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About the Journal

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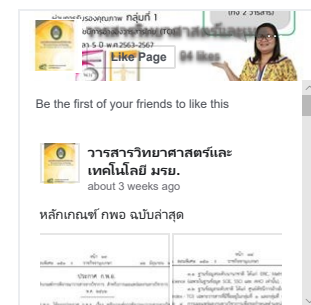
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วารสารวิทยาศาสตร์และเทคโนโลยี มจร. เป็นเอกสารวิชาการ มีวัตถุประสงค์เพื่อส่งเสริม และเผยแพร่ผลงานทางวิชาการที่มีคุณภาพ ในลักษณะของบทความวิชาการ (Academic Article) บทความวิจัย (Research article) บทความปริทัศน์ (Review article) และบทวิจารณ์หนังสือ (Book Review) ในสาขาวิทยาศาสตร์และเทคโนโลยี ได้แก่ วิทยาศาสตร์ เกษตรศาสตร์ วิศวกรรมศาสตร์ และสาขาอื่นๆ ที่เกี่ยวข้อง จัดพิมพ์และออกเผยแพร่ปีละ 2 ฉบับ (ฉบับแรกประจำเดือนมกราคมถึงเดือนมิถุนายน และฉบับที่สองประจำเดือนกรกฎาคมถึงเดือนธันวาคม)

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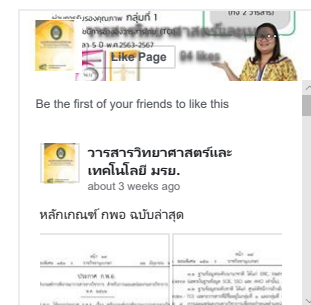
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The Modification of Silica Surfaceseparated from Overflowing Mud in Lapindo Indonesia as Cation Exchange Adsorbent

การปรับเปลี่ยนพื้นผิวของซิลิกาที่แยกจากโคลนทะเล้งในเมืองลาพินโด ประเทศอินโดนีเซีย ให้เป็นตัวดูดซับความสามารถในการแลกเปลี่ยน ประจุบวก

J. Ikhsan^{*}, S. Sulastri and E. Priyambodo

¹The Department of Chemistry Education, Faculty of Mathematics and Natural Sciences,
State University of Yogyakarta, Karangmalang, Yogyakarta 55281, Indonesia

Abstract

The mud overflowing in Lapindo Indonesia was a major disaster for lots of people. In fact, the mud contains silica that is very potential as adsorbents. This research studied the preparation of cation exchange adsorbent from the Lapindo mud-separated silica and the measurement of cation exchange capacity of the adsorbent. The preparation was done by reacting the silica with 3-(Trimethoxysilyl)-1-propanethiol, and the result was oxidized to produce silica whose surface was saturated by sulfonate functional groups. Each step of the preparation was accomplished by spectroscopic analysis of FTIR, and some of them were completed by XRD and SEM-EDX. The cation exchange capacity of the adsorbent was determined by titration, in which the adsorbent was saturated by Na⁺ ions, and the H⁺ ions released were then titrated by OH⁻ ions. This research succeeded to prepare well cation exchange adsorbent. The cation exchange capacity of the mud, of gel silica, of 3-(Trimethoxysilyl)-1-propanethiol-saturated silica, and of sulfonate-saturated silica were 0, 0.32, 0.84, and 4.15 meq/gram of sorbent, respectively. It can be concluded that the preparation of sulfonate-saturated silica can increase significantly the cation exchange capacity, became 13 times larger than that of silica.

Keywords: Mud, Silica, Sulfonate, Cation exchange capacity.

