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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 Na$_2$SO$_3$, as Reaction 1.

\[
\text{Si–(OH)$_4$ + 2 NaOH } \Leftrightarrow \text{ Na}_2\text{SiO}_3 + \text{ H}_2\text{O} \quad (1)
\]

Na$_2$SO$_3$ become H$_2$SiO$_3$ when it was reacted with acid (Reaction 2), and overcome the polymerization reaction.

\[
\text{Na}_2\text{SiO}_3 + 2\text{H}^+ \Leftrightarrow \text{H}_2\text{SiO}_3 + 2\text{Na}^+ \quad (2)
\]

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.
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,[10-13] 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.[13,14] The model of pseudo first order kinetic model was represented by Equation 3.

\[
\frac{dq}{dt} = k_1 (q_e - q_t)
\]  

Where \( q_t \) and \( q_e \) are the capacity of absorbent to absorb 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 \( q=0 \) to \( q=q_t \) produces the Equation 4.

\[
\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2303} t
\]  
The equation of Lagergren Pseudo Second Order Kinetic was expressed by Equation 5.

\[
\frac{dq}{dt} = k_2 (q_e - q_t)
\]  

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.

\[
t = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]  

Plotting \( t/q \) 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]

\[
q_t = k_2 t^{1/2} + c
\]  

Where \( q_t \) is the amount of adsorbates on adsorbent surfaces at the time \( t \) (mmol/g), \( k_2 \) is particle diffusion rate constant (mmol/g min-1). 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 \( k_2 \) and the intercept \( C \) (mmol/g) can be calculated.

Boyd model was expressed by the Equation 8.

\[
B = -0.4977 - \ln \left( \frac{1 - q_t}{q_e} \right)
\]  

From which \( q_0 \) and \( q_e \) are the amount of adsorbates on surfaces at infinite time and at time \( t \), respectively. \( B \) is a mathematical function of fraction \( q_t \) to \( q_e \). Plotting \( t \) versus \( B \) produces lines whose linearity was used to identify whether film diffusion or intraparticle diffusion controls the rate of adsorption.[10] 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.

\[
\ln q_e = \ln q_m - k e^2
\]  

Where \( e \) is equal to RT \( \ln(1+C_0) \), \( C_0 \) is cation concentration at equilibrium time (mol/L), \( q_e \) an \( q_m \) 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]
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 (Na₂SiO₃), 3-(trimethoxysilyl)-1-propanethiol, and H₂O₂ 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 (Na₂SiO₃), 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 H₂O₂ solution. The amount of 2 g of MMS was added to 32 mL H₂O₂ solution and stirred for 1 h until the precipitation was formed. The result was filtered with Buchner, and the precipitate 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.

Adsorption Kinetic of Ca²⁺ and Mg²⁺ onto SMS
The mass of 2 g MMS was added into 0.001 M Ca²⁺ or Mg²⁺ 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 Mg²⁺ or Ca²⁺ using AAS. A similar method was done previously.[18]

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 Ca²⁺ or Mg²⁺ 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 2q of 64°.

After the sugarcane bagasse samples were dried,
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.

\[
\text{SiO}_2(s) + 2 \text{NaOH(aq)} \rightarrow \text{Na}_2\text{SiO}_3(aq) + \text{H}_2\text{O(l)}
\] (11)

After Na$_2$SiO$_3$ 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 (¼SH). The mechanism of reaction was initiated by oxygen protonation on methoxy groups (OCH$_3$) of 3-(trimethoxysilyl)-1-propanethiol. Siloxy (-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$_2$O$_2$ 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. 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](image-url)
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. 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.

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.

