ADSORPTION OF Ca(II), Pb(II) AND Ag(I) ON SULFONATO-SILICA HYBRID PREPARED FROM RICE HULL ASH

Siti Sulastri[1,2], Nuryono[3,*], Indriana Kartini[3], and Eko Sri Kunarti[3]

[1]*Student of Doctorate Program, Department of Chemistry, Faculty of Mathematics and Natural Sciences,*
Universitas Gadjah Mada, Yogyakarta, Indonesia

[2]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, State University of Yogyakarta,*
Karangmalang, Yogyakarta, Indonesia

[3]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada,*
Bls 21, Sekip Utara, Yogyakarta 55281, Indonesia

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ABSTRACT

In this research, adsorption of Ca(II), Pb(II) and Ag(I) in aqueous solution onto sulfonato-silica hybrid (SSH) prepared from rice hull ash (RHA) has been studied. The preparation of SSH adsorbent was carried out by oxidation of mercapto-silica hybrid (MSH) with hydrogen peroxide (H_2O_2) solution 33%. MSH was prepared, via sol-gel process, by adding 3 M hydrochloric acid solution to mixture of sodium silicate (Na_2SiO_3) solution and 3(trimethoxysilyl)-1-propanthiol (MPTS) to reach pH of 7.0. Solution of Na_2SiO_3 was generated from destruction of RHA with sodium hydroxide solution followed with heating at 500 °C for 30 min. The SSH produced was characterized with Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) analyzer, energy dispersive X-ray (EDX) spectroscopy and determination of ion-exchange capacity for sodium ion (Na^+). The adsorption of Ag(I) and Ca(II) were conducted in a batch system in various concentrations for one hour. The adsorbent ion was calculated based on difference of concentrations before and after adsorption process determined using atomic absorbance spectrophotometric (AAS) method. The adsorption character was evaluated using model of isotherm Langmuir and Freundlich adsorption to calculate the capacity, constants and energy of adsorption. Result of characterization by EDX and FTIR showed qualitatively that SSH has been successfully synthesized which were indicated by appearance of characteristic absorbance of functional group namely silanol (Si-OH), siloxane (Si-O-Si), methylene ($-CH_2-$) and disappearance of mercapto group (SH). The XRD data showed amorphous structure of SSH, similar to silica gel (SG) and MSH. The study of adsorption thermodynamics showed that oxidation of MSH into SSH increases the ion-exchange capacity for Na^+ from 0.123 to 0.575 mmol/g. The change in functional group from silanol to mercapto and from mercapto to sulfonato increases the adsorption capacity of Ca(II). However, the capacity order of adsorbents for both ions of Pb(II) and Ag(I) in aqueous solution is MSH > SG > SSH.

Keywords: *adsorption, silica, rice, hybrid, sulfonato*

INTRODUCTION

Rice husk, the predominant byproduct in the milling process of domestic agriculture, is usually either burned or discarded, resulting not only in resource wasting, but also in environmental pollution. As a consequence, especially in the field of material science, it makes sense to prepare rice husk ash (RHA), which is composed of extremely pure amorphous silica extracted from rice husk by a series of process including acid leaching, pyrolysis, and carbon-removing and may be used as silica source for silica based materials.

In recent times, sol-gel methods [1-2] have been considered promising for preparing ultrafine, high purity, single and multicomponent oxide glasses and ceramic composites with the advantages of high purity, lower sintering temperature, a high degree of homogeneity, high yield, small processing time, cost effectiveness and environment friendly [3-4]. Most of the sol-gel methods [5] of preparing LAS glass ceramics are alkoxide based, and therefore, control of hydrolysis and condensation reaction of different metal alkoxide is becoming difficult towards the formation of a common network in which the various metal ions are included. Several attempts have been carried out including matching of hydrolysis rates by chemical modifications with chelating ligands, synthesis of multicomponent alkoxides or partial prehydrolysis of alkoxides [6].

Mechanically stable matrices, such as chemically modified silica gel surfaces, have awakened growing interest because the knowledge acquired with them permits the transfer of some properties found in homogeneous chemistry to the immobilized state. Among the more promising highly developed surfaces

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* Corresponding author. Tel/Fax : +62-274545188
Email address : nuryono_mipa@ugm.ac.id

are the silica-attached organosilanes which are widely used in various technologies [7–9]. These materials enable speciation of trace elements and are useful in solving many problems in nuclear technology, electronics, metallurgy, mining, medicine, agriculture, fisheries and environmental studies. Although a large body of data has been reported about anchored silicas, new applications are continuously demanding further information.