Corresponding Author, e-mail: jikhsan@uny.ac.id



บทคัดย่อ

ปัญหาโคลนทะเลาะในเมืองลาพินโด ประเทศอินโดนีเซีย นับเป็นภัยพิบัติครั้งใหญ่ที่สร้างผลกระทบต่อประชาชนจำนวนมาก ในความจริงแล้วโคลนเหล่านี้มีซิลิกาซึ่งมีศักยภาพในการใช้เป็นตัวดูดซับที่ดี งานวิจัยนี้ศึกษาการเตรียมตัวดูดซับการแลกเปลี่ยนประจุบวกจากซิลิกาที่แยกจากโคลนในเมืองลาพินโด และการวัดความสามารถในการแลกเปลี่ยนประจุบวกของตัวดูดซับดังกล่าว โดยนำซิลิกามาทำปฏิกิริยากับ 3-(Trimethoxysilyl)-1-propanethiol และนำสารที่ได้มาออกซิไดซ์เพื่อผลิตซิลิกาที่มีพื้นผิวที่อิมมัวด้วยหมู่ฟังก์ชันซิลโฟเนต รวมถึงใช้ FTIR ประกอบกับ XRD และ SEM-EDX ในการวิเคราะห์สเปกตรัมในแต่ละขั้นตอนของการเตรียมความพร้อมดังกล่าว ความสามารถในการแลกเปลี่ยนประจุบวกของตัวดูดซับถูกวัดโดยการไตเตรท โดยตัวดูดซับจะถูกทำให้อิมมัวด้วยโซเดียมไอออน (Na^+) ซึ่งไฮโดรเจนไอออน (H^+) ที่ถูกปล่อยออกมาจะถูกนำมาไตเตรทด้วยไฮดรอกไซด์ไอออน (OH^-) งานวิจัยนี้ได้เตรียมตัวดูดซับการแลกเปลี่ยนประจุบวกได้สำเร็จ ซึ่งความสามารถในการแลกเปลี่ยนประจุบวกของโคลน ซิลิกาเจล ซิลิกาที่อิมมัวด้วย 3-(Trimethoxysilyl)-1-propanethiol และซิลิกาที่อิมมัวด้วยซิลโฟเนตมีค่า 0 0.32 0.84 และ 4.15 มิลลิอิควิวเลนต่อตัวดูดซับหนึ่งกรัม (meq/gram) ตามลำดับ สรุปได้ว่า การเตรียมซิลิกาที่อิมมัวด้วยซิลโฟเนตสามารถเพิ่มความสามารถในการแลกเปลี่ยนประจุบวกได้อย่างมีนัยสำคัญ และสูงกว่าความสามารถในการแลกเปลี่ยนประจุบวกของซิลิกาที่ 13 เท่า

คำสำคัญ : โคลน ซิลิกา ซิลโฟเนต ความสามารถในการแลกเปลี่ยนประจุบวก

Introduction

The mud that has been flooding in East Java, Indonesia since 8 years ago was disaster for lots people in that area. In fact, the mud can be used potentially for the need of people, such as adsorbent since the mud contain significant amount of silica and alumina (Amin & Irawan, 2010). It is known that good adsorbents are commonly soil colloid such as aluminosilicate containing aluminium and silica.

This study investigated the separation of silica from the Lapindo mud and the preparation of surfaces of the silica as cation exchange adsorbent which ought to increase its capacity to bind cations via the exchange reactions. Silica contains many functional groups of hydroxyl $-\text{OH}$ (Sposito, 1984), whose hydrogen can be exchanged by other cations. The exchange can be useful for the impregnation of



the cations of micronutrients needed by plants through strong chemisorption and so the bound cations are released slowly when they are dissolved into water. This principle may be suitable to be used for the production of slow release fertilizer. The preparation of cation exchange adsorbent with the materials from Lapindo mud was started by the separation of silica. Previous investigations separated the silica from rice husk (Savita & Proctor 1997, Kalapathy et al., 2000). The husk was soaked into HCl, filtered and rinsed until neutral. The result was then reacted with NaOH solution and heated until it boiled, then filtered. The solution from the filtration was Na_2SiO_3 , following the reaction (1):



Na_2SiO_3 become H_2SiO_3 when it was reacted with acid (reaction (2)), and overcome the polymerization reaction (Figure 1).

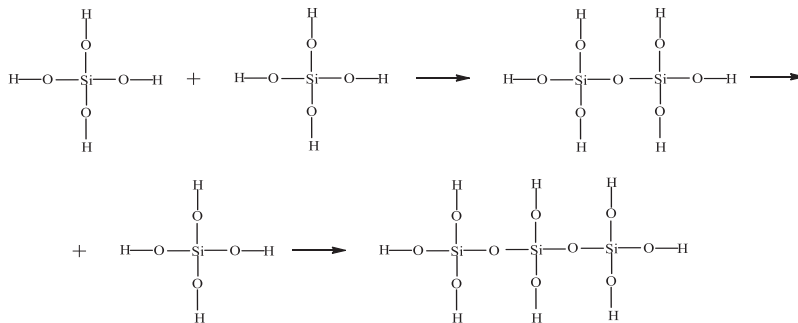


Figure 1 Reaction of polymerization of H_2SiO_3

The modification of the surface of silica occurred by changing $-\text{Si}-\text{OH}$ become $-\text{Si}-\text{OM}$, where M was simple species except hydrogen (El Shafei, 2000). There were two types of compounds can be used to modify silica; they were organic-functionalization and inorganic-functionalization compounds (Jal et al., 2004). The first one was for modifier compounds with organic functional groups, and the later one was for the modifier involving inorganic compounds or metal oxide. The modification technique can be conducted by salinization or sol-gel process. Salinization process was conducted onto gel silica whose medium was not water.

