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Adsorption kinetic and equilibrium of Ca(II) and Mg(II) onto sulfonate-modified silica from sugarcane bagasse

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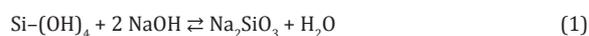
ABSTRACT

Sugarcane bagasse contains silica, which was separated and modified in this investigation. The silica was reacted by 3-(trimethoxysilyl)-1-propanethiol, and the product was oxidized to produce sulfonate-modified silica (SMS). The result of modification was accomplished by spectroscopic analysis of FTIR, XRD, and SEM-EDX. The SMS was used as adsorbent for adsorption kinetic and equilibrium of Ca²⁺ and Mg²⁺. The mechanism of the adsorption can be proposed from these experiments. Adsorption kinetic studied the adsorption of the cations as the function of contact time, and the data were evaluated by intra-particle diffusion model, Boyd equation, and Lagergren pseudo kinetic model. The calculated model fitted well to the experimental data and suggests that both Ca²⁺ and Mg²⁺ were adsorbed by SMS through external mass transfer, and were pseudo-second ordered. Adsorption equilibrium was evaluated using proton stoichiometry, and adsorption isotherms, the adsorption as the function of cation concentration, and the data were analysed using Dubinin-Radushkevich (DR)-Radushkevich. The results showed that the adsorption of Ca²⁺ onto SMS was through cation exchange and, that of Mg²⁺ onto SMS was via physisorption.

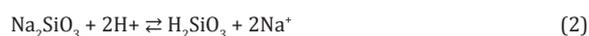
Keywords: Boyd model; Dubinin – Radushkevich; Intraparticle diffusion; Lagergren pseudo kinetic; Proton stoichiometry

INTRODUCTION

This study investigated the separation of silica from sugarcane bagasse, and the modification of its surfaces become sulfonate-modified silica (SMS) which may enable for surface cation exchange. The preparation of SMS adsorbent with the materials from sugarcane bagasse was started by the separation of silica. Previous investigations separated the silica from rice husk.^[1] 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 Na₂SO₃, as Reaction 1.



Na₂SO₃ become H₂SiO₃ when it was reacted with acid (Reaction 2), and overcome the polymerization reaction.



Surface modification of silica can be conducted by changing silanol functional group –Si-OH becomes

–Si-OM, where M was simple species except hydrogen.^[2] There were two types of compounds can be used to modify silica; they were organic-functionalization and inorganic-functionalization compounds.^[3] 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 researchers modified silica by use of 3-(trimethoxysilyl)-1-propanethiol and aerosol in toluene medium.^[4,5] Sol-gel process was conducted to precursor silica. Modifier substituting silanol groups were added to precursor silica in gel formation process, which resulted in a compound containing siloxane group, silanol group, and modified silica represented by –S-OM.

The preparation of silica from sugarcane become SMS adsorbent was done through several steps, but one of the most important steps is the reaction of the silica with modifier of 3-(trimethoxysilyl)-1-propanethiol as conducted by some previous researchers producing mercapto-functional groups (–SH) of the silica.^[6-8] SMS was obtained by oxidation of the –SH functional

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groups and produced sulfonate functional groups (-SO₃H) of the adsorbent that was then called SMS. The proton of the functional groups of SMS can be exchanged by cations that were investigated in this research.

The choice of sugarcane bagasse as the sample of this research was due to the over the availability of the bagasse which may result in serious problems of environment. The cations of Ca²⁺ and Mg²⁺ were chosen because of representation of micronutrients needed by plants. The result of this study may useful to understand the strength the binding and may be relevant to the rate of desorption. The principles can be implemented on the use of modified silica as the sorbent of micronutrients for the slow release fertilizer.

The experiments of adsorption kinetic and equilibrium of Ca²⁺ and Mg²⁺ cations by SMS from sugarcane silica were conducted to study the mechanism of adsorption. Data of adsorption kinetics were modelled using pseudo first order or second order kinetic,^[9-11] intraparticle diffusion model,^[10,12] and Boyd kinetic model.^[11] Data of adsorption equilibrium were collected through proton stoichiometry and adsorption isotherm which was analyzed using DR equation.^[13,14]

The model of Lagergren pseudo first order or second order kinetic model was used by previous investigators to study the adsorption kinetic.^[11,16-18] The model of pseudo first order kinetic model was represented by Equation 3.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

Where q_e and q_t are the capacity of adsorbent to adsorb M²⁺ at equilibrium and time t , respectively (mmol/g), k_1 is the reaction first order constant with the unit of minute⁻¹. Integration to the equation with $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, produces the Equation 4.

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2303} t \quad (4)$$

The equation of Lagergren Pseudo Second Order Kinetic was expressed by Equation 5.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where k_2 is the pseudo second order constant, with the unit of g/mmol/minutes. The integration of the equation of pseudo second order kinetic produced the Equation 6.

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \quad (6)$$

Plotting t/q_t versus t of the equation made a linear line

for reactions with pseudo second ordered.

