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Synthesis of Disulfonato-Silica Hybrid from Rice Husk Ash

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***Abstract*—Disulfonato-silica hybrid (DSSH) has been synthesized through sol-gel process using a silica precursor of sodium silicate solution extracted from rice hull ash (RHA), acid monosodium salt 4-amino-5-hydroxy-2,7-naftalena-disulfonato (AHNSNa) as the sulfonato source, and a crosslinking compound of 3-chloropropyltrimethoxysilane. The hybrid caracteristics were evaluated based on the infrared (IR) spectra, x-ray diffraction (XRD) paterns, Scanning Electron Microscope/Energy Dispersive X-ray spectroscopy (SEM/EDX), Brunauer–Emmett–Teller (BET) and Nuclear Magnetic Resonance-Silica (NMR-Si) spectra. Results show that the binding sulfonato has been happened. DSSH obtained has properties of amorphous, mesoporous size, and the future can be used as an adsorbent. Mainly used adsorbent for metal ions adsorb in accordance with the sulfonato group.**

***Index Terms*—disulfonato silica hybrid, rice husk ash, sol-gel**

I. INTRODUCTION

Indonesia is one of agricultural countries producing about 50 million tons of rice annual. That amount of rice may produce about 3 tons of rice husk ash (RHA) and so far has not been used optimally. The major component of RHA is amorphous silica (above 86-97%); therefore it is potency to be used as the silica source in the synthesis of silica-based materials [1].

Disulfonato-silica hybrid (DSSH) is a hybrid product of silica and organic compounds containing sulfonato groups. The application of DSSH has been reported by Azmiyawati *et al.* [2] for adsorption of Mg (II), Cd(II), and Ni(II). From the study was concluded that the adsorption capacity of the hybrid for Mg (II) is higher than Cd (II) and Ni (II). Another applications have been reported for catalyst [3]-[7], ion exchange and ion transport [8]. Synthesis of DSSH may be carried through two techniques, namely grafting [2]-[6], and sol gel process [7], [8]. One advantage of the synthesis of silica materials via sol-gel process is the possibility to synthesize organic-silica hybrid materials in mild process condition and a low temperature. The attachment of sulfonato groups on silica may be performed through two ways, i.e. by oxidizing the attached thiol groups with hydrogen peroxide [9] and attaching sulfonato groups directly onto the silica. Azmiyawati *et al.* [2] reported synthesis of DSSH through grafting technique using commercial silica gel as the solid support and γ-glycidoxypropyltrimethoxysilane as the connecting bridge with acid monosodium salt 4-amino-5-hydroxy-2, 7-naftalenadisulfonat (AHNSNa) as the sulfonato source.

The paper reports synthesis of DSSH through sol-gel process using silica precursor of sodium silicate solution extracted from RHA, a 3-chloropropyltrimethoxysilane bridge and AHNSNa as the active group source. The structure of DSSH is elusidated based on NMR-Si spectra.

II. EXPERIMENTAL

A. Chemicals

Rice hull ash (RHA) was collected from Jambidan village, Banguntapan, Bantul, Jogjakarta, Indonesia and for extraction of silica was used sodium hydroxide. Chemicals for synthesis of DSSH included 4-amino-5-hydroxy-naphtalene-2,7-disulfonic acid monosodium salt ($C_{10}H_8NNaO_7S_2$) (AHNSNa) as the sulfonato source, 3-chloroprophyltrimethoxy-silane (CPTS), triethylamine ($C_6H_{15}N$), and hydrochloric acid. Sodium bicarbonate solution was used for the solvent of AHNSNa, and diethyl ether, and acetone for washing solvents. All chemicals were of analytical reagent grade (Merck) and used as receipted.

B. Procedure

1) Preparation of silica precursor

The preparation was performed using a procedure reported by Kalapathy *et al.* [10] with litle modification. RHA sample was grounded to obtain powder with the particle size of 106 μm. The powder then was washed by mixing and stirring the sample with 2 M HCl solution for 1 h. The residue was filtered and netralized with distilled water. The washed sample 50 grams was mixed with 500 mL of 1 M NaOH solution and boiled for 2 hours. The resulted slurry was allowed to stand for 24 hours and then filtered. The precipitate obtained was washed again with distilled water and filtered. The filtrate and washing solution were collected to obtain a solution of sodium silicate. The solution was then analyzed with atomic absorbance spectrophotometry (AAS) to determine the content of silica.

