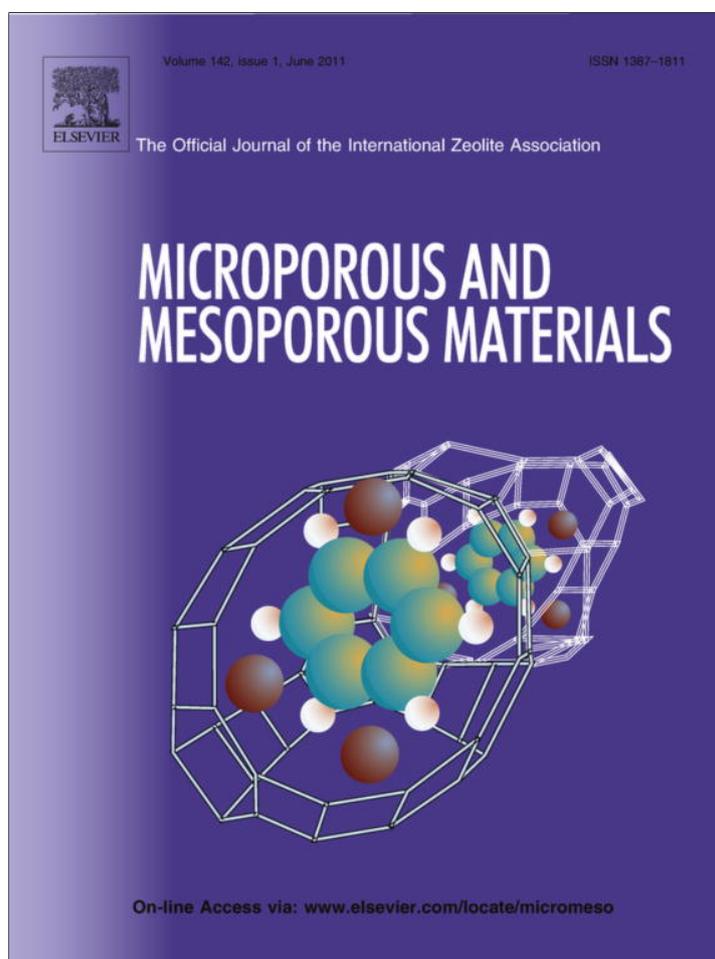


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Utilization of rarasaponin natural surfactant for organo-bentonite preparation: Application for methylene blue removal from aqueous effluent

Alfin Kurniawan^a, Hogiartha Sutiono^a, Yi-Hsu Ju^b, Felycia Edy Soetaredjo^a, Aning Ayucitra^a, Aditya Yudha^a, Suryadi Ismadji^{a,*}

^aDepartment of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia

^bDepartment of Chemical Engineering, National Taiwan University of Science and Technology, 43, Sec. 4 Keelung Rd., Taipei 106, Taiwan

ARTICLE INFO

Article history:

Received 26 May 2010

Received in revised form 24 November 2010

Accepted 26 November 2010

Available online 4 December 2010

Keywords:

Organo-bentonite

Rarasaponin

Adsorption

ABSTRACT

Rarasaponin that belongs to the natural surfactant was used as modifying agent for preparation of organo-bentonite. This surfactant was extracted from wild plant *Sapindus rarak DC*. The modifying process was conducted by microwave thermal irradiation. The characterization of bentonite and its modified form was carried out using FTIR, nitrogen sorption and XRD analysis. In order to test the adsorption capability of organo-bentonite, batch adsorption experiments of methylene blue from aqueous solution using this adsorbent were conducted under several operating conditions. The highest adsorption capacity (q_m) of organo-bentonite obtained in this study was 256 mg/g while for raw bentonite was 194 mg/g at 60 °C. The adsorption isotherm and kinetic data were modeled using several well known models. Freundlich isotherm model represented the adsorption equilibrium data better than the Langmuir isotherm model. For the kinetic model, the pseudo-second order gave reasonable parameters and could correlate the kinetic data well. New mechanisms of organo-bentonite formation as well as adsorption of methylene blue on the surface of organo-bentonite were also proposed in this paper.

© 2010 Elsevier Inc. All rights reserved.

1. Introduction

Dyes, which are usually produced by synthetic process, are generally characterized by complex aromatic molecular structure [1]. The presence of dyes in aqueous effluent such as in river stream can be noticed easily because dyes are colored and highly visible. The discharge of dyes directly into aqueous effluent can endanger living organism and its aquatic ecology because most dyes are toxic. Accumulation of dyes in water reduces the penetration of solar radiation into the body of water and harms the photosynthesis activity by plant and phytoplankton and subsequently significantly affects aquatic life and food web. Some dyes also possess carcinogenic and mutagenic properties which are very harmful to human life if accumulate in their body for a long time [2].

Several conventional methods for the treatment of wastewater containing dyes are available [3], and the most efficient one is the adsorption process, because it is simple in terms of operation and can remove the contaminant even at very low concentration. The success of an adsorption process completely depends on the correct choice of the adsorbent, and the most widely used adsorbent for this purpose is activated carbon. However, the main disadvantage of using activated carbon as the adsorbent is its high cost.

Therefore, the use of activated carbon as adsorbent in large scale treatment of wastewater containing dyes is economically not feasible. In order to overcome this major drawback, a number of studies for searching alternative adsorbents for wastewater treatment purpose have been conducted [4–7].

