



FKIP UNS

Proceeding

The 1ST International Conference on Science, Mathematics,
Environment, and Education (ICoSMEE)

Surakarta, 16-17 September 2017

**"New Challenges and Perspectives of Innovative Research in
Science, Mathematics, Environment and Education for Sustainable
Life continuing the spirit United nation worldwide Decade of
Education for Sustainable Development (DESD)"**



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Faculty of Teacher Training and Education
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CHAIRMAN WELCOME SPEAKS AND REPORT

Assalamu'alaikum Warahmatullahi Wabarakatuh, may peace and God Blessing be upon us all

Honorable chancellor of Universitas Sebelas Maret (UNS) and all Vice-Chancellors, Honorable Dean of Faculty of Teacher Training and Education and all Vice-Deans, Distinguished keynote speakers

Distinguished guests and participants,
Ladies and Gentlemen.

It gives me a great pleasure to welcome all of you and chair this 1st International Conference on Science, Mathematics, Environment and Education (ICoSMEE). This Conference is a collaborative work organized by the department of Mathematics, Chemistry, Biology, Physics and Science Education of the Faculty of Teacher Training and Education of Universitas Sebelas Maret, Surakarta, Indonesia.

The theme of this conference is 'New Challenges and Perspectives of Innovative Research in Science, Mathematics, Environment and Education for Sustainable Life continuing the spirit of United Nation's Decade of Education for Sustainable Development (DESD)'. Indeed, the theme reflects the mission of this conference. This conference attempts to provide holistically novel ideas to address the challenge and issues on global sustainability. The conference is attended by 6 keynote speakers from 4 countries in related disciplines namely:

1. Prof. Amy Cutter-Mackenzie (Southern Cross University, Australia)
2. Prof. Bob Bucat (University of Western Australia)
3. Kathy Malone, Ph. D (Ohio State University, USA)
4. Sidrotun Naim, Ph. D (Universitas Surya, Indonesia)
5. Prof. Steven Gilmour (King's College University, UK)
6. Prof. Sulistyo Saputro, Ph. D (Universitas Sebelas Maret)

According to the theme, this conference covers the interlinked disciplines in mathematics and environmental and natural science and, complements the two side of the DESD's coin with educational discipline. To ensure the contribution of this conference to the scientific world, selected articles will be published in the International Journal of Energy Technology and Policy (INDERSCIENCE Publisher-Scopus Indexed), International Journal of Services Technology and Management (INDERSCIENCE Publisher-Scopus Indexed), Indonesian Journal of Chemistry (Scopus Indexed), IOP Proceedings (Open Access - Scopus Indexed) and regular ICoSMEE Proceedings.

My precious thanks to all the participants who traveled far or near to share experience and to engage with each other. I truly believe the engagement of disciplines from different departments as well universities attending today will certainly make this seminar fruitful and productive. Finally, no chairman's report would be complete without a very sincere word of thank. I would like to thanks the Chancellor of Universitas Sebelas Maret and staffs, the Dean of Faculty of Teacher Training and Education and staffs. I Also indebted to all of my colleagues that work together to organize this conference, many thanks to all the team for a good job. Thank you

Wassalamu'alaikum warrahmatullah wabarakatuh. May peace and God's blessings be upon you all

Surakarta, 16 September 2017
Chairman of the ICoSMEE

Puguh Karyanto, M.Si., Ph.D.

RECTOR SPEAKS

Assalamu'alaikum warahmatullahi wabarakatuh. May peace and God's blessings be upon us

Welcome to Surakarta, Indonesia!

It is a great pleasure to welcome you all to the first International Conference on Science, Mathematics, Environment and Education (ICoSMEE) held in Surakarta, Indonesia. On behalf of Universitas Sebelas Maret (UNS) and the committee, let me express my warmest greetings and appreciation to all speakers and participants (from abroad and within Indonesia) who come to Surakarta to attend this conference to share experiences and works related to Mathematics, Science, Environment and its education. My strong belief is that your safe journey is because of the blessings granted by the Almighty God. It is a honour for this university to have the opportunity to organize this important conference.