2) Synthesis of DSSH

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The synthesis refered to the procedure reported by Azmiyawati *et al.* [11] with litle modification (without reflux process). The first step of synthesis was attachment of sulfonato groups on the CPTS by mixing 50 mL solution of AHNSNa (4.08 %, w/v) in sodium carbonate solution 0.05 M, 4.85 mL triethylamine and 6 mL CPTS added dropwise and constantly stirring for 5 hours. The solution then was added with 100 mL sodium silicate solution (extracted from RHA) and 3 M of HCl solution dropwise; and the suspension was then constantly stired for 24 h at a room temperature (25 ℃) until the gel was formed. This gel was aged for 2 h at 70 ℃, and dried in a vacuum for 24 h. The gel was filtered and the residue was washed with destilled water till free of acid. The gel was dried at 70 ℃ for 2 h to obtain disulfonato-silica hybrid (DSSH).

3) *Characterization*

The amorphous nature and the functional group of the DSSH were evaluated from XRD patterns and FTIR spectra, respectively. The surface topology and porosity (surface area and pore radii) were identified with SEM-EDX and BET techniques, respectively.

III. RESULT AND DISCUSSION

A. *Silica Precursor from RHA*

Sodium silicate solution from extraction of RHA was prepared by heating a suspension of RHA and NaOH solution at high temperature. Silica can be extracted from RHA due to higher solubility at pH above 9 [12]. Therefore, it is necessary to add a strong base to increase the pH. Based on the data obtained from analysis with AAS, the percentage of silica extracted from RHA was approximately 62.61%.

B. *Chemical Structure of DSSH*

The FT-IR spectra of DSSH compared to that of AHNSNa are shown in Fig. 1.

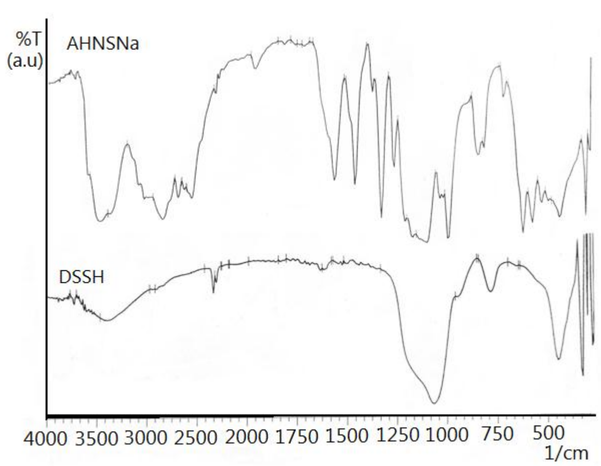


Figure 1. FT-IR spectra of AHNSNa and DSSH

It can be seen from Fig. 1 that absorbance band for DSSH at 972.12 cm^{-1} is broader than that for SG (at 956.69 cm^{-1}). It is probable due to overlaps between of Si-O stretching vibration from Si-OH and symmetric stretching of C-S at around 1,095 ~ 1,085 cm^{-1}. In addition, the two sharp absorbance bands at 2931.80 and 2962.66 cm^{-1} for the DSSH indicate the presence of strectching vibration of C-H from methyl and methylene groups, respectively [13], [14]. Absorption bands for the stretching vibration of S = O characteristic at 1,028, 1,254, and 1,084 cm^{-1} can not be seen because those overlap with broading band of Si-O from siloxane (at around 1,072 cm-1) [3], [15]. Broad absorption band from 3,100 to 3,450 cm-1 is precticted as an overlap peak between the characteristic band for the O-H vibration (3,450 cm-1) and symmetry stretching vibration of N-H (3,270 cm-1) [16].

Sulfonato binding onto the CPTS is confirmed with ^{29}Si-NMR spectra of SG and DSSH presented in Fig. 2.