For instance, previous researches modified silica by use of 3-(trimethoxysilyl)-1-propanethiol and aerosol in toluene medium (Tertyth & Yanishpolski, 2000, Shylesh *et al.* 2004). Sol-gel process was conducted to precursor silica. Modifier substituting silanol groups were added to precursor silica in gel formation process, which resulted in compound containing siloxane group, silanol group, and modified silica represented by $-S-OM$.

The preparation of silica from Lapindo mud become a cation exchange adsorbent was done through several steps, but one of the most important steps are the reaction of the silica with modifier of 3-(trimethoxysilyl)-1-propanethiol as conducted by some previous researchers (Margolese *et al.*, 2000, Serano *et al.*, 2003, Morales *et al.*, 2008), following the reaction as given on Figure 2.

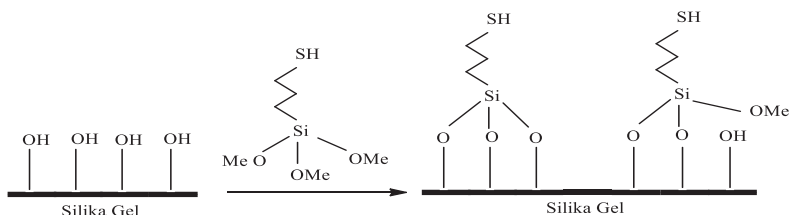


Figure 2 Reaction of silica and modifier of 3-(trimethoxysilyl)-1-propanethiol

One of cation exchange adsorbent is the adsorbent with sulfonate functional groups. It can be provided by oxidizing mercapto-functional groups ($-SH$) of the adsorbent. The oxidation brings about silica which binds sulfonate functional groups ($-SO_3H$). The proton of the groups can be exchanged by cations, with the reaction as illustrated by Figure 3.

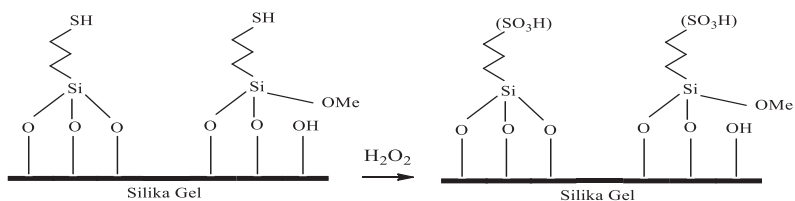


Figure 3 Cation exchange reaction on sulfonated-silica



Investigation about cation adsorption by the surface of aluminosilicate via cation exchange showed that montmorillonite had different cation exchange capacities (CEC) interacted different amount of Zn^{2+} , but when the CEC of the adsorbents were made the same, it lead to the same amount of Zn^{2+} adsorption (Ikhsan *et. al.* 2005a). Therefore, CEC can be used as the indicator of sorbent capacity to bind certain amount of cations interacted by cation exchange.

Objectives

The objectives of the research were to separate silica from Lapindo mud (SG), to modify the surface of the silica to be cation exchange adsorbent (SCE), and to study the cation exchange capacity (CEC) of the adsorbents.

Materials and Methods

Lapindo mud

The samples were Lapindo mud that has been overflowing and destroying some villages and a city in East Java Indonesia since 2006. The mud sample was taken from Jatirejo, Sidoarjo, East Java, Indonesia, that is \pm 500 meters in distance from the source of the flow.

Reagents

Water for all experiments was free of minerals. All other reagents were from Merck of analytical reagent grade.

Experimental Methods

Preparation of sodium silicate

Lapindo mud samples were washed by soaking them into HCl solution, and the resulted residues were dried, grinded, and sieved. The washed mud was reacted with NaOH solution in a fluoro ethylene vessel, and boiled for 1h. The boiled samples were left to reach room temperature, and filtered using Buchner. The filtrate from the filter was sodium silicate.