Global framework of sustainable development proposed by UN has led to several in-depth scientific discussions focused on studies and reviews of the strategies and progress made so far. The main objective of the performed discussions is to examine the progress and seeking appropriate and more operational strategies addressing the challenge of a better global sustainability achievements. In the discussion, university has an important position in providing solution from both, in result-chain area and in causal-chain area.

It cannot be denied that natural, environmental and education science play as a major backbone underpinning effort in seeking the solution of achieving the goal of sustainable development. Scholarly research, reviews and reports from these majors are of valuable scientific databases in achieving the goal of sustainable development. The spirit of having contribution in the aforementioned UN goal has led the UNS and the committee to organize this conference. This conference involving Science, Mathematics, Environment and Education in order to address the challenge of fulfilling holistic approaches Towards the improvement of the quality of human life without ignoring the sustainability of the environmental system.

This first International Conference on Science, Mathematics, Environment and Education (ICoSMEE) aims at bringing together researchers, educators, scientists, and scholar students in the area of Science, Mathematics, Environment and Education to exchange and share their experiences, ideas, and findings and to discuss practical challenges encountered and the solutions to develop humanity and the quality of human life in a sustainable manner. It is expected that this conference will reach its declared objectives successfully. Let me wish you all a fruitful discussion during the conference and an enjoyable stay in Surakarta.

Thank you very much.

Wassalamu'alaikum warrahmatullah wabarakatuh. May peace and God's blessings be upon you all

Surakarta, 16 September 2017

Rector

Prof. Dr. H. Ravik Karsidi. M.S



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The Study of Adsorption Kinetic of Nitrate (NO_3^-) Anion by Gel Silica from Sugarcane Bagasse

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Abstract. This research aimed to synthesize silica from sugarcane bagasse and to determine adsorption kinetics model. Synthesis of silica was prepared by sol-gel method by adding HCl 1 M into Na_2SiO_3 solution from the synthesis of sugarcane bagasse. The synthesized silica was characterized by FTIR spectroscopy and XRD. The product was then used for the adsorption of NO_3^- anion. Result of characterization by FTIR showed that the silica was successfully synthesized by the presence of the absorption of silanol (Si-OH) and siloxane (Si-O-Si) groups. XRD characterization showed that silica had amorphous structure. The optimum time for the adsorption of anion NO_3^- by silica was 2880 minutes or 2 days. From the results of the study it was found that the adsorption kinetic follows the Lagergren Pseudo-Second-Order model with the rate constant (k_2) of $-3.120 \times 10^3 \text{ min}^{-1}$. Based on the Elovich equation, the initial adsorption rate of $-6.054 \times 10^{-14} \text{ mg g}^{-1} \text{ min}^{-1}$ and the magnitude of surface area and activation energy (β) were $-1.415 \times 10^6 \text{ g mg}^{-1}$. Based on the intra-particle diffusion kinetics and Boyd model, mechanism of nitrate anion adsorption by silica sorbent occurred through two stages of the reaction controlled by intra-particle diffusion and the rate of adsorption process was controlled by the mass transfer rate of the external anion nitrate molecule onto the silica adsorbent.

Keywords: silica; adsorption kinetics; nitrate anion; intra-particle; Boyd

1. Introduction

One of most widely used adsorbents for the adsorption process is silica gel. Silica gel is one of synthetic amorphous silica compounds. One of the solids that can be synthesized become silica gel is sugarcane bagasse. Bagasse is a solid of sugarcane obtained from the remaining sugar production. It is estimated that about 40% of the bagasse produced is still not well utilized. Based on research conducted by Cordeiro et al. (2010), the bagasse of sugarcane processed at 600°C contained of SiO_2 (60.96%), K_2O (9.02%), MgO (8.65%), P_2O_5 (8.34%), CaO (5.97%), Na_2O (0.70%), MnO (0.48%), Al_2O_3 (0.09%), Fe_2O_3 (0.09%), and the lost content in the combustion process (5.70 %). The high content of silica in bagasse can be used as a source of silica for the preparation of sodium silicate solution (Worathanakul et al, 2009). The silica in the bagasse of sugarcane is extracted using NaOH solution into a precursor of sodium silicate to be used as silica gel (Nazriati et al., 2014). Silica gel is a synthesis of synthetic compounds which can be extracted by sol-gel method (de Lima et al., 2011). The formed silica gel can be used as adsorbent for adsorption process.