Modification of various kinds of clay and clay minerals using various kinds of chemical modifying agents for the removal of various organic compounds from water or wastewater has been widely studied, and the results also had been summarized by several authors [8–10]. The use of chemicals for modification of clays and clay minerals often creates more serious problem to environment and commonly needs expensive waste treatment system for unused or excess chemicals. Therefore, research on the utilization and modification of clays and clay minerals for wastewater treatment purpose (especially for dyes removal) should be directed towards the application of environmental friendly or natural chemicals as modifying agents. In this study we employed rarasaponin extracted from *Sapindus rarak DC* as a natural surfactant for bentonite modification. To the best of our knowledge, there is no information available regarding the use of this natural surfactant as modifying agent for organo-bentonite preparation. Furthermore, the chemical reaction mechanism between rarasaponin and silanol group of bentonite during modification is presented in this paper. New adsorption mechanism between methylene blue and carbonyl group from organo-bentonite is also proposed.

* Corresponding author. Tel.: +62 313891264; fax: +62 313891267.

E-mail address: suryadiismadji@yahoo.com (S. Ismadji).

2. Materials and methods

2.1. Chemicals

Methylene blue (basic blue 9, C.I. 52015; chemical formula $C_{16}H_{18}N_3SCl \cdot 3H_2O$; MW, 373.90 g/mol) was purchased as analytical-laboratory grade from Sigma–Aldrich and used without any further treatment.

2.2. Rarasaponin extraction

Rarasaponin was extracted from dried fruits of wild plant *S rarak DC*. *S rarak DC* is a tall tree which originated in South East Asia and is now widely distributed in Asia and Africa. The fruits were obtained from Klaten, Central Java, Indonesia. The extraction procedure of rarasaponin from fruits of wild plant *S rarak DC* was carried out as follows: the dried fruits of *S rarak DC* were crushed by a micro-hammer mill (JANKE AND KUNKEL) and sieved in vibration screen (RETSCH) to obtain powder with particle size of 106–150 μm . Twenty grams of *S rarak DC* powder was added to 200 mL of distilled water. The mixture was then heated at 80 °C for 60 min. The extract was then separated from the solid using centrifugation (Hettich Zentrifugen EBA-20) for 10 min at 4000 rpm. The supernatant was then concentrated by vacuum evaporation (BUCHI RE 121) and dried in a vacuum drying oven. The rarasaponin crystal were collected and crushed by using micro-hammer mill, sieved using vibration screen (RETSCH) until its particle size was between 106–150 μm .

2.3. Organo-bentonite preparation

Raw bentonite used in this study was obtained from mining site located in Pacitan, East Java, Indonesia. The cation exchange capacity (CEC) of bentonite was determined using ASTM C837-99 method. The CEC value of the bentonite was 67.2 meq/100 g. The point of zero charge (pH_{pzc}) of raw bentonite was 3.71. This value was determined by pH titration procedure [11]. The chemical element composition of raw bentonite used in this study was analyzed by atomic absorption spectrophotometer (AAS SHIMADZU AA6200) with flame emission. The results are summarized in Table 1.

Prior to modification, bentonite was purified using hydrogen peroxide solution to remove any organic and inorganic impurities; raw bentonite was suspended in hydrogen peroxide solution for 18 h. After the purification was completed, the mixture was heated to remove excess hydrogen peroxide. Subsequently, the bentonite was repeatedly washed with distilled water, separated from solution, and dried in a force circulation oven at 110 °C for 24 h. The dried bentonite was then crushed into powder.

The preparation of organo-bentonite was conducted using the following procedure: 0.5 g of rarasaponin was dissolved in 25 mL of distilled water. Subsequently, 5 g of bentonite powder was

added to the solution. The mixture was then heated by microwave thermal irradiation (InexTron) for 90 s at 700 watt. The irradiation time above 90 s caused the destruction of bentonite as well as rarasaponin structure, while irradiation time below 90 s didn't allow the attachment of rarasaponin structure onto bentonite. The solid was then separated from the mixture, repeatedly washed using distilled water, and dried at 110 °C for 24 h.

2.4. Characterization of raw bentonite and organo-bentonite

The characterization of raw bentonite and its modified form was conducted using techniques such as FTIR, nitrogen sorption, and X-ray diffraction (XRD). The FTIR qualitative analysis was carried out in FTIR SHIMADZU 8400S using KBr method. The pore characteristic of bentonite and organo-bentonite was measured by nitrogen adsorption at $-196\text{ }^\circ\text{C}$ in a Quadrasorb SI. Prior to the gas adsorption measurements, the samples were degassed at 150 °C in vacuum condition for 24 h. The nitrogen adsorption-desorption isotherms were measured over relative pressure (P/P_0) from approximately 10^{-3} to 0.998. The pore size distribution of raw bentonite and organo-bentonite was determined by density functional theory (DFT) model in which the software available within the instrument, and medium regularization was used for the calculation. The X-ray diffraction (XRD) patterns of powder were recorded on a Rigaku Miniflex Goniometer instrument at 30 kV and 15 mA, using $\text{Cu}\alpha$ K radiation at a step size of 0.01°.