The preparation of gel silica (SG)

Into (Na_2SiO_3) solution was added HCl drop-by-drop while stirred until the gel was formed and the pH reached 7. The solution was left over night, added boiled water, stirred for 15 mins., and washed for free chloride ions. The residue was then dried in an oven at 70 °C until the mass was constant, and gel silica (SG) was obtained.

The modification of silica surfaces with 3-(trimethoxysilyl)-1-propanethiol

The step was similar to the preparation of SG, but the reagent that was added Na_2SiO_3 solution was 3-(trimethoxysilyl)-1-propanethiol instead of HCl. From this preparation the residues obtained were silica containing mercapto functional groups (-SH) on its surfaces. This sorbent was then called mercapto-modified-silica sorbent (SMM).

The preparation of cation exchange adsorbent

The sorbent was prepared by oxidating the mercapto functional groups (-SH) on the surfaces of silica using HNO_3 solution. The oxidation reaction was conducted and stirred for 1 h. When the reaction was completed, the result was filtered with Buchner and washed until pH 4.0 with water. The residues from the filtration were cation exchange adsorbent (SCE).

The determination of cation exchange capacity of the SCE sorbent

The SCE sorbent was saturated by Na^+ ions to replace H^+ ions from sulfonate ($-\text{SO}_3\text{H}$) bound by the surfaces of silica. The H^+ ions replaced and released by the surfaces were titrated by OH^- ions with universal indicator, and it represented the cation exchange capacity of the surfaces of the sorbent.

Results

Lapindo mud sample

The Lapindo mud sample before and after heating of 700 °C for 3 hrs were measured by XRD. The result was given in Figure 4.

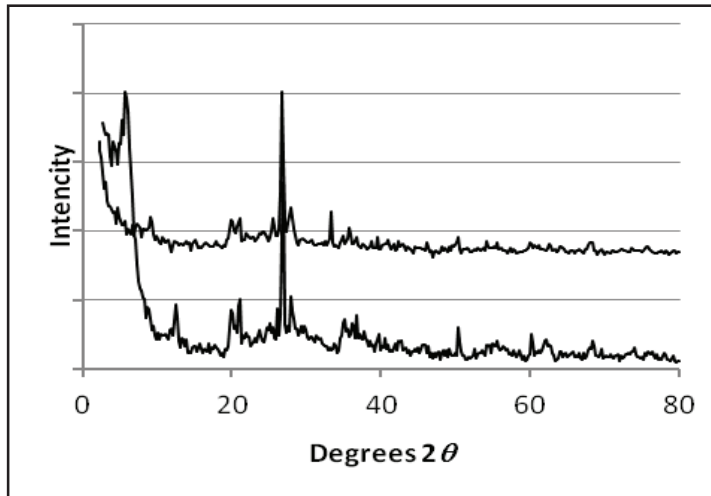


Figure 4 Diffractogram of washed Lapindo mud before and after 3hrs heating at 700 °C: (top line) was washed Lapindo.

The chemical contents of Lapindo mud were measured using *Energy Dispersive X-Ray Spectroscopy* (EDX), with the result was given in Figure 5. The result showed that Lapindo mud contained 11.11% mass of Si.

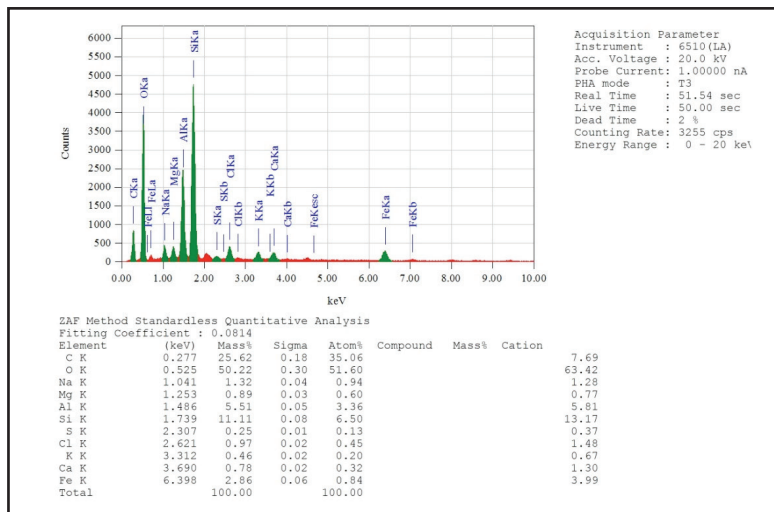


Figure 5 EDX of washed Lapindo mud

Modification of Silica from Lapindo mud

The preparation of cation exchange adsorbent (SCE) was done through four steps of experiments. The steps were (a) preparation of SG from Lapindo mud, (b)

modification gel silica by 3-(trimethoxysilyl)-1-propanethiol, and (d) the preparation of silica to be SCE. To confirm the results of synthesis as expected, Fourier Transform Infrared Spectrophotometry (FTIR) and Scanning Electron Microscope Energy Dispersive X-Ray Spectroscopy (SEM-EDX) measurements were done to the result of each step.