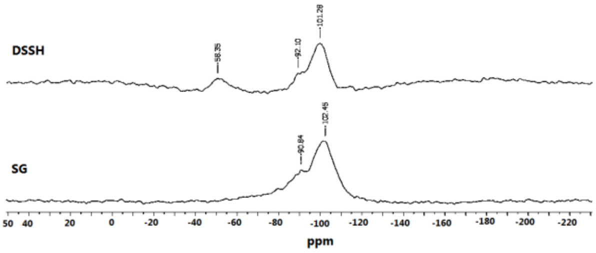
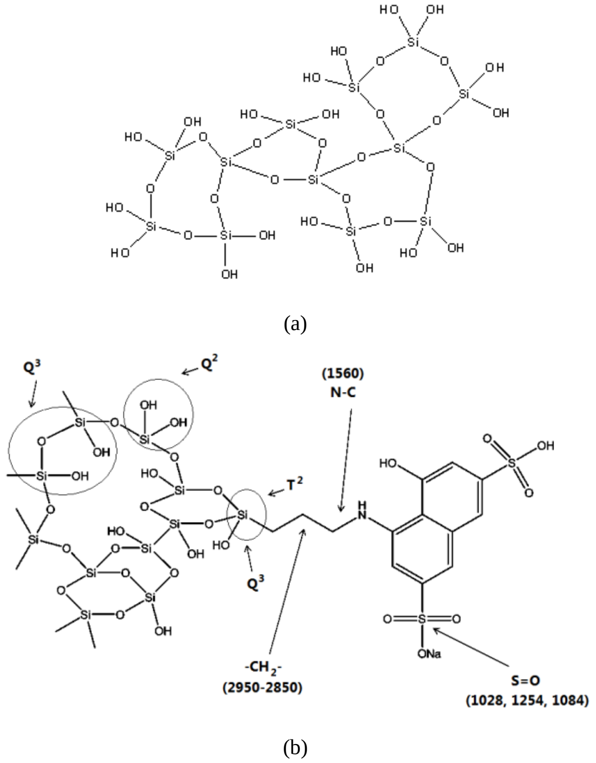


Figure 2. ^{29}Si NMR spectra of SG and DSSH.



(a)

(b)

Figure 3. Proposed structure of (a) silica gel and (b) DSSH synthesized.

DSSH adsorbent analysis using ^{29}Si-NMR propyl-trimethoxysilanedisulfonat aims to confirm the incorporation of silica gel with the framework and determine sheath surface of the silica sulfonato [17]. Determined chemical shifts (in ppm) relative to external TMS standard. Shifts in the spectra of these bands can also identify type of hydroxyl species that exist in the silica gel and HDSS. Two band sharp shift in the spectra observed for SG is -90.84 and -102.45 ppm ppm. Chemical shift at -90.84 ppm from silicon representing SG of Q^2, ie geminal silanol groups:-O_2Si-$(OH)_2$ is characterized by the wide peak between -90 to -91 ppm [9], [17]-[19]. While the chemical shift of -102.45 ppm representing the Q^3 silicon, namely single silanol, -O_3SiOH [17], [18]. At DSSH there are three major bands in the spectra, showing two additional silica chemical environment. The band on chemical shift around -58 ppm is considered to represent the structure of T^2 (-O_2Si (OH) R) and T^3 (-O_3SiR), where R is a propyltrimethoxy-silanesulfonat group [17], [18]. The band presence affects the covalent bridges between groups propyltrimethoxy-silanedisulfonat and silica framework. The second and third peaks appeared in the region around -91 ppm and -101 ppm for the DSSH respectively represent the structure of Q^2 and Q^3 [3], [17]-[21]. Of all these explanations have seen that SG type geminal silanol, which means one Si atom, has two functional groups OH. In depictions of the structure of the silica gel can be estimated as follows Fig. 3.

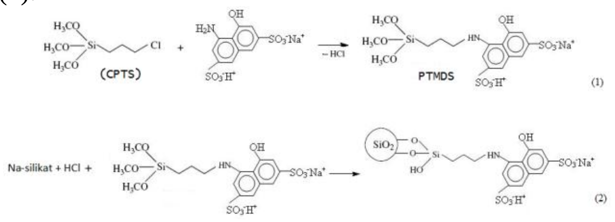
The success of the DSSH synthesis can be observed from the composition of the hybrid material by a destruction and EDX (Table I). If the material contains sulfur, can be expected to emerge successful synthesis. Based on the data obtained by destruction, the sulfur content in DSSH 2825.05 ppm with existing sulfur percent is 2.8733% c/c [11]. The binding sulfur atom is supported by the emergence of other atoms as a supplement, such as the addition of an oxygen atom and a chlorine atom rest of CPTS.