Silica gel is an inorganic support widely used in many chemical processes aiming several scientific and technical applications [10–11]. This support has been increasingly used because its surface offers many advantages due for example, to its thermal and chemical stabilization during the reaction process [12]. It has a high surface area (~500 m^2/g), micropores size in the range 5–500 °A and it can be used at a relatively low cost [13]. Silanol groups on silica gel surface behave like a weak acid ($pKa=9.4$); thus they can interact with polar compounds through both strong hydrogen bonds and dipole–dipole interactions as the well known Brønsted acid [14-15]. Due to the presence of these groups of acids, silica gel is able to adsorb the most varied of chemical species such as cyclic amines [16], amides [17], proteins [18], biologically active phosphates [19], and also for sorption in the separation process of the platinum metal [20], without previous modification with an organomolecule. The modification of the silica gel surface is usually done by using an appropriate molecule denominated silylating agent, and as a consequence, stable covalent bond are formed [10]. However, to increase the chain can be overcome by further reaction, in a subsequent post-reaction step, with a variety of organic functions, for the many desired purposes. Thus, modified silica is widely used in chromatography [10], as support for materials with catalytic properties [11], as sequestration agent of metals [21], for ion-exchange [22], also for contaminants removal from waste effluent streams [23], and for many other purposes.

In previous reports we described the investigations of synthetic schemes aiming at the preparation of organic–inorganic polymer hybrids by using traditional heterogeneous routes [24]; and for the study of adsorption equilibrium processes of the divalent cations cobalt, nickel, and copper from aqueous solution. Homogenous routes using RHA as the silica source for preparation of amino- and mercapto-silica hybrids; and the adsorption study of several metal ions also had been reported [25-26]. The results of the adsorption capacity of the hard divalent clearly showed that amino modified silica tends to adsorb hard base cations in higher amount than mercapto modified silica.

In the present work we investigated the adsorption processes of Ca(II), Ag(I) and Pb(II) in aqueous solution on sulfonato modified silica prepared from rice hull ash as the silica source. The present study aims to evaluate the influence of silica modification with mercapto and sulfonato groups on the adsorption capacity using two isotherm models (Freundlich and Langmuir).

EXPERIMENTAL SECTION

Chemicals

Precursor of sodium silicate (Na_2SiO_3) solution for sol-gel process was prepared from rice hull ash (RHA) using a procedure reported by Nuryono [13]. Sample of RHA was mixed with NaOH solution 2 M and the mixture was mechanically stirred in a hotplate till dry and then was heated at 500 °C for 30 min in a furnace. The residue was dissolved in water to obtain solution of Na_2SiO_3.The reagent grade of 3-(trimethoxysilyl)-propane-1-thiol (MPTS) from Aldrich, cations of Ca(II), Ag(I), and Pb(II) in chloride and nitrate salts (greater than 98% purity from Merck), and hydrogen peroxide 33% (Merck) were used as supplied.

Procedure

Sol-gel process for preparation of sulfonato silica hybrid

Precursor of Na_2SiO_3 solution 25 mL was mixed with 4 mL MPTS and then the mixture was added with hydrochloride acid 3 M drop by drop and was stirred slowly till the pH of 7.0. The gel formed was kept overnight and then was washed with water in order to be free of acid by monitoring with a universal pH indicator paper. The gel was dried at 70 °C and was grounded into 200 mesh in particle size. The product obtained was silica modified with mercaptopropyl group (mercapto silica hybrid, MSH). The similar work was repeated without addition of MPTS to obtain silica gel (SG) as the control product. The silica modified with mercaptopropyl groups was oxidized with H_2O_2 to produce sulfonic acid moieties on the silica surface. Typically, 1.0 g of MSH was suspended in 16 mL of aqueous 33% (wt) H_2O_2 with continuous stirring at room temperature for 1 h [30]. The produced material was filtered, washed several times with water and ethanol and then dried at 100 °C overnight. The sulfonic acid groups attached to the pore walls were converted into sodium sulfonate groups through ionization with NaOH solution (0.1 M). The solid product was filtered off, washed with deionized water, and dried at room temperature overnight. The sample was characterized using XRD, FT-IR spectroscopy and by determination of cation-exchange capacity in proton (H^+) form.