Based on above mentioned short description, the study of nitrate (NO_3^-) anion adsorption rate by the silica adsorbent at various contact time need to be conducted to describe the nitrate adsorption rate through kinetic modeling of Lagergren pseudo kinetic, intra-particle, and Boyd equations.

2. Research Methods

The materials used in this research were sugarcane bagasse; HCl and NaOH for the separation of silica; HCl and NaOH solutions for maintaining pH; KNO_3 as nitrate source (NO_3^-), free ion water, Whatman filter paper No. 42. Tools used include muffle furnace; Buchner filter device; magnetic stirrer and heater; Shaker; 200 mesh sieve; mortar; and supporting glassware.

Sugarcane bagasse was dried under the sun and then burned. The combustion ash was then calcined at 600°C for 5 hours. The ash was then pounded and sieved to homogenize the ash with a 200 mesh sieve. Twenty grams of homogeneous ash were put into a plastic jar and treated with 1 L HCl 0.1 M. The mixture is stirred with a magnetic stirrer for 2 hours. The mixture is further filtered with a Buchner filter and washed with free-ion-water until neutral. The residue of the filtrate was ash that was free of impurities. Then the ash was put into the oven at 80°C until the mass was constant. The touched ash was incorporated teflon and heated, while it was continuously stirred at 90°C for 1 hour. The ash was then filtered and the filtrate obtained was solution of sodium silicate. The sodium silicate solution was then reacted with HCl 1M while it was stirred constantly until the mixture was gel and pH 7 was formed. The mixture was then filtered off and the residue of silica hydrogel was collected. The silica hydrogels was then washed with water until neutral and dried in the oven at 80°C . The dried silica hydrochlor was a silica gel subsequently characterized by FTIR and XRD. The silica obtained was then used as adsorbent for the nitrate anion adsorption experiments.

The amount of 0.2 gram of silica gel from the synthesis was dissolved into 200 ml of 0.0002 M nitrate solution and stirred with shaker. Each time variation of 5, 10, 15, 30, 60, 120, 180, 1440, 2880, and 5760 min, a 10 mL sample was taken and centrifuged. The centrifuged solution was taken with the volume of 1 mL, and 100x diluted. The solution was then added by 1 mL of 1 M HCl and free concentrations of each contact time of the nitrate ion was measured by UV-Vis spectroscopy. The addition of a given amount of HCl solution was to maintain the system pH which may shifted due to the adsorption of nitrate ions by silica gel. The data were analyzed using the equations of Lagergren pseudo kinetics, Elovich, intra-particle, and Boyd to describe the adsorption process.

3. Results and Discussion

3.1. Results of X-Ray Diffraction Analysis

The XRD diffractogram of silica gel synthesized from the sugarcane bagasse was shown in Fig. 1, whose slope peak appears in the range of $2\theta = 22.9484^\circ$. It is indicated that the resulting silica gel is amorphous. Based on research from Musić *et al.* (2011), the amorphous peak at region $2\theta = 23^\circ$. The peak can shift even lower if the heating increases.. According to Indriyanti *et al.* (2011), the amorphous silica structure can be applied as an adsorbent, better than of the structure of crystalline, this is because the amorphous structure has larger surface areas.