Intraparticle diffusion model was expressed by Equation 7.^[10,12,19]

$$q_t = k_1 t^{1/2} + c \quad (7)$$

Where q_t is the amount of adsorbates on adsorbent surfaces at the time t (mmol/g), k_1 is particle diffusion rate constant (mmol/g min^{1/2}). If the plot of q_t versus t is linear, it means the adsorption mechanism follows the intraparticle diffusion model, and the values of the constant k_1 and the intercept C (mmol/g) can be calculated.

Boyd model was expressed by the Equation 8.

$$B_t = -0.4977 - \ln\left(1 - \frac{q_t}{q_\infty}\right) \quad (8)$$

From which q_∞ and q_t are the amount of adsorbates on surfaces at infinite time and at time t , respectively. B_t is a mathematical function of fraction q_t to q_∞ . Plotting t versus B_t produces lines whose linearity was used to identify whether film diffusion or intraparticle diffusion controls the rate of adsorption.^[11] The linearity lines can be (a) linear lines and pass at the initial point of zero, (b) linear lines that do not pass through zero point, or (c) not linear. Linear lines pass initial point of zero means the rate determining step of the adsorption is intraparticle process. Linear lines that do not through zero point means adsorption of a cation by SMS occurred through cation exchange. Not linear lines indicated the adsorption of cation by SMS was through external mass transfer.

To describe the adsorption equilibrium, proton stoichiometry was measured, and DR equation was used to model the adsorption isotherm data. Proton stoichiometry is the number protons that are taken up or released by adsorbent surfaces to bind 1-mole adsorbate.^[20-22] DR was used to understand adsorption equilibrium between adsorbed cation on SMS surfaces and cations in solution. The DR model was expressed by Equation 9.

$$\ln q_e = \ln q_m - ke^2 \quad (9)$$

Where e is equal to $RT \ln(1+1/C_e)$, C_e is cation concentration at equilibrium time (mol/L), q_e an q_t were the amount of cation on SMS surfaces and on solution at equilibrium time (mol/g), respectively, and k is a constant related to adsorption energy (mol² kJ⁻²). Linear plots of $\log q_e$ versus e^2 , gave the value of the constant k that is related to adsorption free energy (E), expressed by Equation 10.^[14] When E was in the range of 8-16 kJ/mole, the adsorption was through cation exchange, but if it was <8 kJ/mole, the adsorption was by physical forces.^[14]

$$E = \frac{1}{\sqrt{2k}} \quad (10)$$

EXPERIMENTAL SECTION

Materials

The samples were sugarcane bagasse which was the rest product of cane sugar factory in Yogyakarta, Indonesia. Water for all experiments was free of minerals, and all other reagents were from Merck of analytical reagent grade. The materials needed were HCl solution, NaOH solution, sodium nitrate solution (Na_2SiO_3), 3-(trimethoxysilyl)-1-propanethiol, and H_2O_2 solution.

Instrumentation

Instruments were needed in this investigation were Perkin Elmer 3110 AAS, Shimadzu Prestige 21 Fourier transform infrared (FTIR), Rigaku Multiflex S-6000 X-ray diffraction (XRD), and Jeol JSM 6510 LA scanning electron microscopy (SEM).

Procedure

The preparation of SMS

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

Into sodium nitrate solution (Na_2SiO_3), 3-(trimethoxysilyl)-1-propanethiol was added. HCl was added in drops-by-drops to the solution, while stirred until the gel was formed and the pH reached neutral. The results were left at the room temperature for 18 h. The gel was washed with water and stirred, and filtered with Buchner. The gel was then dried in the oven at 80°C , and mercapto-modified-silica (MMS) was obtained.

The SMS was prepared by oxidation of mercapto functional groups (-SH) of MMS using H_2O_2 solution. The amount of 2 g of MMS was added to 32 mL H_2O_2 solution and stirred for 1 h until the precipitation was formed. The result was filtered with Buchner, and the precipitate was soaked into 10% of H_2SO_4 for 1 h, washed with water until pH was neutral, and it was finally dried in the oven until the mass was constant. The product obtained was SMS adsorbent.

Adsorption Kinetic of Ca^{2+} and Mg^{2+} onto SMS

The mass of 2 g MMS was added into 0.001 M Ca^{2+} or Mg^{2+} and was stirred at constant temperature 30°C and pH 5.00. After equilibrium duration of times, the sample was taken, centrifuged, and the

supernatant was analyzed for free concentration of Mg^{2+} or Ca^{2+} using AAS. A similar method was done previously.^[18]

Adsorption equilibrium of Ca^{2+} and Mg^{2+} onto SMS

The experiments were conducted by varying concentration of Ca^{2+} or Mg^{2+} to describe the effect of concentration on the adsorption. The concentration of Ca^{2+} or Mg^{2+} was increased in steps from 0.1 mM to 2 mM, and the pH was kept constant of 5.00 by addition of 0.1 M HCl/NaOH solution. A sample was taken after the equilibrium time, was centrifuged, and the supernatant was analyzed for free concentration of Ca^{2+} or Mg^{2+} . The amount of added HCl/NaOH solution following each addition of Ca^{2+} or Mg^{2+} concentration was recorded as proton stoichiometry, the proton that was needed/released in the adsorption mechanisms of Ca^{2+} or Mg^{2+} by SMS. The method was used in previous investigations.^[20,21]