2.5. Adsorption studies

The adsorption process was conducted by adding a known amount of raw bentonite or organo-bentonite into 250 mL iodine flasks containing 100 mL of methylene blue solution with an initial concentration of 500 mg/L. The solutions were shaken in water-bath shaker (Memmert) at 100 rpm for 35 min at various temperatures (30, 45, and 60 °C). After the process was completed, the flasks were then removed from the bath and the mixtures were centrifuged at 3500 rpm for 5 min to separate the solution from the organo-bentonite. The concentration of methylene blue solution was measured quantitatively with spectrophotometer (SHIMADZU UV/VIS-1700 PharmaSpec) at maximum wavelength (664.1 nm). The amount of methylene blue adsorbed at equilibrium was determined by the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where q_e is the amount of methylene blue adsorbed at equilibrium (mg/g organo-bentonite), C_0 and C_e (mg/L) are the liquid phase concentrations of methylene blue at initial and equilibrium, respectively. V is the volume of methylene blue solution (L) and m is the mass of organo-bentonite used (g).

For kinetic study, the adsorption process was conducted by adding a fixed amount of organo-bentonite (0.5 g) into a series of 250 mL iodine flasks that containing 100 mL methylene blue solution at various initial concentrations of 300, 500, and 700 mg/L. The flasks containing the mixtures were then shaken in a temperature controlled water bath at a certain temperature. At certain time interval (every 5 min for the first 30 min, and subsequently the samples were analyzed every 1 min until 35 min), the concentration of methylene blue in the solution was measured quantitatively with spectrophotometer (SHIMADZU UV/VIS-1700 PharmaSpec). The amount of methylene blue adsorbed at a time interval t (q_t) was calculated using the equation

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

Table 1
Chemical element analysis result of raw bentonite.

Element	Percentage of mass fraction (w/w)
Si	60.79
Al	20.84
Ca	4.77
Mg	1.21
Fe	0.31
Na	0.28
K	0.24
Mn	0.07

Here q_t is the amount of methylene blue adsorbed at time t (mg/g organo-bentonite), and C_t (mg/L) is the liquid phase concentrations of methylene blue at time interval t .

3. Results and discussion

3.1. Rarasaponin

Rarasaponin belongs to alkaloids group which has one or more oligosaccharide [12]. The FTIR spectra of rarasaponin and its functional group are given in Fig. 1 and Table 2, respectively. From Table 2, it can be seen that rarasaponin has functional groups such as hydroxyls, ester carbonyls, aromatic rings, and also alkanes group both in aliphatic and alicyclic structure. The absorption peak around 2345 cm^{-1} which belong to nitrile group may be due to impurities or some type of contaminants.

3.2. Characterization of bentonite and organo-bentonite

FTIR absorption spectra of bentonite and its modified form are given in Fig. 2, while the functional groups and its corresponding wave number values are summarized in Table 3. Fig. 2 and Table 3 reveal that the specific surface functional groups exist in raw bentonite and organo-bentonite. Table 3 indicates that the absorption peak at 1257.23 cm^{-1} appears only in organo-bentonite spectra, this wave number is assigned to the asymmetrical stretching vibration of C–O from carbonyl group from rarasaponin. The stretching vibration of C–O found in organo-bentonite indicates that carbonyl group from rarasaponin was intercalated into raw bentonite, leading to the formation of organo-bentonite.

The nitrogen sorption isotherms of raw bentonite and its modified form are depicted in Fig. 3 Both raw bentonite and organo-bentonite possess mesoporous structure as indicated by the presence of hysteresis that lies between adsorption and desorption isotherm curve at relative pressures above 0.5. The BET surface area of raw bentonite and organo-bentonite are 92.3

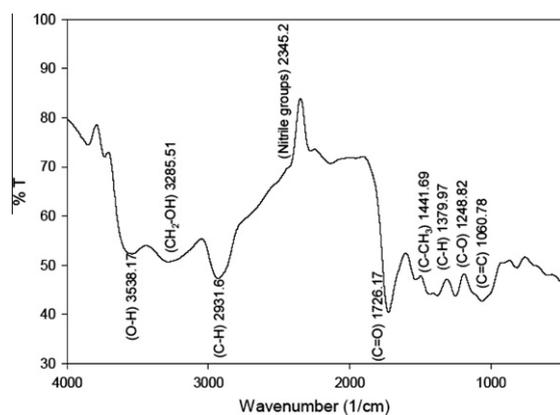


Fig. 1. The FTIR absorption spectra of rarasaponin derived from *Sapindus rarak DC*.

Table 2
Functional groups that contained in rarasaponin derived from *Sapindus rarak DC*.

Functional groups	Wavenumber (1/cm)
O–H stretch, free hydroxyl	3538.17
CH ₂ stretch bonded with hydroxyl group	3285.51
C–H stretch	2931.6
C=O stretch (ester carbonyls group)	1726.17
C–CH ₃ bend	1441.69
C–H bend bonded with hydroxyl group	1379.97
C–O stretch (carbonyls group)	1248.82
C=C stretch (aromatic rings group)	1060.78

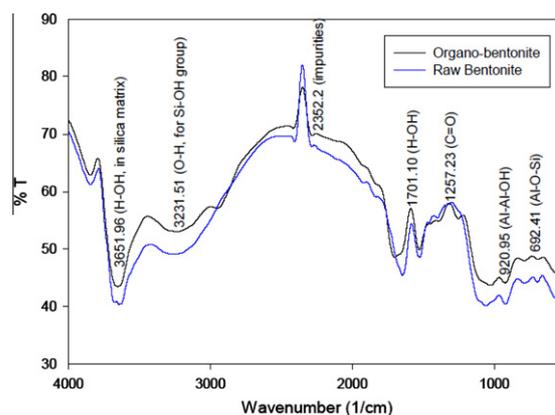


Fig. 2. The FTIR absorption spectra for raw bentonite and organo-bentonite.

Table 3
The functional groups of raw bentonite and organo-bentonite.