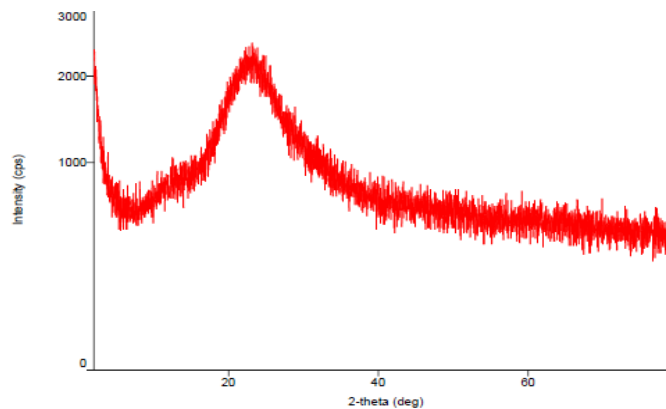


Figure 1. XRD diffractogram of silica gel from sugarcane bagasse

3.2. Spectroscopic Analysis Result of FTIR

Fourier Transform Infrared Spectroscopy (FTIR) is used to determine the presence of functional groups in the material (Mansur et al. 2002). Silica gel is a material having active surface side ie silanol (Si-OH) and siloxane (Si-O-Si) groups having good mechanical stability, large porosity and surface area. Therefore, silica gel can be used as an adsorbent (Istiningrum et al., 2015). The spectrogram of FTIR of silica gel from the bagasse was compared with that of FTIR of Kiesel silica gel 60G to know the quality of synthesis results as can be seen in Figure 2.

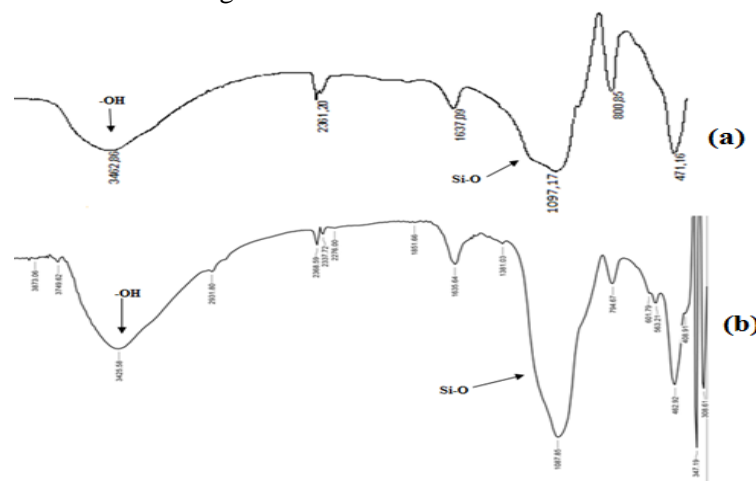


Figure 2. FTIR spectra (a) Kiesel Gel 60G and (b) silica gel from sugarcane bagasse.

The interpretation of the FTIR spectrogram of silica gel was depicted in Table 1.

Table 1. Interpretation of FTIR silica gel from sugarcane bagasse

No.	Functional Groups	Wave Number (cm ⁻¹)	
		Silica Gel Result of Synthesis	Kiesel Gel 60G
1.	Bending vibration ≡Si-O on ≡Si-O-Si≡	462,92	471,16

2.	Symmetrical stretching vibration of $\equiv\text{Si-O}$ on $\equiv\text{Si-O-Si}\equiv$	794,67	800,85
3.	Asymmetric stretching vibration of $\equiv\text{Si-O}$ on $\equiv\text{Si-O-Si}\equiv$	1087,85	1097,17
4.	Vibration stretching $-\text{OH}$ on $\equiv\text{Si-OH}$	3425,58	3462,86
5.	Bending vibration $-\text{OH}$ on the water molekul	1635,64	1637,09
6.	Stretching vibration C-H	2931,80	-

In general, the absorption bands appearing on silica gel spectra of synthesis results from the bagasse show functional groups of silanol (Si-OH) and siloxan (Si-O-Si) groups (Mujiyanti *et al*, 2013). Based on the Table 1, the functional groups shown by FTIR of silica gel from bagasse was closely similar to that of silica Kiesel gel 60 spectra. The main peak of silica gel spectra was the vibration of the -OH group (hydroxyl group), and $\equiv\text{Si-OH}$ groups which appears at 3425.58 cm^{-1} wave numbers. The second peak represents functional group of siloxane groups ($\equiv\text{Si-O-Si}\equiv$) which appears at 1087.85 cm^{-1} wave numbers. The presence of functional groups $\equiv\text{Si-O-Si}\equiv$ is amplified by a peak at 462.92 cm^{-1} wavelength indicating $\equiv\text{Si-O}$ bond (Suka *et al.*, 2008). In addition to the functional groups possessed by silica gel, the silica gel FTIR spectra of the synthesized product also have other functional groups derived from impurities, which can not be completely cleaned. Therefore, it can be concluded that the functional group of silica gel from bagasse was similar to that of the Kiesel gel 60G.