Analysis of adsorption data

The intraparticle diffusion model, diffusion-chemisorption model, and Boyd equation were used to evaluate the data of adsorption kinetics. The analysis of Lagergren pseudo kinetic model was used to model the order kinetic of Ca^{2+} or Mg^{2+} adsorption by SMS. The isotherm equation of DR was used to describe the adsorption mechanism of both cations onto SMS either through physisorption or cation exchange. The proton stoichiometry was calculated to support the proposal of the adsorption mechanism. Both models of adsorption kinetics and equilibrium must be inline and relevant one another for the description of adsorption mechanism.

RESULTS AND DISCUSSION

The Synthesis of Silica from Sugarcane Bagasse and Its Modification Become the SMS

Sugarcane bagasse contained silica insignificant amount whose surfaces can be modified using sol-gel process since the silica was amorphous in structure as shown in Figure 1, whose typical 2θ of 64° .

After the sugarcane bagasse samples were dried,

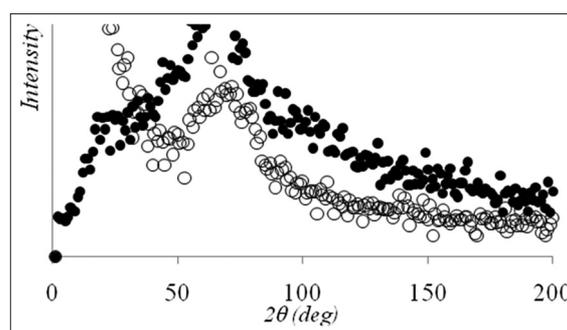


Figure 1: Diffractogram of gel silica (filled circles) and sulfonate-modified silica (blank circles)

grinded, sieved, and reacted with NaOH solution in a certain condition, the supernatant from the filtration of sodium silicate was found as the Reaction 11.



After Na_2SiO_3 was treated with 3-(trimethoxysilyl)-1-propanethiol and HCl solution to get MMS. The MMS is silica on which its surfaces bind mercapto (-SH) functional groups. Hence, the modification to get SMS was done by replacing silanol group of silica (-SOH) with mercapto groups ($\frac{3}{4}\text{SH}$). The mechanism of reaction was initiated by oxygen protonation on methoxy groups (OCH_3) of 3-(trimethoxysilyl)-1-propanethiol. Siloxy ($-\text{SiO}^-$) of silica then attacked and replaced the protonated oxygen of methoxy, and bound silica on 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 2. The SMS was prepared by oxidizing MMS using H_2O_2 32%, with reaction as given in Figure 3.

Spectroscopic Analysis on Modification Process

Spectroscopic analysis of FTIR was done to confirm the results of modification process including the preparation of silica that was synthesized in this study, MMS, and SMS. The spectra were compared to that of gel silica Kiesel 60 Merck as depicted in Figure 4. There were few differences of wavelength shift and new peaks amongst the spectrograms.

The synthesis result of MMS was indicated by FTIR spectrogram on the availability of -CH group from propyl chain, -SH, mercapto groups, and C-O-C.^[6] FTIR measurement in this study has shown all the groups as listed in Table 1. The groups of -CH was shown by stretching vibration on wavelength of 2970/cm, 2931.80/cm, and 2873/cm. The group of mercapto -SH was shown generally by weak peaks in the wavelength between 2600 and 2450/cm, and