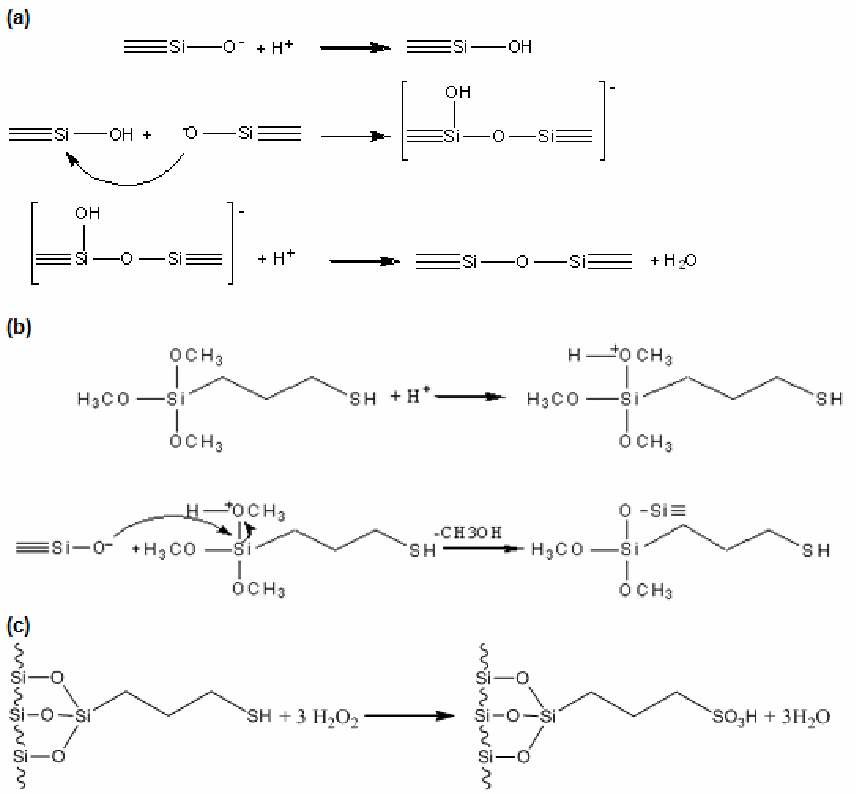

Fig 1. Reaction of sulfonato-silica hybrid formation steps. (a) formation of siloxane bonding; (b) modification of silica with mercapto group, and (c) oxidation of mercapto group with hydrogen peroxide

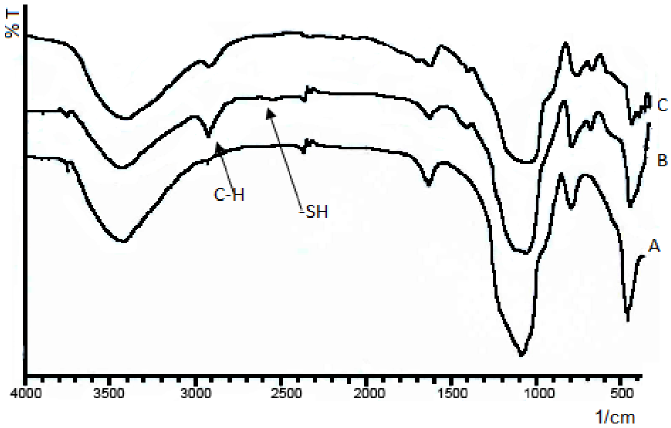

Fig 2. Infrared spectra of products; silica gel (A), mercapto silica Hybrid (B) and sulfonato silica hybrid (C)

Isotherms of adsorption

The batch adsorption method was used for determining the isotherms of adsorption consisting of 100 mg of adsorbent suspended in 50.0 mL of an aqueous metal ion at various initial concentrations. They were mechanically stirred for 1 h at a room temperature (298 K). The solutions were centrifuged and the supernatant was determined by atomic absorption spectroscopy. The amount of metal ions adsorbed (mmol/g) was calculated from the expression:

$$m = \frac{(C_o - C)V}{M}$$

where C_0 and C are the initial and equilibrium concentrations of metal ions in mmol/L, respectively. V is the volume of the aqueous solution (*L*) and M is the mass of adsorbent (g). The above procedure was carried out with all adsorbents (SG, MSH, and SSH). The adsorption capacity (*b*) was calculated from these isotherm data.