3.3. Kinetics of NO_3^- Anion Adsorption

Contact time is crucial in the adsorption process. This is because the contact time allows the diffusion process and the adherence of the adsorbate molecule to take place better, unless it reaches optimum. The longer the contact time, the more substances were adsorbed (Mar'atus S. & Saputro, 2012). In this research, the adsorption process was carried out by introducing 0.2 gram of adsorbent (synthetic silica gel) into 200 mL anion solution of NO_3^- 0,001 M with variation of contact time 5, 10, 15, 30, 60, 120, 180, 1440, 2880, and 5760 minutes at 30°C and pH 5.

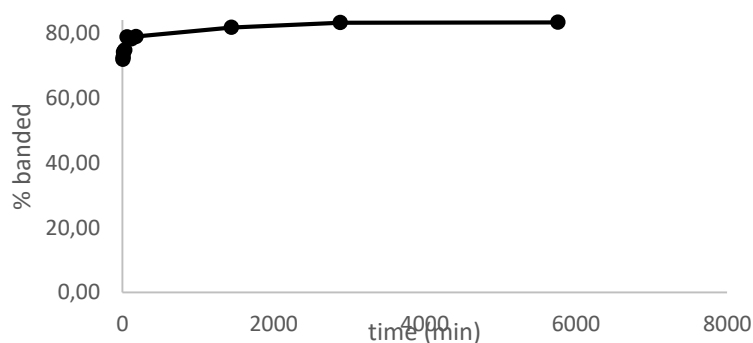


Figure 3. The effect of contact time (minutes) to percentage of nitrate anions adsorbed

Figure 3 shows that the longer the contact time, the higher the percentage of NO_3^- anions bonded by the silica gel adsorbent. During the entire adsorption contacts, the percentage of adsorption was slight different with few increment in later time duration. From the slight different, the optimum time determination on NO_3^- anion adsorption was based on the highest percentage of NO_3^- anion bonding. It was 83.31%, which occurred at 2880 minutes or 2 days. At 5 minute contact, the adsorbed nitrate anion was in high amount, then slightly increased at contact time of 10 min. The adsorbed nitrate number increased significantly until it reached the optimum contact time. According to Mohamad (2013), after

the equilibrium time, the adsorption of nitrate anion was about constant as the relevant adsorbent surface active groups.

3.4. Kinetic Model of Anion NO_3^- Adsorption

In the adsorption process, a reaction rate equation which depended on the adsorption capacity of an adsorbent might be comply the information of the adsorption process and the reaction mechanism (Ikhsan *et al.*, 2013). The adsorption kinetics model used in this research data were Lagergren pseudo first order, Lagergren pseudo second order, Elovich, Intra-particles diffusion, and Boyd.

Lagergren pseudo kinetic model showed poor fit for first-ordered kinetic, but it fitted with good straight line for the second ordered kinetic, as given in Figures 4 and 5. The equation of the straight line is then interpreted so that the adsorption kinetics parameter will be obtained as in Table 2 which will determine the binding reaction order in silica gel.

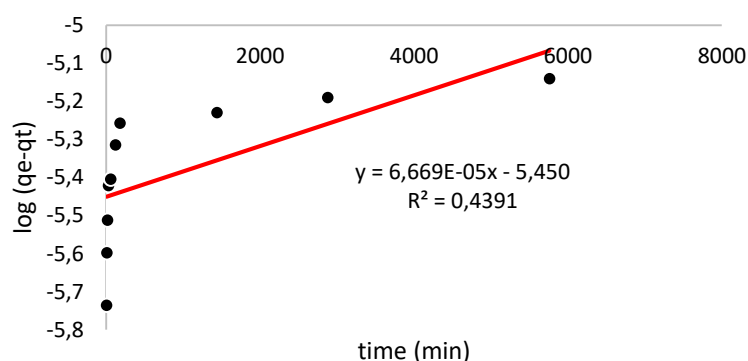


Figure 4. Lagergren Pseudo-First-Order Kinetic model of anion nitrate binding.