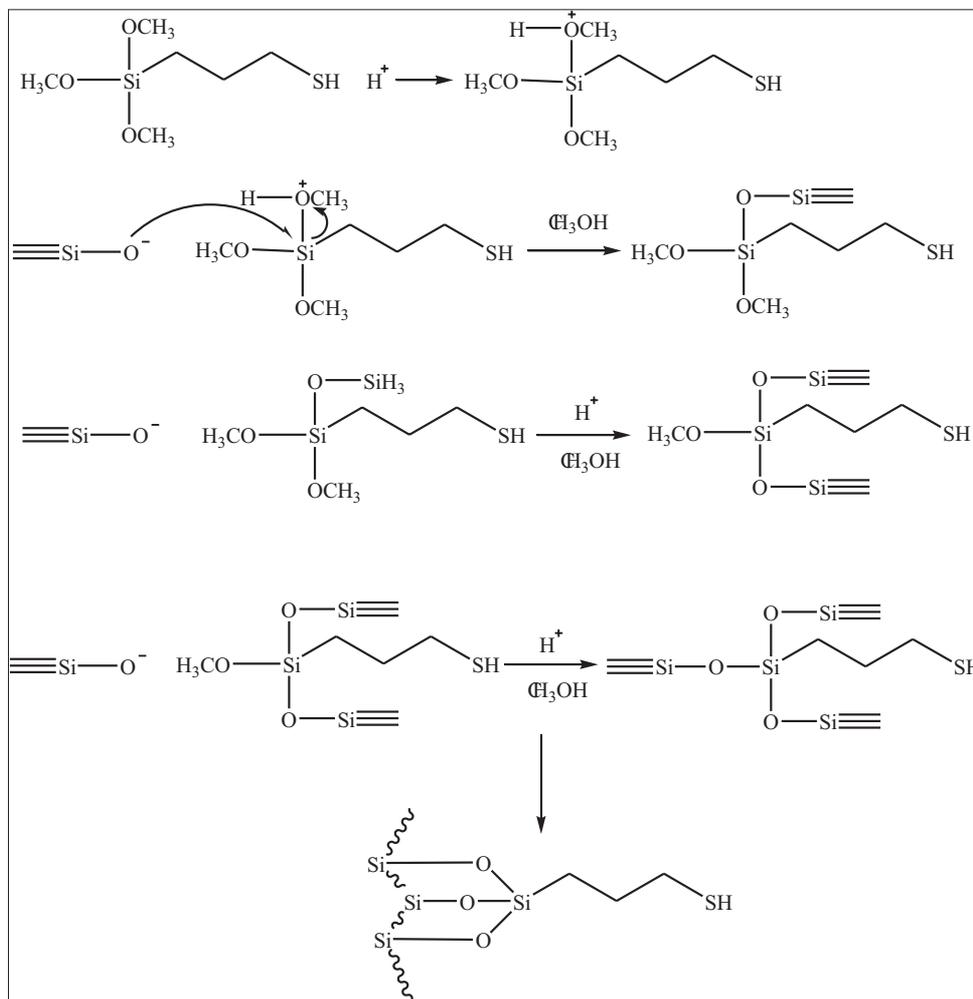


Figure 2: Reaction mechanism on mercapto-modified silica

Table 1: FTIR of gel silica Kiesel 60 (Merck), gel silica (this study), MMS, and SMS

Functional groups	Wavenumbers (cm ⁻¹)			
	A ^{a)}	B ^{a)}	C ^{a)}	D ^{a)}
Stretching vibration –OH of Si-OH	3448.5	3472.39	3448.72	3425.58
Asymmetric stretching vibration Si-O of Si-O-Si	1101.3	1097.43	1049.28	1041.56
Symmetric stretching vibration Si-O of Si-O-Si	800.4	799.06	802.39	601.79
Bending Vibration –OH of H ₂ O	1637.5	1639.88	1635.64	1635.64
Stretching vibration Si-O of Si-OH	970.1	970	910.4	910.4
Bending vibration Si-O-Si	472.5	465.57	470.63	470.63
Stretching vibration –CH ₂	-	-	2931.8	2931.8
Stretching vibration –SH	-	-	2569.18	-
Vibration –SO of –SO ₃ H	-	-	-	1404.18

^{a)}: (A): Gel silica Kiesel 60 (Merck), (B): Gel silica (this study), (C): MMS, and (D): SMS. FTIR: Fourier transform infrared, MMS: Mercapto-modified-silica, SMS: Sulfonate-modified silica

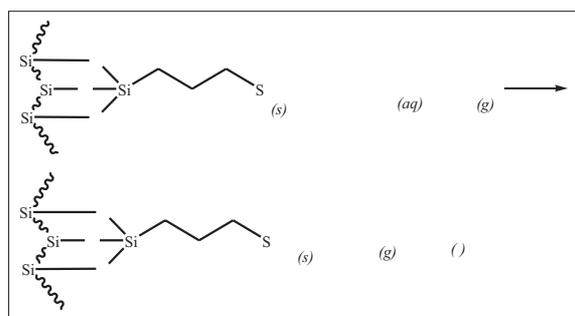


Figure 3: Sulfonate-modified silica adsorbent, the result of oxidation of mercapto-modified silica

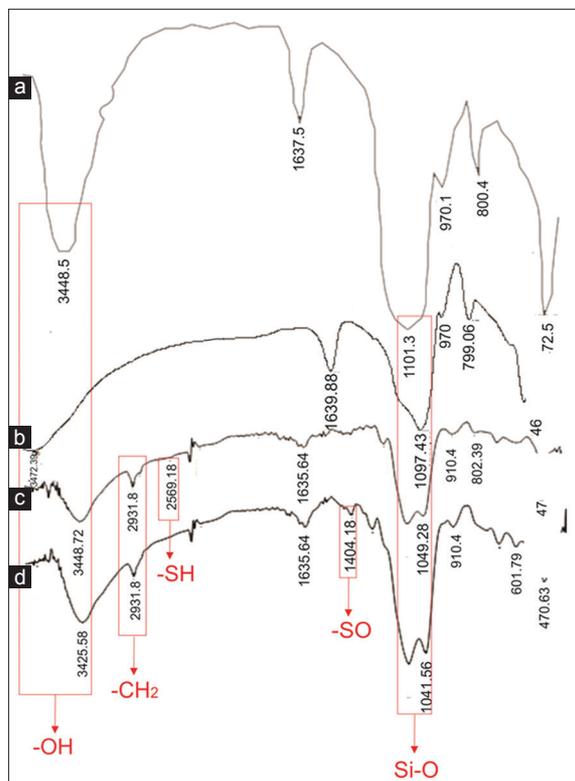


Figure 4: Fourier transform infrared spectrogram of (a) gel silica Kiesel 60 (Merck), (b) gel silica (this study), (c) mercapto-modified silica, and (d) sulfonate-modified silica

this study found the –SH groups were indicated by stretching vibration in the wavelength of 2580/cm and

2569.18/cm. While vibration of C-O-C appeared in the wavelengths of 1375/cm and 1456/cm.