FTIR spectrogram of SG, SMM, and SCE were depicted in Figure 6. There are few differences of wavelength shift and new peaks amongst the spectrograms. SEM-EDX measurements for SG and SCE were given by Figures 7 and 8 with 1000 times zoom out.

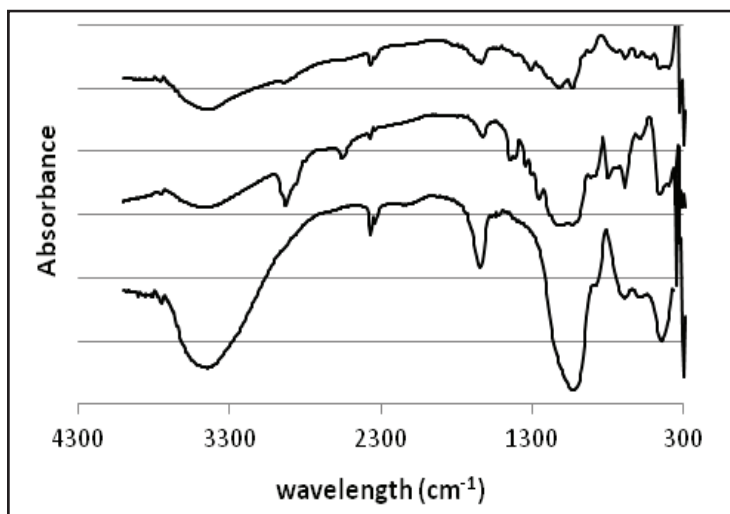


Figure 6 FTIR Spectrogram on the preparation of (bottom) SG, (middle) SMM, and (top) SCE

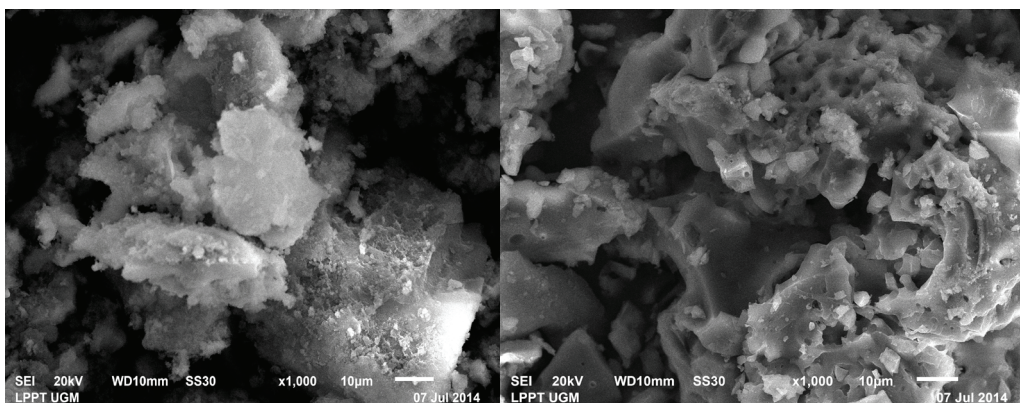


Figure 7 (left) SEM-EDX of SG and **Figure 8** (right) SEM-EDX of SCE

Measurement of Cation Exchange Capacity (CEC)

The CECs of Lapindo mud, SG, SMM, and SCE were measured by titration. Each adsorbent was saturated by NaOH solution. H⁺ ions that were released by the surface of adsorbent were titrated by NaOH solution. The results of the analysis were listed on Table 1.

Table 1 CEC of adsorbent

No	Adsorbent	CEC (mmole/gram)
1.	Lapindo mud	0.00
2.	SG	0.32
3.	SMM	0.84
4.	SCE	4.15

Discussion

The preparation of gel silica from Lapindo mud

Lapindo mud contained silica in significant amount of 11.11% as measured by EDX (Figure 5). The surface of silica that was separated from the mud was able to be modified using sol-gel process. The silica was amorphous as shown by Figure 4, on which typical 2θ of silica shifted from 17 Å to 15 Å after the heating at 700 °C, indicating the shift of the structure of silica.