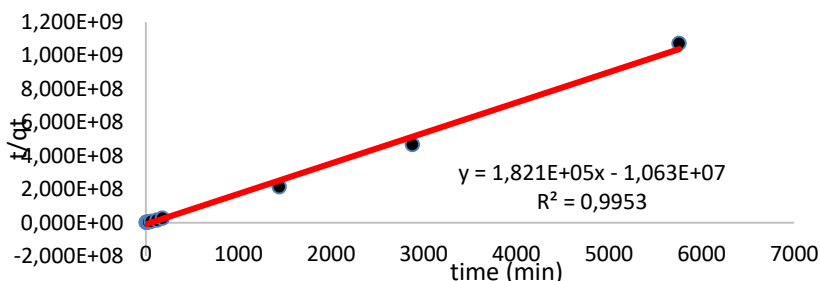


Figure 5. Graph of kinetic model Lagergren Pseudo-Second-Order binding of anion nitrate.

Table 2. Lagergren Kinetics Parameters on Anion Nitrate Adsorption

Kinetic Models	Parameter	Value
<i>Lagergren Pseudo-First-Order</i>	q_e experiment (mg g^{-1})	$1,263 \times 10^{-5}$
	k_1 (min^{-1})	$1,536 \times 10^{-4}$
	q_e (mg g^{-1})	$3,548 \times 10^{-6}$
	R^2	0,4391
	R	0,6626
<i>Lagergren Pseudo-Second-Order</i>	k_1 (min^{-1})	$-3,120 \times 10^3$
	q_e (mg g^{-1})	$5,491 \times 10^{-6}$
	R^2	0,9953
	R	0,9976
	h	$-94,071 \times 10^{-9}$

Based on the parameter of the correlation coefficient (R) in Table 2 above, the adsorption kinetics follows the Lagergren pseudo second order equation. The Lagergren pseudo second order equation was given by

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t$$

Where q_e and q_t are the capacity of SiO₂ to adsorb nitrate ions at equilibrium time t , respectively (mmol g⁻¹), k_1 and k_2 are the reaction first and second order constants, respectively, whereas h is initial adsorption rate with the value of $(k_2 q_e^2)$. The value of q_e calculations from Lagergren pseudo second order kinetics was also close to the value of q_e experiments. The high correlation rates of the results in this research assured that the reaction of nitrate anion binding to the silica gel sorbent reacts through a two-order reaction. The adsorption process following the Lagergren pseudo second order kinetic model means that the velocity of silica gel adsorption to the nitrate anion per time unit is directly proportional to the quadratic empty adsorbent capacity ($q_e - q_t$). The high adsorption initial rate (h) indicates that the adsorption progresses rapidly. This was supported by the results of this study as given by Figure 3 from which the adsorption occurred significantly since the start of contact time. Adsorption of nitrate anion by rapid silica gel adsorbent is possible because of the abundance of active site availability and the porous structure of the silica gel sorbent causing large surface area (Ejikeme *et al.*, 2014). The binding rate constant (k_2) that occurs in accordance with the Lagergren Pseudo-Second-Order model was $-3,120 \times 10^3 \text{ min}^{-1}$.

The plot of q_t versus $\ln t$ is used to identify Elovich's kinetic model (Figure 6). The equation of Elovich's kinetic model was as following.

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$$

The kinetic graph of Elovich describes the linear line with the slope $1/\beta$ and the intercept $\frac{1}{\beta} \ln(\alpha\beta)$ where α is the initial adsorption rate and β is the surface area and the activation energy. $\frac{1}{\beta}$ indicates the number of active sites on the surface of the sorbent that can absorb adsorbate. Whereas $\frac{1}{\beta} \ln(\alpha\beta)$ shows the amount of adsorption at $\ln t=0$ or $t=1$ min where the value is used to understand the adsorption behavior in the early stages (Zuas *et al.*, 2014). Based on Table 3, it was found that the initial adsorption rate (α) was $-6.054 \times 10^{-14} \text{ mg g}^{-1} \text{ min}^{-1}$. While the magnitude of surface area and activation energy (β) is $-1.415 \times 10^6 \text{ g mg}^{-1}$. The Elovich equation assumes that the solid surface is actually heterogeneous (Munifah *et al.*, 2011).