Previous researchers stated that sulfonated silica to which it was abbreviated by SMS in this study was indicated by peak at wavelength of 1028/cm, which was the peak of sulfuric acid, and by C-S stretching vibration at a wavelength of 1095–1085/cm, and by asymmetric stretching peak C-S at 960–950/cm. Stretching S=O at wavelengths of 1028, 1254, and 1084/cm cannot be separated from wide and strong peak of siloxane because they were overlapping at similar areas of wave bands.^[6] Main indicator of SMS formation was disappearance of –SH groups at wavelength 2500/cm indicating the success of sulfonation reaction whose –SH groups changed into –SO₃H functional groups. The formation SMS was also indicated by the appearance of broad bands and relative increase of frequency at wavelength areas 3400–3200/cm which was suitable to the absorbance of –OH from sulfonate groups. Weak absorbance of C-H or methylene groups at 2932/cm also support the formation of SMS. The formation of SMS in this study was also indicated well by the shift of absorbance at wavelength area of 2553.75/cm, which was the area of –SH group vibration, and indicated by the increase of frequency from 3441.01/cm to 16.624/cm as the absorbance of –OH from sulfonate groups. This study also showed the absorbance of –OH group at a wavelength of 3448.72/cm with the intensity of 3.193. Weak absorbance of C-H or the methylene appeared at 2939.52/cm¹.

SEM analysis showed visualization of the surface in detail so the surface of SMS and silica (SG) as the comparison and can be compared visually. From Figure 5, SMS has a smaller particle size and more pores compared to SG. The amount of pores on the 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 adsorbates. Light intensity shown in the pictures from SEM might indicate the mass of molecules of the samples.

Figure 5 showed that SMS had more bright areas than SG, indicating that SMS had higher molecular mass and contained more functional groups than SG. While energy dispersive X-ray showed the amount of silica in the adsorbents of sugarcane bagasse, SG, and SMS as it is given in Table 2. The analysis showed that 16.42% sulfur was available in the sample of SMS, meaning that SMS contained a significant amount of 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. However, the percentages of silica in SMS (17.20%) was less much than that in SG (36.51%) which resulted from the availability of other atoms bound by the surfaces following the interaction of sulfur atom. Average mass of O atoms was higher than Si, and the mass ratio of Si:O in SMS and in SG was about 1:2 and 1:1, respectively. It can be stated that the mass of O atom in SMS was twice higher than Si, but it was only about the same in SG. Since O atom of sulfonate groups whose lone pair electron play a significant role in the cation exchange reaction on adsorbent surfaces, the modification should increase the cation exchange capacity of SMS.

Adsorption Kinetics of Ca²⁺ and Mg²⁺ by SMS

The Lagergren pseudo kinetic model showed that the adsorption of Ca²⁺ and Mg²⁺ was second ordered, with the parameters listed in Table 3. The intraparticle diffusion of both Ca²⁺ and Mg²⁺ by SMS was given in Figure 6. The plots of *qt* versus *t*^{0.5} were multilinear for both Ca²⁺ and Mg²⁺ adsorption.

Boyd equation was used to further model of the cations adsorption. The plot was given in Figure 6, and suggest that both lines on the plot that were calculated using Boyd equation was not linear and did not fit well to the

experimental data. However, on Ca²⁺ adsorption, it showed the line pass through the *qt* axis at the much smaller number (-0.1) than that of Mg²⁺ adsorption (-0.4).

Based on the model of pseudo kinetic model, the adsorption of Ca²⁺ and Mg²⁺ by SMS was second ordered. Table 3 shows that the adsorption rate of Ca²⁺ was 37 times slower than that of Mg²⁺, even though the initial adsorption rate (*h*) of Ca²⁺ was 30 times higher than Mg²⁺. This phenomenon explains that the adsorption included multi-step reactions as shown by intraparticle diffusion model from which both Ca²⁺ and Mg²⁺ adsorption by SMS were not solely controlled by intraparticle diffusion, but also on extra particle mass transfer. The adsorption process occurred both on the surfaces and in pores of SMS, and as represented by two lines of adsorption models [Figure 6]. First line showed the importance of boundary layer effect, and the second line showed pore diffusion and extra particles diffusion. Slope of the second lines is diffusion coefficient in which Mg²⁺ was higher than Ca²⁺. The intercept of the plot showed the effect of boundary layer effects suggesting the higher value of the slope, the stronger diffusion takes role in the adsorption process, which controlled the rate of the adsorption process.