Functional groups	Wavenumber (1/cm)	
	Raw Bentonite	Organo-bentonite
O–H stretch for H ₂ O in the silica matrix	3635.57	3651.96
O–H stretch of silanol (Si–OH) groups	3279.73	3231.51
O–H bend, for adsorbed H ₂ O at bentonite interlayer	1646.13	1701.10
C=O stretch of deacylated carbonyl group	–	1257.23
Si–O–Si stretch of the tetrahedral sheet	1027.88	1057.99
Al–Al–OH bend	920.95	922.87
Al–O–Si bend (for octahedral Al)	697.22	692.41
Si–O–Si bend	437.81	466.74

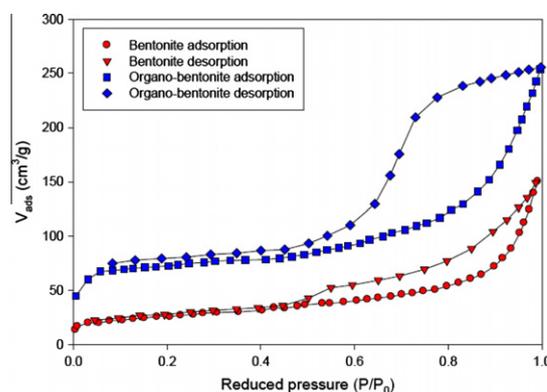


Fig. 3. Nitrogen adsorption–desorption isotherms of raw bentonite and organo-bentonite.

and $84.6\text{ m}^2/\text{g}$, respectively. Total pore volume for raw bentonite is $0.61\text{ cm}^3/\text{g}$, while the organo-bentonite has higher pore volume ($0.87\text{ cm}^3/\text{g}$). The higher pore volume of organo-bentonite than that of raw bentonite was due to the intercalation of rarasaponin molecules into the structure of bentonite and causing the expansion of interlayer spacing of bentonite. The pore size distribution of raw bentonite and its modified form was determined by DFT (Density Functional Theory) analysis and the results are shown in Fig. 4. This figure clearly shows that both of these materials have pore width that distribute mainly from 15 to 80 \AA , which confirmed the mesoporous nature of both adsorbents. This result was in agreement with other previous works [13,14].

Physical characterization of layer structure for bentonite and organo-bentonite was conducted by X-ray diffraction. The XRD

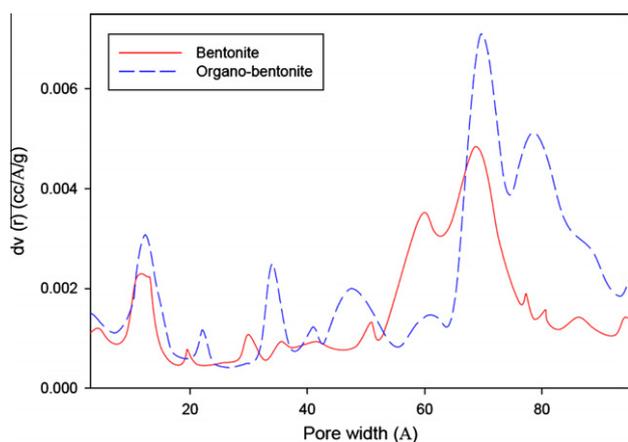


Fig. 4. Pore size distribution of raw bentonite and organo-bentonite.

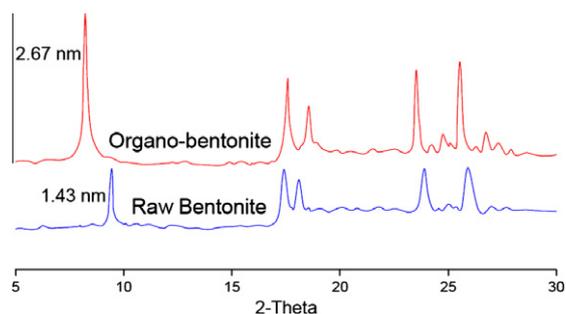


Fig. 5. XRD analysis results for raw bentonite and organo-bentonite.