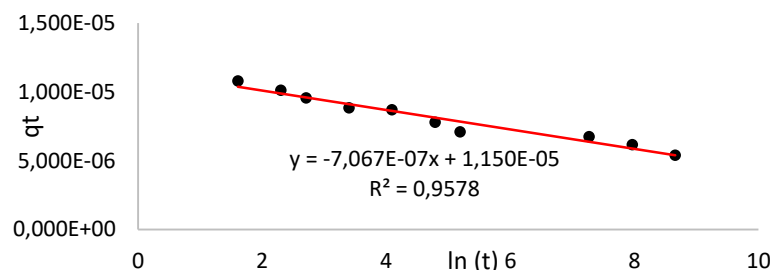


Figure 6. Elovich Kinetic Model Binding of Nitrate Anion

Table 3. Elovich's kinetic model parameters

Kinetic Model	Parameter	Value
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Elovich	α (mg g ⁻¹ min ⁻¹)	$-6,054 \times 10^{-14}$
	β (g mg ⁻¹)	$-1,415 \times 10^6$
	R ²	0,9578
	R	0,9787

Intra-particle diffusion model can be used to explain the adsorption mechanism. The intra-particle equation is given below.

$$q_t = k_{id}t^{1/2} + C$$

The calculation using intra-particle equation provides certain numbers of linear line which describes the number of stages of the adsorption occurred. The adsorption process of nitrate anions by silica consisted of two stages, namely the movement of particles from outside the adsorbent to the surface of the adsorbent and followed by the diffusion of the molecules into the pores. Intra-particle diffusion is generally a slow process and is considered a rate-determining stage in the adsorption process (Ho & McKay, 2000).

Table 4. Parameters of the intra-particle diffusion diffusion kinetics model in the adsorption process of anion nitrate

Kinetic Model	Parameter	Value
Intra-Particle Diffusion	k_{id1} (mg g ⁻¹ min ^{-0,5})	$-2,973 \times 10^{-7}$
	C_1 (mg g ⁻¹)	$1,097 \times 10^{-5}$
	R_1^2	0,9413
	R_1	0,9702
	k_{id2} (mg g ⁻¹ min ^{-0,5})	$-2,778 \times 10^{-8}$
	C_2 (mg g ⁻¹)	$7,599 \times 10^{-6}$
	R_2^2	0,958
	R_2	0,9788

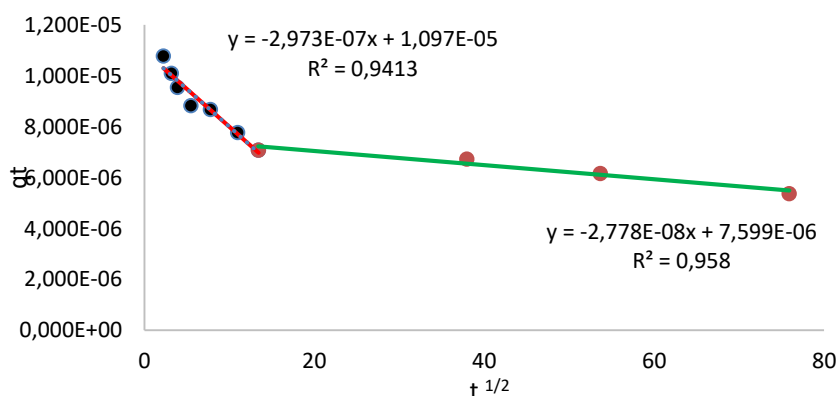


Figure 7. Two stages calculated from the intra-particle diffusion equation

Figure 7 shows the presence of gradient variations and this suggests that intra-particle diffusion is not the only rate-determining stage in this adsorption process (Holle *et al.*, 2013). From plot q_t to $t^{1/2}$ (Figure 7) shows that the resulting plot has two linear portions, indicating that the adsorption process of nitrate anion by silica gel sorbent occurs in two stages of reaction. The first linear part (k_{id1}) corresponds to the diffusion of the boundary layer (film diffusion) occurring on the external surface of the adsorbent.