Two lines of a model of diffusion brought about further analysis to propose the step with the slowest speed of adsorption process. The model for this calculation was Boyd equation. The plot was given in Figure 6, and suggest that both lines on the plot were not linear and did not fit well to the experimental data. However, on Ca²⁺ adsorption, it showed the line pass through the *Bt* axis at much closer to zero (-0.1) than that of Mg²⁺ adsorption (-0.4). The value of *Bt* is the proposal of the adsorption mechanism. When *Bt* is close to the “zero,” the rate of adsorption was predominantly determined by extra particle diffusion, but if the value is high, the adsorption rate was mostly determined by external mass transfer. Since Ca²⁺ adsorption has a smaller value of *Bt* than Mg²⁺, proposing that the adsorption of Ca²⁺ by SMS was through extra particle diffusion. On the other hand, Mg²⁺ was adsorbed SMS by external mass transfer.^[15]

Table 2: Chemical contents of SG and SMS by EDX spectroscopy

Elements	% mass	
	SG	SBS
Si	36.51	17.20
O	41.94	45.29
S	0.18	16.42

SMS: Sulfonate-modified silica, EDX: Energy dispersive X-ray

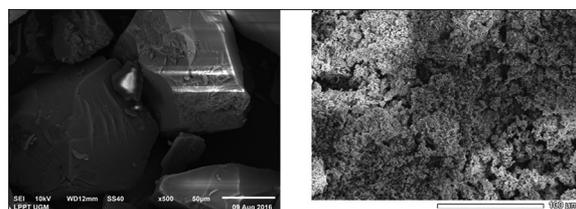


Figure 5: Scanning electron microscopy of SG and sulfonate-modified silica

Adsorption Equilibrium and Mechanism

The effect of the concentration of Ca²⁺ or Mg²⁺ on the adsorption experiments was conducted to confirm the results of the kinetic model for the description of the adsorption mechanism. The parameters of the isotherm DR model were given in Table 4. The DR isotherm equation suggests higher energy involved on the adsorption of Ca²⁺ than that of Mg²⁺. Process of adsorption involved protons because the experiments needed the addition of base when the experiments of adsorption were conducted at pH 5.0. The amount of protons taken up or released in the adsorption process

Table 3: Lagergren pseudo second order kinetic model parameters

Cation	k_2 (g/mol/min)	h (g/mol/min)	q^e , calc.(mol/g)	q_e , exp(mol/g)	R^2
Ca ²⁺	0.07503	0.00116	0.12415	0.12083	0.99971
Mg ²⁺	2.73839	5.55885×10 ⁻⁵	0.00451	0.00454	0.99778

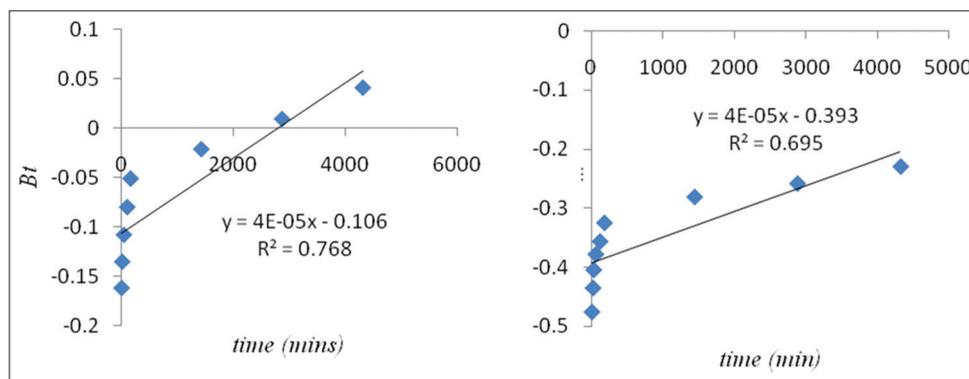


Figure 6: Boyd model of Ca²⁺ and Mg²⁺ by sulfonate-modified silica

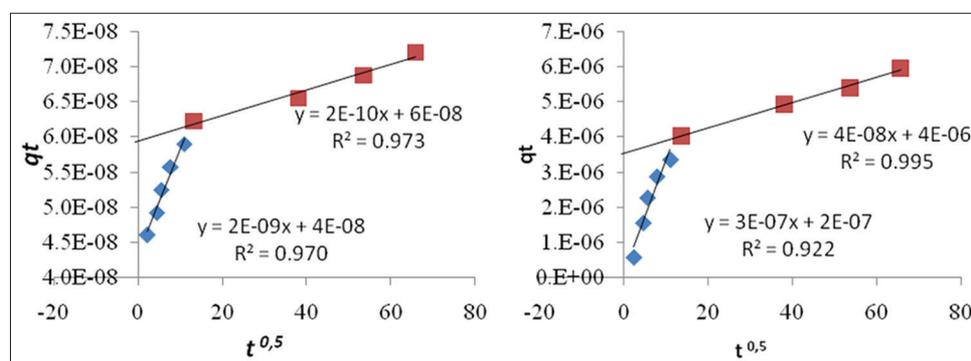


Figure 7: Intraparticle diffusion plot of Ca²⁺ and Mg²⁺ by sulfonate-modified silica