RESULT AND DISCUSSION

The reaction for the formation of sulfonato modified silica through a novel sulfonation route is presented in Fig. 1 consisting of three steps. Those include formation of siloxane as framework of silica by adding acid in solution of silicate anion (Fig. 1(a)), immobilization of mercapto groups the silica during formation of gel (Fig. 1(b)), and is oxidation of the immobilized sulfhydryl groups to the corresponding sulfonic acid moieties with H_2O_2 (Fig. 1(c)). Experiment with volumetric method shows that in the investigated condition oxidation of MSH to become SSH increased

Table 1. Freundlich and Langmuir parameters of metal ion adsorption on adsorbents

Ion	Adsorbent	Freundlich			Langmuir		
		K_f	*n*	R^2	*b (mmol/g)*	*K (L/mmol)*	R^2
Ca(II)	SG	89.89	3.786	0.980	1.00	2.16	0.994
	MSH	4.246	2.429	0.954	0.22	0.44	0.878
	SSH	122.0	5.283	0.809	0.67	3.12	0.996
Pb(II)	SG	17.58	1.692	0.949	2.20	1.10	0.988
	MSH	95.06	2.801	0.926	2.50	2.16	0.998
	SSH	52.48	2.513	0.966	1.67	1.82	0.992
Ag(I)	SG	220.4	4.072	0.996	0.19	4.66	0.941
	MSH	97.81	1.862	0.988	2.00	7.76	0.901
	SSH	220.4	4.072	0.996	1.67	4.83	0.994

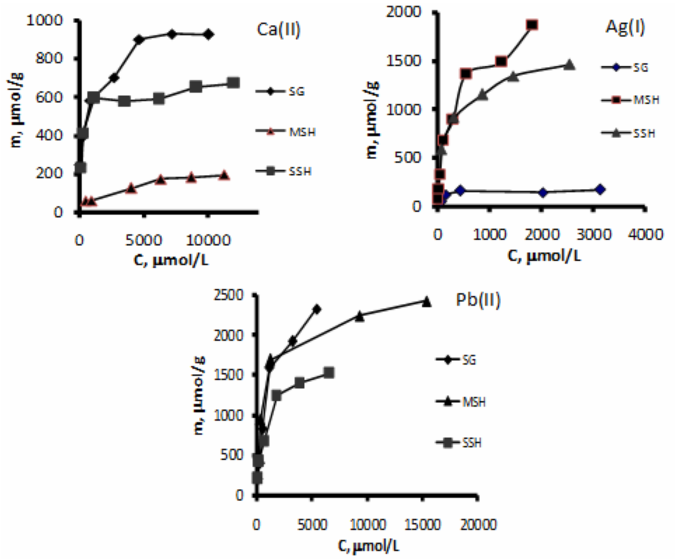

Fig 3. Correlation curves of the amount of metal ions adsorbed versus concentration of metal ions at equilibrium

the cation exchange capacity for Na^+ from 0.123 to 0.575 mmol/g.

Physical character of products

Infrared spectra of the products at various stages of its modification by the sulfonation reaction were performed to monitor changes on its surface (Fig. 2). Silica gel is identified with the presence of specific spectra of stretching vibration from –OH from silanol group (3425 cm^{-1}). Bending vibration of that group appears at 1636 cm^{-1}. Spectra at 1080 and 795 cm^{-1} comes from stretching and bending vibrations, respectively, of Si–O from siloxane (Si–O–Si). The presence of the mercaptopropyl groups in the functionalized material was evidenced by the presence of strong C-H stretching vibrations of the propyl chains at 2900 cm^{-1} [27] and a weak vibration corresponding to the -SH group at 2580 cm^{-1}. As indicated in Fig. 2, for the sulfonation reaction, the thiol groups in the MSH were oxidized by H_2O_2 to sulfonic acid units. However, sulfonic acid peaks at 1028 cm^{-1}, peaks at 1095~1085 cm^{-1} corresponding to symmetric C-S stretching vibrations, peaks at 960~950 cm^{-1} for asymmetric C-S stretching, and peaks at 1028, 1254, and 1084 cm^{-1} for S=O stretching cannot be distinguished from the broad and strong siloxane absorption peak because of the overlapping of bands [28]. However, the relative increase of the intensity of the hydroxyl band frequency between 3200 and 3400 cm^{-1} and the disappearance of the weak -SH peak at 2580 cm^{-1} indicates that the sulfonation reaction had indeed occurred, with the subsequent oxidation of -SH groups to $-SO_3H$ groups.

