C had the same molecular weight distribution range (12-298 Kda). While gelatin extracted at 90 °C had a molecular weight distribution range 9-298 Kda. However, the molecular weight distribution range of gelatin extracted at 70 and 80 °C were focused on 44-85 Kda and 60-85 Kda. Gelatin extracted at 90 °C had a molecular weight distribution range with a lower limit that was smaller at 9 Kda than others. These data supported the phenomenon of decreasing in the intensity of the peaks of the five amide functional groups of gelatin at 90 °C when compared with gelatin extracted at 80 °C. These results lead to the breaking of the amide bond in gelatin with a single polypeptide chain into an amino acid residue of gelatin (glycine, proline and hydroxyproline). Gelatin is extracted at 80 °C had the second highest yield of 8.1333%, the highest peak intensity of five amide functional groups of gelatin and narrower molecular weight distribution range (12-289 Kda) that was focused on 60-85 Kda. These results made gelatin extracted at 80 °C was better to be used as a template in the synthesis of mesoporous silica alumina.

**Table 3.** Molecular weight distribution of gelatin extracted from catfish bone

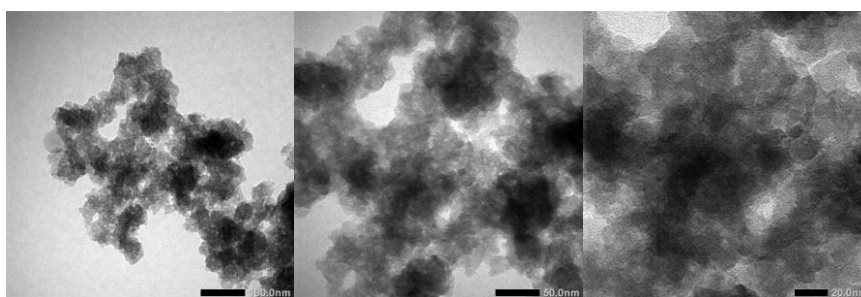
Hydrolysis temperature of gelatin (°C)	Molecular weight range (Kda)
60	12 – 298
70	12 – 298
80	12 – 298
90	9 – 298

**Table 4.** Chemical composition of silica and alumina extracted from lapindo mud

Silica		Alumina	
Element	Quantity	Element	Quantity
Si	100%	Al	89,69%
		Si	5,94%
		Cr	1,24%
		Fe	2,35%



**Figure 2.** N<sub>2</sub> adsorption-desorption of mesoporous silica-alumina



**Figure 3.** TEM micrograph of mesoporous silica alumina

The mesoporous silica-alumina shown the type IV isotherm typical of mesoporous materials. The mesoporous silica-alumina presented average pore diameter of 105.14 Å, total pore volume of 0.1974 cc/g and BET surface area of 75.105 m<sup>2</sup>/g. TEM micrographs of mesoporous silica alumina is shown in Figure 3. Overall, the structure of mesoporous silica- alumina synthesized in this study had wormhole-like pore. The pore size was relatively not uniform. This makes sense considering the gelatin used as template had a wide molecular weight distribution range.

#### 4. Conclusion

Extraction of gelatin from catfish bones using alkaline and acid pretreatment was successful. Molecular weight range gelatin extracted was widening with increasing temperature of hydrolysis. Gelatin is extracted at 80 °C was used as template in the synthesis of mesoporous silica alumina because it had a high yield, highest intensity of five amide functional groups and narrower molecular weight distribution range. Silica and alumina were also successfully extracted from Lapindo mud using acid leaching method. Silica and alumina obtained had a purity of respectively 100% and 89.69%. Catfish bone gelatin, silica and alumina successfully converted into mesoporous silica alumina. TEM micrograph showed that mesoporous silica alumina had wormhole-like mesoporous structure. The mesoporous silica-alumina had pore diameter of

105.14 Å, pore volume of 0.1974 cc/g and BET surface area of 75.105 m<sup>2</sup>/g.

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