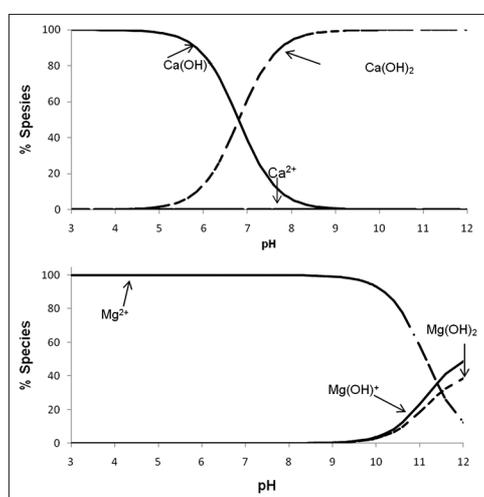


Figure 8: Species distribution of (a) Ca²⁺ and (b) Mg²⁺. The stability constants of the hydrolysis of Ca²⁺ were Stumm and Morgan,[27] and Mg²⁺ from Baes and Mesmer,[28] whose species distribution was calculated using the computer program GRFit[29]

were called proton stoichiometry [Table 5]. The measurement of proton stoichiometry was needed to support the proposal of the binding process between adsorbate and adsorbent.^[20,22]

At pH of 5.0, proton stoichiometry showed that H⁺ was released in significant amount when cation Ca²⁺ or Mg²⁺ was adsorbed by SMS. Adsorption was affected by charges of adsorbent-adsorbates, radius of adsorbates, and concentration of adsorbate.^[20] Charges of surface were affected by pH. At lower pH values, the surfaces of SMS were protonated and positively charged, and at higher pH values they were deprotonated and negatively charged.^[20,23] The point at which net charges of the surfaces were zero is called point zero charge (PZC). The PZC of SMS was not measured, but that of silica was reported very low.^[24] It means that at pH 5, the pH at which the experiments of adsorption kinetic and isotherm were carried out, the charges of surfaces of SMS were negative. On the other hands, for the