From the x-ray diffraction pattern (data is not shown), three products (SG, MSH and SSH), that are similar to those reported everywhere, show a broad peak with maximum intensity around 2θ = 21–23°. According to Kalaphaty et al. [29], silica with the wide band and the maximum peak at 2θ = 20–22° is characteristic of silica for amorphous structure. Thereby, result of characterization with XRD indicates that modification of silica with both mercapto and sulfonato groups do not cause the change of the silica structure.

Adsorption Isotherm

To investigate the adsorption capacity, various concentrations of Ca(II), Pb(II) and Ag(I) solutions were stirred for 1 h with adsorbent at room temperature. The experiment data is expressed in Fig. 3 as curves correlating the amount of metal ions adsorbed versus concentration of metal ions at equilibrium. For interpretation of the adsorption experimental data, two isotherm (Langmuir and Freundlich) models were used [30]. The expression of the Langmuir model is:

$$m = \frac{bKC}{1 + KC}$$

where m is the amount of metal ions adsorbed (mmol/g) at equilibrium; C is the concentration of metal ions at equilibrium; K represents the Langmuir constant (L/mmol) that relates to the affinity of binding sites and b is the theoretical saturation adsorption capacity of the monolayer (mmol/g).

The Freundlich model assumes heterogeneous adsorption due to the diversity of the adsorption sites or the diverse nature of the metal ions adsorbed, free or hydrolyzed species. The Freundlich model is expressed as:

$m = K_f\ C^{1/n}$

where *Kf* is the Freundlich constant related to adsorption capacity of adsorbent and *n* is the Freundlich exponent related to adsorption intensity. K_f and *n* can be calculated from the slope and intercept of the linear plot of log *m* vs. log *C*. Table 2 displays the coefficients of the Langmuir and Freundlich models along with regression coefficients (R^2).

As seen from Table 1, the R^2 values for both the Langmuir and Freundlich isotherm models were mostly above 0.90, suggesting that both models closely fit the experimental results. The adsorption capacity of the monolayer (*b*) values for Ca(II) on adsorbents was in order: SG > SSH > MSH. This fact can be explained using hard acid property of Ca(II) and site actives of the adsorbents. Addition of mercapto groups to the silica increases the softness of the adsorbent. Hence, the capability of Ca(II) to interact with mercapto groups clearly is weak. However, by oxidation process leading to formation of sulfonato ($-SO_3H$) the hardness of adsorbent is improved, and the capacity is increased, as well. Different phenomena occurs on soft metal ions of Ag(I) and Pb(II), with the similar capacity value order for two first adsorbents (SG < MSH). However, the increase of capacity for Ag(I) is higher than Pb(II) and this result is similar to the previous one reported [26]. The change of site actives from mercapto to sulfonato by oxidation leads to decline the adsorption capacities. It is clear that oxidation causes improvement of hydrophilic property of adsorbent which is in line with the capability to adsorb hard metal ions. If the adsorption capacity values of three metal ions on SSH are compared, the order of Ag(I) ~ Pb(II) > Ca(II) is obtained. It is probably due to the bonding type of Ca(II) (ionic) and incompleteness of oxidation. Ionic bond may be ready to be broken down in aqueous (polar) solution via solvation and the un-oxidized mercapto groups interact with Ag(I) and Pb(II) better than with Ca(II).

CONCLUSION

Chemical surface modification is used widely to obtain the desired properties and performance of materials. In the present study, the chemical (sulfonato) modification of silica was undertaken through sol-gel process followed with sulfonation reactions. The results clearly indicate the successful surface modification of silica particles. The modified silica bearing the sulfonated moiety and the presence of the functional groups had no effect on the structure of silica. Hence, the conclusion drawn from the present study is that this sulfonation route can be utilized for the generation of hydrophilic (ionic) property of adsorbent surfaces. Improvement of the ionic property is also expected to be able to increase easiness in desorbing metal ions adsorbed, as well as, enhance the reversibility of adsorbent

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