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

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Wavenumbers (cm⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>Stretching vibration –OH of Si-OH</td>
<td>3448.5</td>
</tr>
<tr>
<td>Asymmetric stretching vibration Si-O of Si-O-Si</td>
<td>1101.3</td>
</tr>
<tr>
<td>Symmetric stretching vibration Si-O of Si-O-Si</td>
<td>800.4</td>
</tr>
<tr>
<td>Bending vibration –OH of H₂O</td>
<td>1637.5</td>
</tr>
<tr>
<td>Stretching vibration Si-O of Si-OH</td>
<td>970.1</td>
</tr>
<tr>
<td>Bending vibration Si-O-Si</td>
<td>472.5</td>
</tr>
<tr>
<td>Stretching vibration –CH₂</td>
<td>-</td>
</tr>
<tr>
<td>Stretching vibration –SH</td>
<td>-</td>
</tr>
<tr>
<td>Vibration –SO of –SO₃H</td>
<td>-</td>
</tr>
</tbody>
</table>

*: (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 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.

### 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

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

<table>
<thead>
<tr>
<th>Elements</th>
<th>% mass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SG</td>
</tr>
<tr>
<td>Si</td>
<td>36.51</td>
</tr>
<tr>
<td>O</td>
<td>41.94</td>
</tr>
<tr>
<td>S</td>
<td>0.18</td>
</tr>
</tbody>
</table>

SMS: Sulfonate-modified silica, EDX: Energy dispersive X-ray
Table 3: Lagergren pseudo second order kinetic model parameters

<table>
<thead>
<tr>
<th>Cation</th>
<th>k₂ (g/mol/min)</th>
<th>b (g/mol/min)</th>
<th>qₑ, calc. (mol/g)</th>
<th>qₑ, exp (mol/g)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>0.07503</td>
<td>0.00116</td>
<td>0.12415</td>
<td>0.12083</td>
<td>0.99971</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2.73839</td>
<td>5.5885×10⁻⁵</td>
<td>0.00451</td>
<td>0.00454</td>
<td>0.99778</td>
</tr>
</tbody>
</table>

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
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 \( \text{M}^{2+} \) and \( \text{M(OH)}^+ \).[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 \( \text{Ca}^{2+} \) adsorption was faster, but at the overall adsorption mechanism [Table 3], the rate was slower than \( \text{Ca}^{2+} \). 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 \( \text{Mg}^{2+} \) was higher than \( \text{Ca}^{2+} \) at pH 5.0 for the same concentration. The higher was the amount of \( \text{Mg}^{2+} \) species; the higher was the rate of the adsorption. Since the radii of sorbates were important in the adsorption,[18] and the radii of \( \text{Mg}^{2+} \) was smaller
through extra particle diffusion and Mg showed that Ca showed that modification of silica sinthesized Adsorption kinetic of intraparticle diffusion model from sugarcane baggase can be done well. confirmed that modification of silica sinthesized CONCLUSION exchange, but Mg was smaller for the adsorption of Ca adsorption energy support the mechanisms. It was DR, model on isotherm experimental data suggest the adsorption mechanisms of Ca and Mg was through different adsorption mechanisms, extra particle diffusion for Ca and external mass transfer for Mg [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 Ca; but it was smaller for the adsorption of Mg. It means that the adsorption of Ca tends to occur through cationic exchange, but Mg through physisorption.[14] CONCLUSION The spectroscopic analysis FTIR and XRD confirmed that modification of silica sinthesized from sugarcane baggase can be done well. Adsorption kinetic of intraparticle diffusion model showed that Ca was adsorbed by SMS adsorbent through extra particle diffusion and Mg through Table 5: Proton stoichiometry for the adsorption of Ca and Mg onto SMS

<table>
<thead>
<tr>
<th>Cation</th>
<th>Proton stoichiometry, ( \chi ) (number of mole of protons released per mole cation adsorbed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(^{2+})</td>
<td>0.05425</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>0.0177299</td>
</tr>
</tbody>
</table>