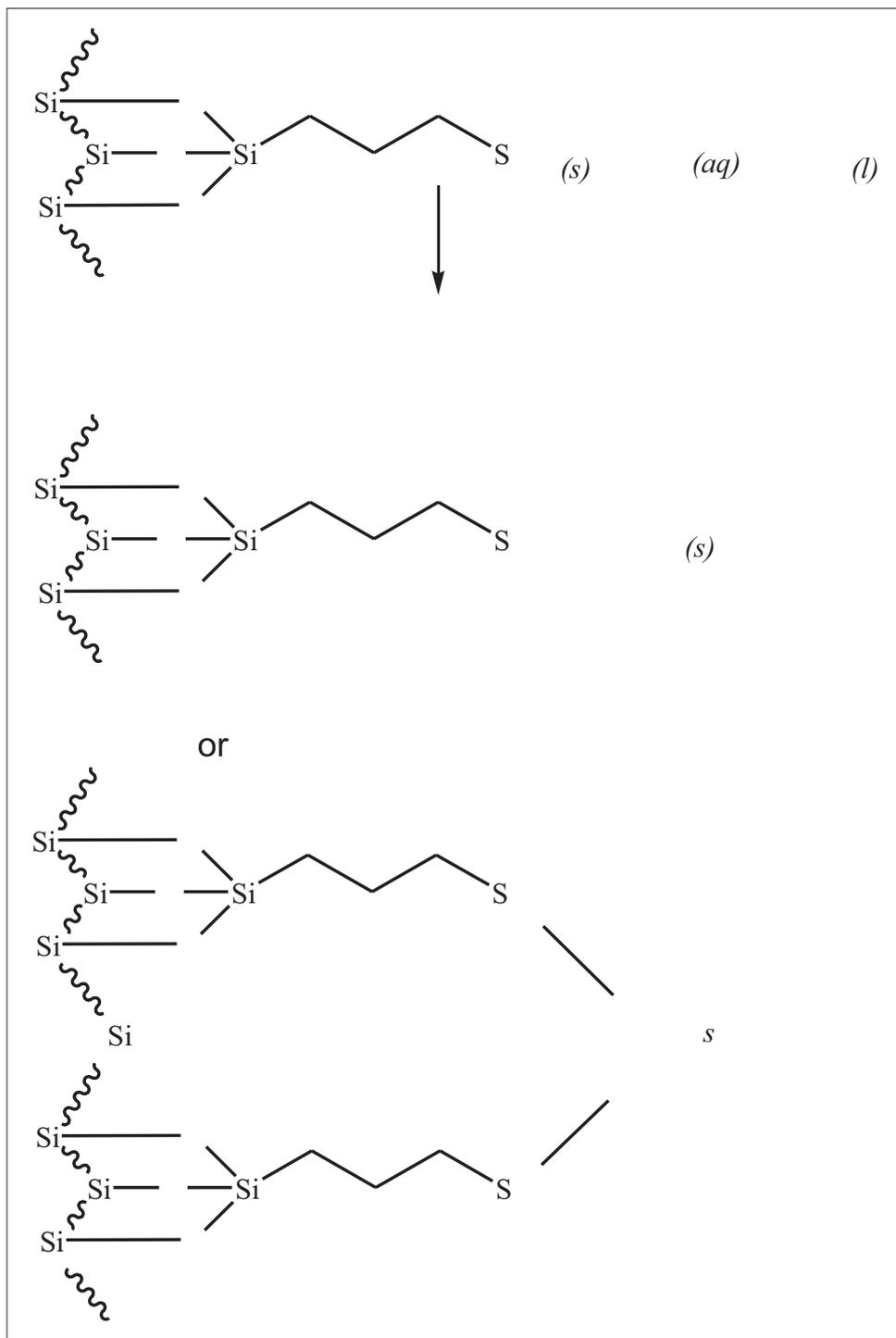


Figure 9: Adsorption of a cation by sulfonate-modified silica (SMS); (a) reaction of SMS and cation solution, (b) surface complexes formed by SMS and Ca²⁺ cation, and (c) surface complexes formed by SMS and Mg²⁺ cations

sorbates of the cations, the charges that appeared to have an important role on the adsorption process by SMS were positive of the species of M²⁺ and M(OH)⁺.^[25]

Two steps of adsorption occurred in the adsorption process as shown by intra-extra particle diffusion [Figure 7]. It fitted to the results of Lagergren pseudo second order kinetic from which at initial contacts, the rate of Ca²⁺ adsorption was faster, but at the overall

adsorption mechanism [Table 3], the rate was slower than Ca²⁺. It can be explained by the availability of the cations species. The species distribution was described in Figure 8. From Figure 8, the availability of species of Mg²⁺ was higher than Ca²⁺ at pH 5.0 for the same concentration. The higher was the amount of Mg²⁺ species; the higher was the rate of the adsorption. Since the radii of sorbates were important in the adsorption,^[18] and the radii of Mg²⁺ was smaller

Tabel 4: Parameters of isotherm DR model

Parameter	DR	
	Ca ²⁺	Mg ²⁺
qmax (mol/g)	7.38E-06	0.003072
KL (L/mol)	-	-
KF (L/g)	-	-
1/n	-	-
N	-	-
E (kJ/mol)	13.8675	7.61431
R ²	0.8586	0.8992

DR: Dubinin-Radushkevich

Table 5: Proton stoichiometry for the adsorption of Ca²⁺ and Mg²⁺ onto SMS

Cation	Proton stoichiometry, χ (number of mole of protons released per mole cation adsorbed)
Ca ²⁺	0.05425
Mg ²⁺	0.017299

SMS: Sulfonate-modified silica

than Ca²⁺ [26] then Mg²⁺ should have the higher potency to be adsorbed by SMS than Ca²⁺ at initial contact. However, in fact, that Ca²⁺ adsorption was faster at first. It may result from the strength of interaction of the surface, where toward Ca²⁺ the interaction was stronger than Mg²⁺. As the adsorption took place after sometime, the availability of one positively charged hydroxyl species of M(OH)⁺ took over the control of the adsorption, at which the distribution of Mg(OH)⁺ at pH 5 was very few, but Ca(OH)⁺ was insignificant amount. This distribution may lead to faster overall adsorption process as indicated the value of k₂ [Table 3]. It was the reason why at initial adsorption, Ca²⁺ has higher adsorption rate than Mg²⁺ [value of h in Table 3], but the rate of overall adsorption showed that Ca²⁺ was slower than Mg²⁺ [value k₂ in Table 3]. From the reasons of the kinetics and based on the analysis of DR, it can be concluded that the adsorption mechanisms of Ca²⁺ and Mg²⁺ was through different adsorption mechanisms, extra particle diffusion for Ca²⁺ and external mass transfer for Mg²⁺ [Figure 9]. DR, model on isotherm experimental data suggest adsorption energy support the mechanisms. It was shown by the parameter of energy for which it was higher than 8 kJ/mole for the adsorption of Ca²⁺, but it was smaller for the adsorption of Mg²⁺. It means that the adsorption of Ca²⁺ tends to occur through cationic exchange, but Mg²⁺ through physisorption.^[14]

CONCLUSION

The spectroscopic analysis FTIR and XRD confirmed that modification of silica synthesized from sugarcane baggase can be done well. Adsorption kinetic of intraparticle diffusion model showed that Ca²⁺ was adsorbed by SMS adsorbent through extra particle diffusion and Mg²⁺ through

external mass transfer. The adsorption kinetic also found that the adsorption of both cations onto SMS was second ordered. To confirm the adsorption kinetic, adsorption isotherm model using the DR equation showed that adsorption of Ca²⁺ onto SMS occurred through that cationic exchange and Mg²⁺ was through physisorption.

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