The second linear part (k_{id2}) is a slow adsorption stage, which is related to intra-particle diffusion. This suggests that the adsorption process is not only through the process of intra-particle diffusion but also through the film diffusion process (Nethaji *et al.*, 2013). Table 4 shows that linear thickness of the first linear portion relative to the film diffusion (C_1) is greater than the thickness of the boundary layer in the second linear portion relative to the intra-particle diffusion (C_2). Consequently the rate constant of the intra-particle diffusion stage (k_{id2}) is smaller than that of the film diffusion rate (k_{id1}). Therefore, the adsorption process of nitrate anion by sorbent silica gel is controlled by intra-particle diffusion (Zulfikar, 2012). The rate of adsorption process is controlled by the mass transfer rate of the external anion nitrate molecule into the silica gel adsorbent (Zuas *et al.*, 2014).

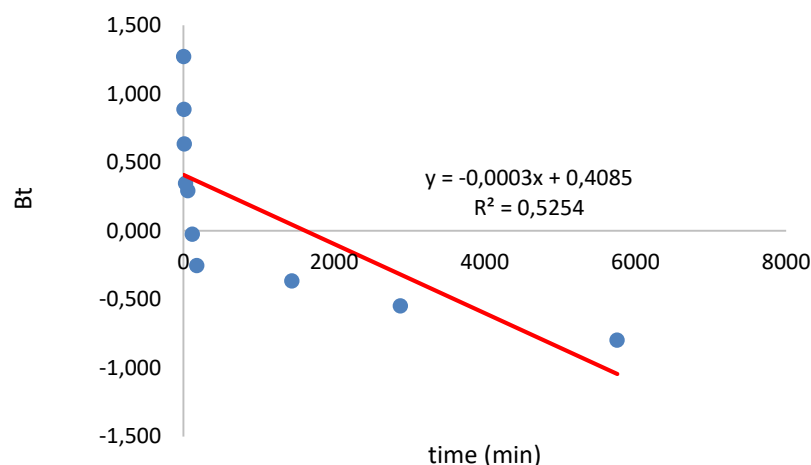


Figure 8. Boyd kinetic model on nitrate adsorption by silica

To confirm the actual slow phase as the determining stage of the adsorption process of nitrate anion by the silica gel sorbent, Boyd kinetic model were used. The Boyd kinetic equation can be expressed as follows

$$B_t = -0,4977 - \ln(1 - F)$$

According to Figure 8, the line that calculated from the Boyd equation do not pass through the origin (0,0), and do not show linear line fitting the experimental data, meaning that the main process of the adsorption by silica gel sorbents are through external mass transfer (Nethaji *et al.*, 2013). Based on the modeling using the intra-particle and Boyd equations, the nitrate anion adsorption kinetics model by the silica gel sorbent follows the intra-particle diffusion model. Thus the adsorption mechanism of nitrate anion by silica gel sorbent occurs through two stages of the reaction controlled by intra-particle diffusion and the rate of adsorption process is controlled by the mass transfer rate of the external nitrate anion molecule into the silica gel adsorbent.

4. Conclusion

The results of silica gel characterization of bagasse through FTIR and XRD spectroscopy, synthetic silica gel having silanol and siloxy functional groups, as well as amorphous structures showing patterns similar to the 60G gel Kiesel.

The models by Lagergren pseudo order kinetics, Elovich, intra-particle, and Boyd explains that nitrate anion adsorption mechanism by silica gel sorbent occurred with high initial rate, and through two stages of the reaction controlled by intra-particle diffusion, with the rate of adsorption process was controlled by the mass transfer rate of the external anion nitrate molecule into the silica gel adsorbent.

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