Gel silica was prepared from Na₂SiO₃ solution by reacting washed Lapindo mud and NaOH solution following the reaction (3). The mechanism of the reaction was given by Figure 9.



The yield obtained from this study was 25 mL Na₂SiO₃/g Lapindo mud.

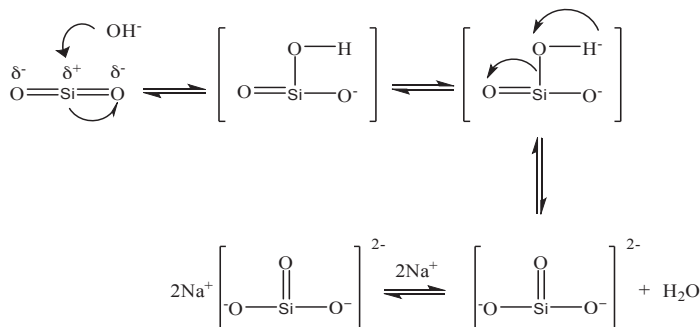


Figure 9 Reaction mechanisms on the formation of Na₂SiO₃ solution from silica



3-(trimethoxysilyl)-1-propanethiol compound. This can occur since protonated oxygen of methoxy group resulted in positive polarization of Si that bound it, and therefore it was easier to be attacked by negative charged species, silicate anion, SiO^- , and formed siloxane species by releasing methanol. The reaction occurred continuously because of the availability of methoxy groups on 3-(trimethoxysilyl)-1-propanethiol, that was ready to bind silicate anion. The mechanism can be illustrated by Figure 11.

This study found the yield of SMM of 1.054 g SMM/g Lapindo mud.