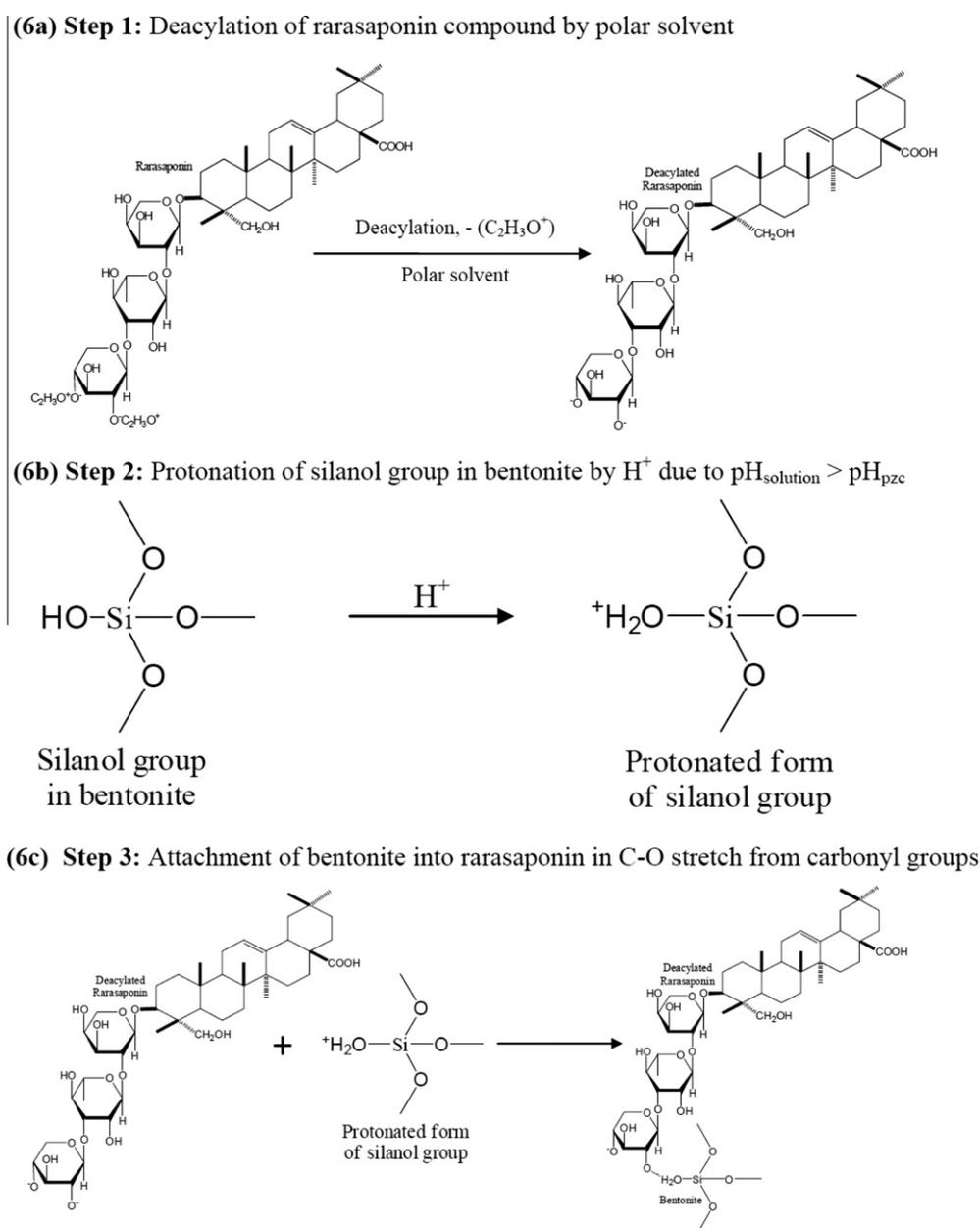


Fig. 6. The formation mechanism of organo-bentonite.

results for raw bentonite and organo-bentonite are shown in Fig. 5. The diffraction peaks of both raw bentonite and organo-bentonite appear at 9.44° and 8.22° , respectively. Other peaks are also observed in the angle range of $5\text{--}30^\circ$. The basal spacing (d_{001}) of raw bentonite and organo-bentonite are 1.42 and 2.67 nm, respectively. The increase of basal spacing in organo-bentonite indicates that rarasaponin molecules were partially intercalated at bentonite interlayer spaces and expanded its interlamellar spacing and the later will promote methylene blue removal from aqueous solution.

3.3. Formation mechanism of organo-bentonite

In this paper, the formation mechanism of organo-bentonite from bentonite and rarasaponin as a natural surfactant was proposed based on the following steps: the first step is the deacylation reaction of rarasaponin structure as indicated in Fig. 6. Rarasaponin, which belongs to biomacromolecules that contains two acyl groups ($\text{C}_2\text{H}_3\text{O}^+$) attached in carbonyl structure. This acyl group attached to carbonyl structure will be deacylated when it is diluted

in polar solvents such as water, sodium methoxide, or methanol as reported by Asao et al. [12]. This phenomenon will cause an imbalance negative charge on oxygen atom in both carbonyl surfaces. This negatively charge of oxygen atoms in carbonyl groups will become the active binding sites for raw bentonite during the next step of reaction.

The second step (Fig. 6b), the surface of silanol group (Si–OH) in tetrahedral sheet of bentonite will be protonated by the excess of H^+ ions due to $\text{pH}_{\text{solution}} > \text{pH}_{\text{pzc}}$ [15]. The excess of H^+ ions in solution will penetrate into raw bentonite surface and then attack the hydroxyl groups in silanol, causing an imbalance positive charge on its surface. The successive of protonation in silicate layer of bentonite can be readily followed by the changes in characteristics of absorption spectra corresponded to vibration of OH groups and octahedral exchangeable cations, leading to the formation of Si-rich phase in bentonite structure [16–18]. The protonation of silanol group in raw bentonite produce water molecules (H_2O) with imbalance positive charge on its surface as indicated in step 2 in Fig. 6b. In the final step, the balancing of the negative charge