TABLE I. THE AVERAGE MASS (IN % W/W) OF THE ELEMENTS C, O, NA, SI, AND CL IN DSSH BASED ON DATA FROM EDX

Element	Mass of SG (%b/b)		average	Mass of DSSH (%b/b)		average
	I	II		I	II	
C	-	-	-	25,79	28,19	26,99
O	53,15	37,61	45,38	47,42	34,34	40,88
Na	0,29	0,37	0,33	0,30	0,31	0,305
Si	46,56	62,02	54,29	31,36	33,05	32,205
Cl	-	-	-	6,71	7,11	6,91

The presence of carbon indicate that group of organic compounds has been tacked on silica gel. While the presence of chloro group showed a residual CPTS are not substituted by sulfonato groups. The mass percentage of silicon was decrease indicates the weight of the same sample, the number of silicon atoms in the silica gel more than the number of silicon atoms in the DSSH. This suggests that there are other atoms in the DSSH, made possible by the presence of sulfonato group. The average mass of O and Si in comparison to SG and DSSH obtained that contains silica on DSSH is lower than oxygen, on the contrary for SG. The ratio Si:O about 6:5 and 3:4 for SG and DSSH, respectively. The main composition of the SG was Si and O, which dominate the entire network of silica. While the ratio Si/O of DSSH increased, which was the number of oxygen atoms is much higher than silicon atoms. The presence of siloxane and silanol groups has been disturbed by the formation of bonds between Si from silica gel with organic compounds. It is increasingly clear conviction that no additional oxygen atoms of sulfonate groups attached to the silica gel.

The above structure eludation supports the reaction model proposed by Azmiyawati *et al.* [11] that the attachment of AHNSNa onto silica gel occurs in a sequence of two distinct steps. The first step is consisted of binding CTS onto AHNSNa to form disulfonato-aminopropyltrimethoxysilane (PTMDS), Eq. (1), and the second stage, APTMDS reacts with sodium silicate (from RHA) to produce disulfonato-silica hybrid (DSSH), Eq. (2).



C. Topology of DSSH

Fig. 4 present XRD patterns SG and DSSH.

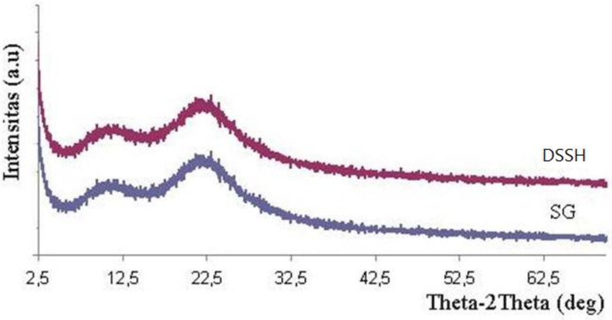
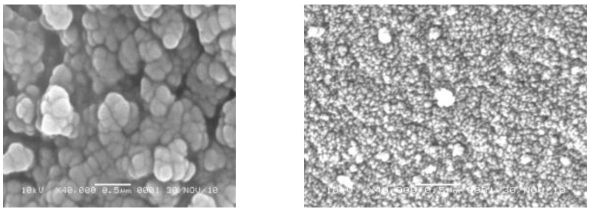


Figure 4. X-ray diffraction patterns of SG and DSSH

Diffractogram shows the pattern of the two materials are very similar, there are two broad absorption band, indicating no crystalline rest of the metal in the initial in both material. According Kalapathy [10], a wide absorption band obtained indicates that the material tends to be amorphous structure.



(a) (b)

Figure 5. Surface topology of (a) SG and (b) DSSH from SEM to 40,000 times magnification.

FT-IR spectra is supported by the data of SEM (Fig. 5) which shows that the surface topology of the SG looks and does not accumulation for globular.

Based on Fig. 5 shows differences in the surface topology of the two materials. SG looks to have larger grains than the DSSH. This size difference may be result in the gel formation of those materials. SG formation occurs continually and grow produce siloxane bonding, leading to formation of larger ball polymer [22]. DSSH formation bonding with a sulfonato compound, formation of siloxane framework stop when Si atom bonds to organic groups. Resulting the growth smaller ball polymer. The increasing number of organic groups, the smaller ball polymer formed.