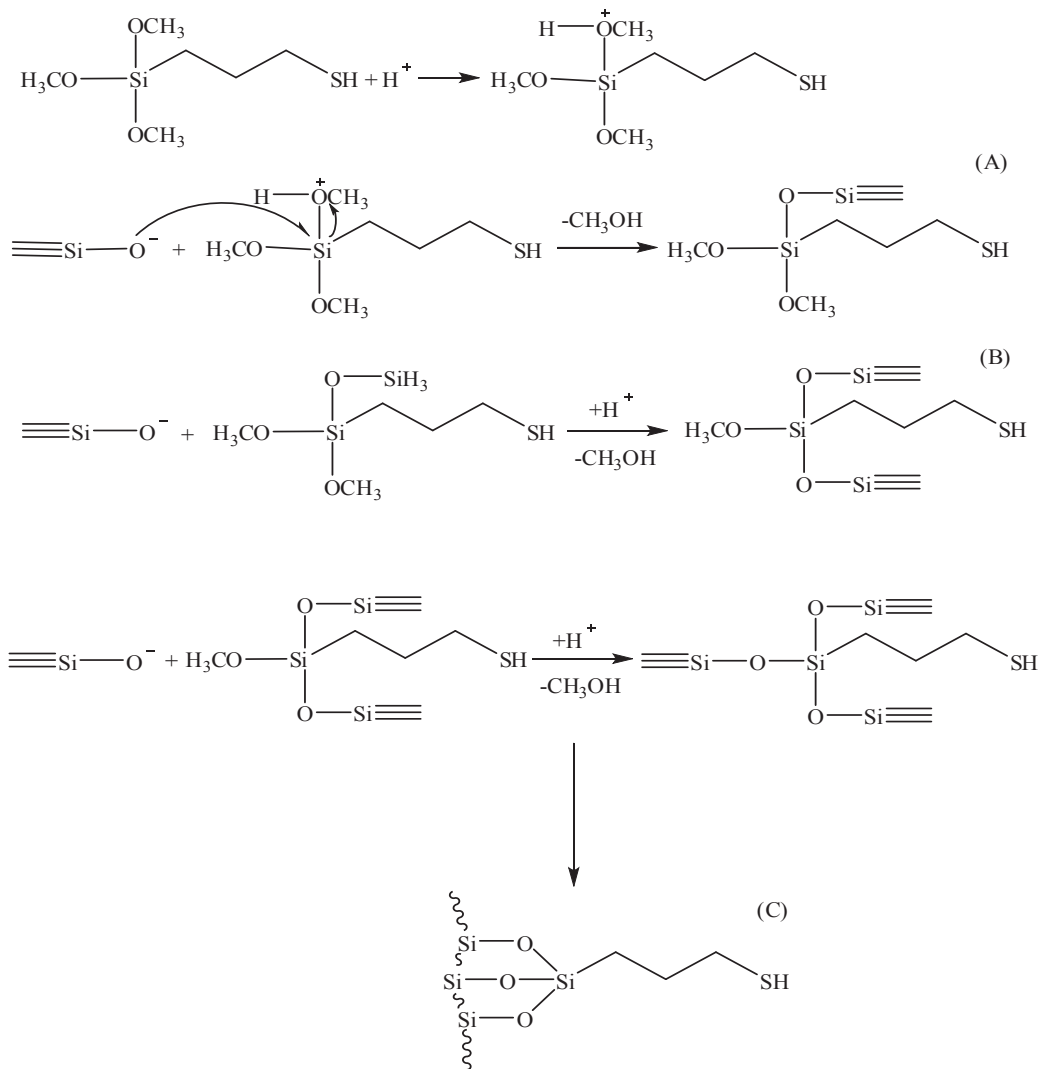


Figure 11 Reaction mechanism on the formation of SMM

The preparation of SCE

The SCE was prepared by oxidizing SMM. The oxidator was HNO_3 65% solution. Side product on the oxidation was NO_2 gas, with the reaction mechanism given in Figure 12. The yield obtained from this study was 0.00751 g SCE per gram Lapindo mud.

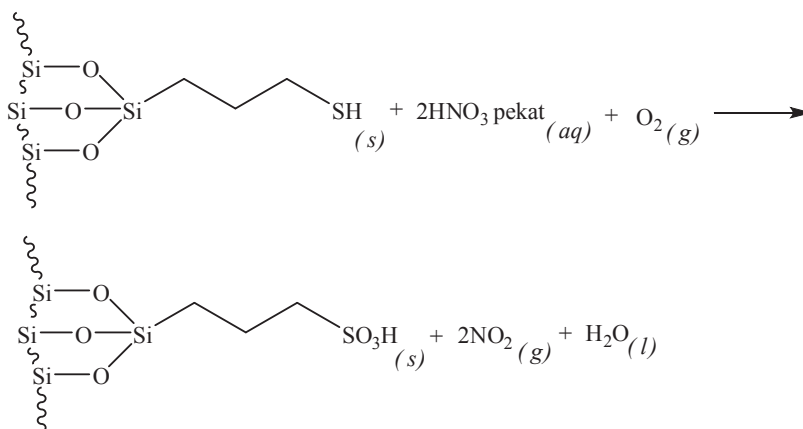


Figure 12 Oxidation reaction on the formation of SCE

Spectroscopic Analysis on modification process

Spectroscopic analysis was done in the modification process including the preparation of gel silica, SMM, and SCE. Synthesis of gel silica from the Lapindo mud was confirmed by the typical group of silanol as shown in the Table 2.

Table 2 FTIR for SG and SMM

No.	SG	Type of vibration	SMM
	Wavelength (cm^{-1})		Wavelength (cm^{-1})
1.	3448.72	Stretching vibration -OH of Si-OH	3448.72
2.	1643.35	Bending vibration of -OH dari Si-OH	1627.92
3.	1026.13	Internal asymmetric stretching vibration Si-O of Si-O-Si	1033.85



No.	SG	Type of vibration	SMM
	Wavelength (cm ⁻¹)		Wavelength (cm ⁻¹)
4.	894.97	external symmetric	802.39
		stretching vibration Si-O of Si-O-Si	
5.	447.49	Bending vibration Si-O of sharp bands Si-O-Si	
	---	Vibration of C-O-C	1442.75
	---	Stretching vibration of -CH	2931.80
	---	Stretching vibration of C-S	694.37
	---	Stretching vibration of -SH	2553.75

The success of synthesis of SMM can be indicated by FTIR spectrogram on the availability of -CH group from propyl chain, -SH, mercapto groups, and C-O-C8. FTIR measurement in this study has shown all the groups as listed in Table 2. The groups of -CH was shown by stretching vibration on wavelength of 2970 cm⁻¹, 2931,80 cm⁻¹ and 2873cm⁻¹. The group of mercapto-SH was shown generally by weak peaks in the wavelength between 2600-2450 cm⁻¹, and this study found the -SH groups were indicated by stretching vibration in the wavelength of 2580 cm⁻¹ and 2569,18 cm⁻¹. While vibration of C-O-C appeared in the wavelengths of 1375 cm⁻¹ and 1456 cm⁻¹.