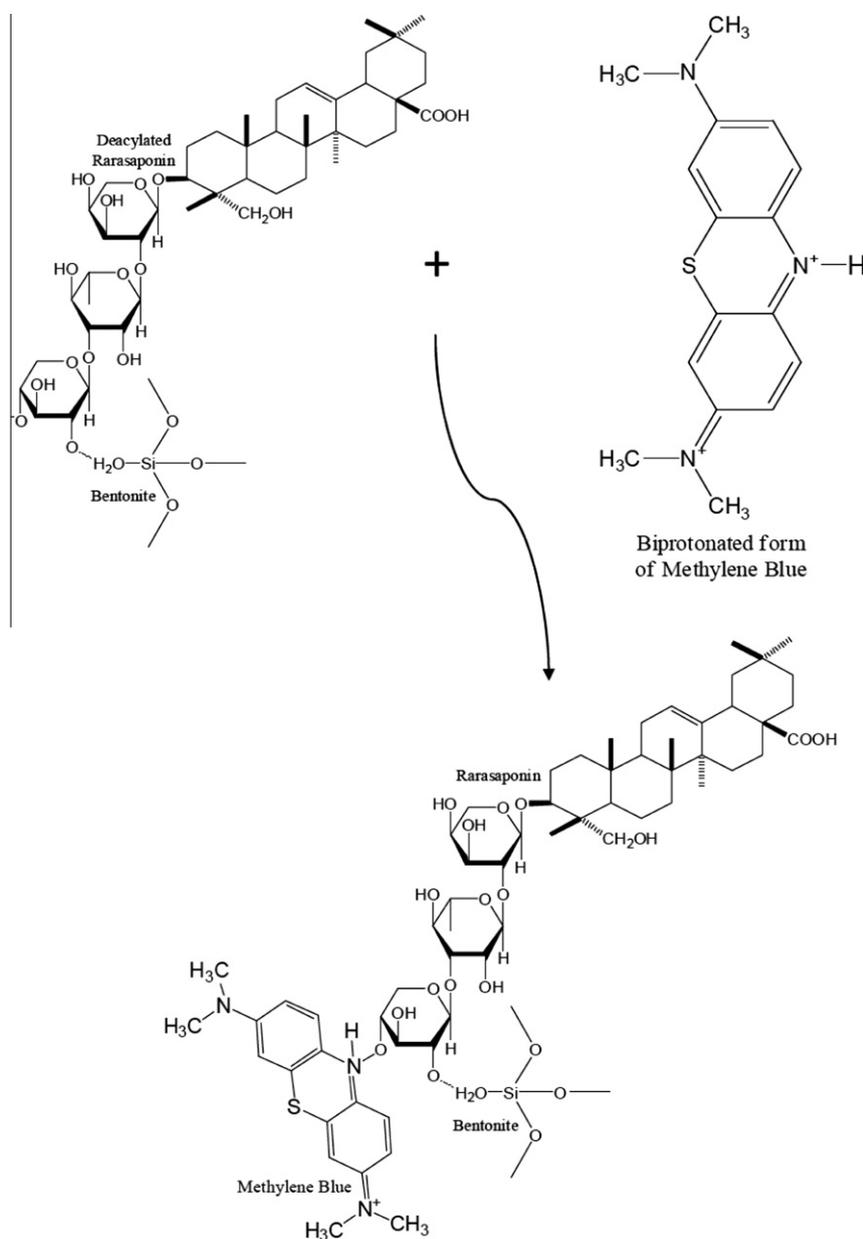


Fig. 7. The proposed mechanism of methylene blue chemisorptions onto the surface of organo-bentonite.

of oxygen atom in one side of deacylated carbonyl group with protonated silanol group (Si-OH_2^+) in tetrahedral sheet of raw bentonite occurred leading to the formation of rarasaponin organo-bentonite as shown in Fig. 6c.

3.4. Chemisorption mechanism between methylene blue and organo-bentonite

Rarasaponin organo-bentonite contains unoccupied side of deacylated carbonyl groups as indicated in Fig. 6. Methylene blue is a cationic dye and has positive charged surface generated from nitrogen center on its organic framework. Biprotonation form of this dye usually occurs at low pH or acid condition as illustrated in Fig. 7 [19]. The double positive charge of nitrogen center available in methylene blue structure plays an important role during the adsorption of this dye in the surface of organo-bentonite. The imbalance negative charge of oxygen atom in unoccupied deacylated carbonyl group will be neutralized by immonium atom (N^+) generated in the cyclohexene structure of methylene blue.

3.5. Adsorption studies

3.5.1. Effect of initial solute concentration

The initial solute concentration provides a necessary driving force to overcome mass transfer resistance between the liquid and the solid phase [1]. The variation in initial solute concentration influences the amount of methylene blue adsorbed and its removal efficiency. Fig. 8 shows the effect of initial concentration of meth-

ylene blue on the amount uptake by raw bentonite and organo-bentonite. The increase of initial solute concentration caused an increase on the amount of methylene blue adsorbed onto the raw bentonite and organo-bentonite surface.

By increasing the initial concentration, the mass transfer resistance (k_x) in the liquid phase becomes smaller because the mass transfer driving force (concentration gradient) in the solution becomes greater, thereby providing faster adsorption rate of methylene blue (MB) onto both of the raw bentonite and organo-bentonite pore structure.

3.5.2. Effect of temperature

Temperature is one of the most important factors in adsorption process. The effect of temperature (30, 45, and 60 °C) as a function of time on the methylene blue adsorption is given in Fig. 9. Generally, temperature has two major effects on the adsorption process. Increasing the temperature induces an increase in the diffusion rate of adsorbate molecules onto adsorbent surface, thereby diminishing mass transfer resistance in liquid phase as a result of the reduced viscosity of bulk solution [1].

Increasing in temperature also enhances the equilibrium adsorption capacity for the particular adsorbate, especially if chemisorption is the control mechanism [1]. It is well known that organo-bentonite, which belongs to montmorillonite clay (MC), has a lattice with positive of thermal expansion coefficient, so that any temperature increase in the system will promote penetration process of adsorbate onto adsorbent surface layer [4,20].