SMS: Sulfonate-modified silica than Ca\(^{2+}\);[26] then Mg\(^{2+}\) should have the higher potency to be adsorbed by SMS than Ca\(^{2+}\) at initial contact. However, in fact, that Ca\(^{2+}\) adsorption was faster at first. It may result from the strength of interaction of the surface, where toward Ca\(^{2+}\) the interaction was stronger than Mg\(^{2+}\). 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 \( h \) in Table 3. It was the reason why at initial adsorption, Ca\(^{2+}\) has higher adsorption rate than Mg\(^{2+}\) [value of \( h \) in Table 3], but the rate of overall adsorption showed that Ca\(^{2+}\) was slower than Mg\(^{2+}\) [value \( k \), 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 Ca\(^{2+}\) and Mg\(^{2+}\) was through different adsorption mechanisms, extra particle diffusion for Ca\(^{2+}\) and external mass transfer for Mg\(^{2+}\) [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 Ca\(^{2+}\); but it was smaller for the adsorption of Mg\(^{2+}\). It means that the adsorption of Ca\(^{2+}\) tends to occur through cationic exchange, but Mg\(^{2+}\) through physisorption.[14] ACKNOWLEDGMENTS This research was funded by DRPM-DIKTI, DGHE, Ministry of Research, Technology and Higher Education of Republic of Indonesia, Authors would like to thank to DRPM-DIKTI. REFERENCES 1. Kalapathy U, Proctor A, Shultz J. A simple method for production of pure. silica from rice hull ash. Bioresour Technol 2000;73:257-62. 2. El Shafei GM. Adsorption on Silica Surfaces. New York: Marcel Dekker; 2000. p. 35-62. 3. Jal PK, Patel S, Mishra BK. Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions. Talanta 2004;62:1005-28. 4. Tertyth VA, Yanishpolsky VV. Adsorption on Silica Surfaces. New York: Marcel Dekker; 2000. p. 504-58. 5. Shylesh S, Sharma S, Mirakjar SP, Singh AP Silica functionalised sulphonic acid groups: Synthesis, characterization and catalytic activity in acetalization and acetylation reactions. J Mol Catal 2004;212:219-28. 6. Margelese D, Melero JA, Christiansen SC, Chmelka BF, Stucky GD. Direct syntheses of ordered SBA-15 mesoporous silica containing sulfonic acid groups Chem Mater 2000;12:2448-59. 7. Cano-Serrano E, Campos-Martín JM, Fierro JL. Sulfonic acid-functionalized silica through quantitative oxidation of thiol groups. Chem Communications 2003;2:246-47. 8. Morales G, Athens G, Chmelka BF, van Grieken R, Melero JA. Aqueous-sensitive reaction sites in sulfonic acid-functionalized mesoporous silicas. J Cата 2008;254:205-17. 9. Ho YS, McKay G. A comparison of chemisorption kinetic models applied to pollutant removal on several sorbents, Transactions of IChemE. Process Saf Environ Prot 1998;763:332-40. 10. Crini G, Peindy NH, Gimbert F, Robert C. Removal of C.I. basic green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies. Sep Purification Technol 2007;53:97-110. 11. Ngah WS, Hanafiah MA. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents. J Environ Sci 2008;20:1168-76. 12. Kavitha D, Nasimivayam C. Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. Bioresour Technol 2007;98:14-21. 13. Kundu S, Gupta AK. Investigation on the adsorption efficiency of iron oxide coated cement (IOCC) towards As (V)-kinetics, equilibrium and thermodynamic studies. Colloids Surf A Physicochem Eng Asp 2006;273:121-8. 14. Xu D, Tan XL, Chen CL, WangXK. Adsorption of Pb(II) from aqueous solution to MX-80 bentonite: Effect of pH, ionic strength, foreign ions and temperature. Appl Clay Sci 2008;41:37-46. 15. Sivaprakash A, Aravindhan R, Ranghavarao J, Nair BU. Kinetics and equilibrium studies on the biosorption of hexavalent chromium from aqueous solutions using bacillus subtilis biomass. Appl Environ Res 2009;7:45-57. 16. Renugadevi N, Sangeetha R, Lalitha P. Kinetics of the adsorption of methylene blue from an industrial dyeing effluent onto activated carbon prepared from the fruits of minimus

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