In addition, the active force and the surface topology, playing a role in the adsorption process are the surface area and the average pore size. Based on the data from nitrogen adsorption isotherms of SG and DSSH calculated with the BET method, a curve of volume versus pressure is expressed in Fig. 6.

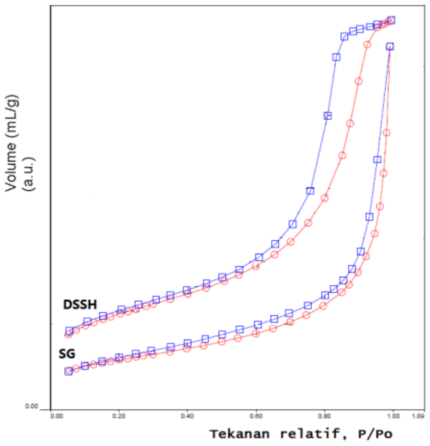


Figure 6. Nitrogen adsorption isotherm of SG and DSSH at 77.350 K

Furthermore, the application of the BJH desorption methods of the nitrogen isotherm at 77.350 K reveals that pore shape is cylindrical and the pore size distribution area is calculated and pointed in Fig. 7. In general, the surface area and pore size for the two materials are shown in Table II.

TABLE II. SURFACE AREA AND MEAN PORE OF SG AND DSSH BASED ON DATA FROM GSA.

	Characterization	SG	DSSH
BET	Surface area (m^2/g)	80.031	417.597
	Total pore volume (cc/g)	2.622×10^{-1}	9.188×10^{-1}
	Pore smaller than (Å)	972.0	971.0
	Average pore radius (Å)	6.553×10^{1}	4.401×10^{1}
BJH	Surface area (m^2/g)	45.841	320.060
	Pore volume (cc/g)	0.243	0.861
	Pore Radius Dv(r) (Å)	15.186	74.898

From the BET pattern (Fig. 6), both SG and DSSH do not show different significantly values, like surface area of SG show smaller than that of DSSH. The result is agreed with the SEM data, in such the poe size of SG is smaller than that of DSSH.

The addition of active groups in sol-gel process leads to the formation of larger pores in DSSH (417.597 m^2 / g) than in SG (80.031 m^2 / g). Larger pore sizes can be formed process of the formation of the silica framework in which binding of the active sites leads to larger pore size by considering the steric hindrance factor. This fact support to the research conducted by Kul, *et al.* [23] that the addition of active groups in sol-gel process enlarge the pore size.

The surface area data does not provide a detailed description of the texture of the materials. Pore and that distribution are required. By applying BJH method [23] for the branching of nitrogen desorption isotherm at 77K with regard pore shape of cylindrical, pore size distribution area can be calculated and includes microporous type (1.5186 nm and 7.4898 nm for SG and DSSH, respectively). Fig. 7 presents the pore size distribution for SG and DSSH.

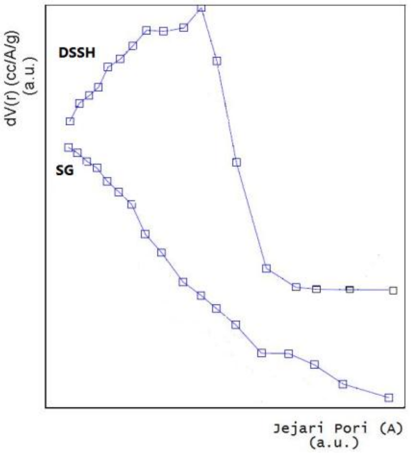


Figure 7. Pore size distribution of SG adsorbent and DSSH.

Similar result based the BJH method, pore size distribution of SG is also smaller (45.841 nm) than that of DSSH (320.060 nm). This difference may arise for the distribution of the sulfonato groups bonded on the pore surface. Another possibility may be explained by the existence of bonds between the sulfonato with SG on the DSSH causing the change of the pore size and pore size distribution.

IV. CONCLUSION

Rice husk ash (RHA) which is agricultural waste can be used as material for the synthesis of silica-based material, such as silica gel and disulfonato silica hybrid (DSSH). The attached of sulfonato group on silica gel will increase the size of the pores in the DSSH. The proposed structure of silica gel synthesis was Q^2 (geminal silanol group) and DSSH was T^2 ($-O_2Si(OH)R$) and T^3 ($-O_3SiR$), where R is a propyltrimethoxysilanesulfonat group.

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