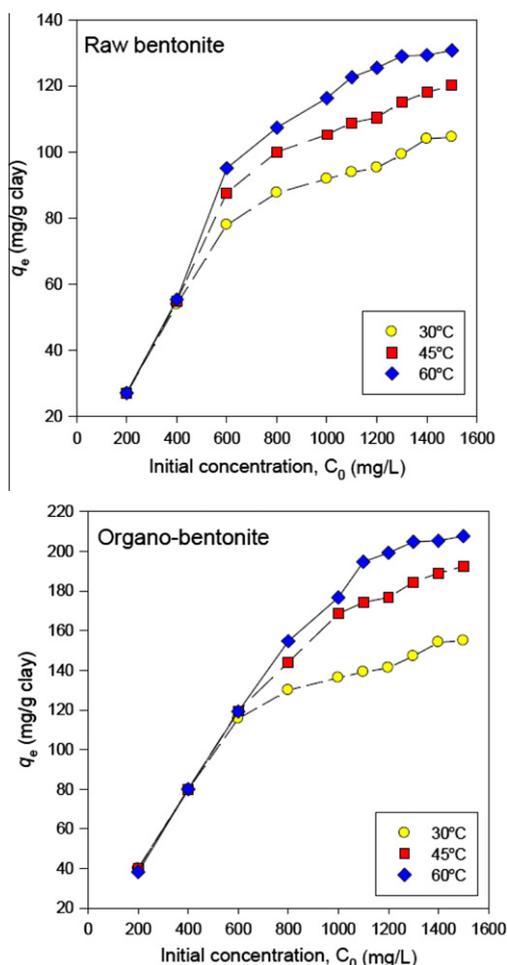


Fig. 8. Effect of initial solute concentration to the amount of methylene blue uptake at various temperature.

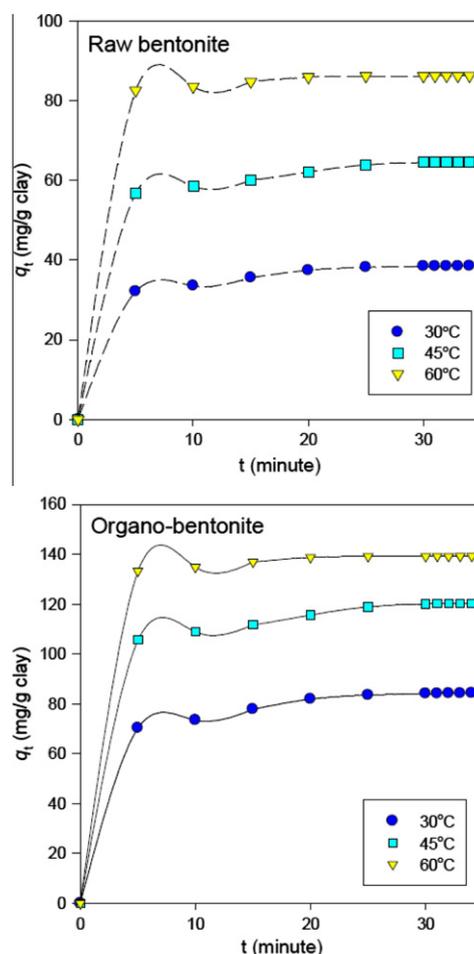


Fig. 9. Effect of temperature as a function of time in methylene blue uptake at initial concentration of 70 mg/L.

3.5.3. Adsorption isotherm

Adsorption isotherm is the most important part for illustrating the mechanism of distributed adsorbate molecules between the liquid phase and the solid phase at equilibrium state [1,4]. Equilibrium adsorption isotherm is vital to the design in adsorption systems and provides valuable information in determining adsorbent surface characteristics whether it is homogeneous or heterogeneous [2].

In this study, adsorption isotherms data were correlated using two well known adsorption equations, Langmuir [21] and Freundlich [22] models. Freundlich equation has the following form

$$q_e = K_F C_e^{1/n} \tag{3}$$

where q_e is the amount of MB uptake per mass of adsorbent (mg/g), K_f and n are both Freundlich temperature dependence constants, relating to adsorption affinity (mg/g).(mg/L)⁻ⁿ and adsorption intensity, respectively. Greater value of n indicates that the adsorption isotherm becomes more nonlinear while if n close to 10, the adsorption process exhibits irreversible isotherm [23].

The Langmuir isotherm is also one of the most popular adsorption models in illustrating adsorption phenomena. This model has been successfully applied to many adsorption processes for liquid system [4,24,25]. This equation has the following form

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{4}$$

Here q_e is the amount of dye adsorbed at equilibrium per mass of adsorbent (mg/g), C_e is the liquid phase concentration at equilibrium (mg/L), K_L and a_L are Langmuir equilibrium constants related

to the attraction of an adsorbate molecule onto an adsorbent surface (L/g) [23], and a constant that related to the net enthalpy of adsorption (L/mg) [4,26], respectively. The constant q_m is equal to K_L/a_L (mg/g) and defined as the monolayer saturation capacity of adsorbent for particular adsorbate [4]. The essential characteristics of the Langmuir isotherm model can be also determined from the dimensionless constant called equilibrium parameter, R_L , expressed by the following equation [14]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

The value of R_L indicate the various nature of adsorption isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 0$), or unfavorable ($R_L > 1$).