Previous researches stated that sulfonated silica to which it was called SCE in this study was indicated by peak at wavelength of 1028cm⁻¹, which was the peak of sulfuric acid, and by C-S stretching vibration at wavelength of 1095-1085cm⁻¹, and by asymmetric stretching peak C-S at 960- 950 cm⁻¹. Stretching S=O at wavelengths of 1028, 1254 and 1084 cm⁻¹ cannot be separated from wide and strong peak of siloxane because they were overlapping at similar areas of wave bands (Margolese et al., 2000, Oh et al., 2006). Main indicator of SCE formation was disappearance of -SH groups at wavelength 2500 cm⁻¹ indicating the success of sulphonation reaction whose -SH groups changed into -SO₃H functional groups. The formation SCE was also indicated by the appearance of broad bands and



relative increase of frequency at wavelength areas $3400\text{-}3200\text{ cm}^{-1}$ which was suitable to the absorbance of -OH from sulfonate groups. Weak absorbance of C-H or methylene groups at 2932 cm^{-1} also support the formation of SCE. The formation of SCE in this study was also indicated well by the shift of absorbance at wavelength area of 2553.75 cm^{-1} , which was the area of -SH group vibration, and indicated by the increase of frequency from 3441.01 cm^{-1} to 16.624 cm^{-1} as the absorbance of -OH from sulfonate groups. This study also showed the absorbance of -OH group at wavelength of 3448.72 cm^{-1} with the intensity of 3.193. Weak absorbance of C-H or the methylene appeared at 2939.52 cm^{-1} .

SEM analysis showed visualization of the surface in detail so the surface of each adsorbent SG, SMM, and SCE can be compared visually. From the Figures 7 and 8, SCE seemed to have more pores compared to the others. The amount of pores on surface might affect significantly to the areas of surfaces which were significantly influence surface adsorption behavior because higher surface areas had more active sites and higher affinity to the adsorbate (Ikhsan et al., 2005b).

Light intensity shown in the pictures from SEM might indicate the mass of molecules of the samples. Figure 7 and 8 showed that SCE had more bright areas than the others, indicating that SCE contained more functional groups than the others.

While EDX showed the amount of silica in the adsorbents of Lapindo mud, SG, and SCE as it is given by Figures 5, 7 and 8. The analysis showed that 5.05% Sulphur were available in the sample of SCE, meaning that SCE contained sulfonate groups. Binding the sulphur from sulfonate groups was followed by the other elements' bond, such as oxygen and carbon. The availability of carbon indicated that organic compound was bound by surfaces of silica. But, the percentages of silica in SCE (6.90%) was less much than that in SMM (22.40%) which resulted from the availability of other atoms bound by the surfaces following the interaction of sulphur atom. Average mass of O atoms was higher than Si, and the mass ratio of Si:O in SCE and in SG was about 12:2 and 3:1 respectively. It can be stated that the mass of O in SCE was 6 times higher than Si, but it was only twice higher in SG. Since atom O in sulfonate groups play significant role in the cation exchange reaction on adsorbent surfaces, the modification can increase the cation exchange capacity.

Determination of cation exchange capacity of adsorbent

The cation exchange capacity (CEC) of adsorbent was measured to predict the ability of the adsorbent silica to bind cations through cation exchange. The determination of CEC was initiated by saturating each kind of adsorbent by use of Na⁺ ions. The saturation reaction to SCE surfaces could be written as Figure 13.



Figure 13 Saturation reaction of SCE by Na⁺ cation

The concentration of H⁺ ions that were released from sulfonate functional groups of SCE and replaced by Na⁺ ions was measured by neutralization titration using NaOH standard solution with addition of universal indicator. The results of CEC determination were given below.

Lapindo mud < SG < SMM < SCE = 0 < 0,32 < 0,84 < 4,15 mmole/gram adsorbent

SCE had greatest CEC, meaning that SCE released most H⁺ ions which were replaced by Na⁺ ions. From this study, CEC of SCE was 13 times greater than that of SG and 5 times greater than SMM.

Conclusion

Lapindo mud contained silica that can be separated and transformed into gel silica. The gel silica from Lapindo mud can be modified to be cation exchange adsorbent. Cation exchange capacity of sulphate-modified silica or cation exchange adsorbent was 4.15 mmole/g adsorbent, or 13 times greater than that of gel silica.

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