Figs. 10 and 11 show the adsorption equilibrium of methylene blue on rarasaponin organo-bentonite at various temperatures, and the fits using Freundlich and Langmuir models. In these figures, the experimental data are represented as symbols and isotherm fitting as solid lines. The parameters for Freundlich and Langmuir were estimated using non-linear least square method. The optimal parameters from the fitting of Freundlich and Langmuir equations with experimental data are summarized in Tables 4 and 5, respectively. From Figs. 10 and 11, and Tables 4 and 5, it is clear that Freundlich model gave better representation for adsorption data. This evidence was confirmed by better coefficient value (R^2) of Freundlich isotherm than Langmuir isotherm for both

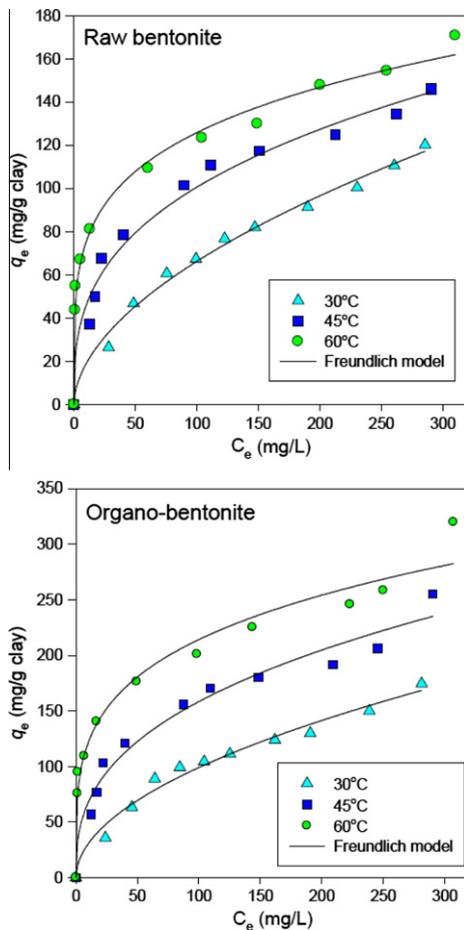


Fig. 10. Experimental adsorption data at initial methylene blue concentration of 50 mg/L and the fit of Freundlich isotherm model.

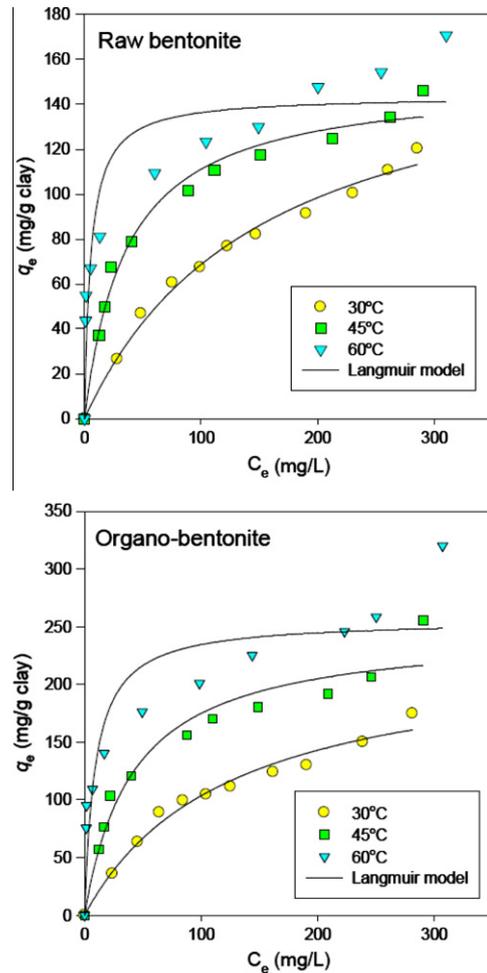


Fig. 11. Experimental adsorption data of methylene blue at initial concentration of 50 mg/L and the fit of Langmuir isotherm model.

Table 4
The Freundlich isotherm parameter for adsorption of methylene blue onto raw bentonite and organo-bentonite.

T (°C)	Raw bentonite Freundlich parameter			Organo-bentonite Freundlich parameter		
	K_F (mg/g).(mg/L) ⁻ⁿ	n	R ²	K_F (mg/g).(mg/L) ⁻ⁿ	n	R ²
30	5.4269	1.8407	0.9919	9.2979	1.9469	0.9816
45	21.0227	2.9423	0.9857	28.7116	2.6975	0.9730
60	45.1755	4.4969	0.9924	68.7154	4.0515	0.9742

Table 5
The Langmuir isotherm parameter for adsorption of methylene blue onto raw bentonite and organo-bentonite.

T (°C)	Parameter of Langmuir isotherm				
	K_L (L/g)	a_L (L/mg)	q_m (mg/g)	R_L	R ²
<i>Raw bentonite</i>					
30	1.1344	0.0065	175	1.76×10^{-3}	0.9895
45	4.1802	0.0230	181	4.78×10^{-4}	0.9846
60	26.5672	0.1372	194	7.52×10^{-5}	0.8798
<i>Organo-bentonite</i>					
30	1.8737	0.0081	231	1.07×10^{-3}	0.9794
45	5.9551	0.0241	247	3.35×10^{-4}	0.9549
60	27.9961	0.1094	256	7.14×10^{-5}	0.8460

raw bentonite and organo-bentonite. Since the parameter K_F in Freundlich equation cannot adequately represent the adsorption capacity of the adsorbent, therefore the adsorption capacity (mg/g) of raw bentonite and organo-bentonite was determined based on Langmuir isotherm constant (q_m). It can be seen that the maximum adsorption capacity of organo-bentonite was higher than raw bentonite at all temperatures. For comparison, the Langmuir based maximum adsorption capacity of several clay adsorbents for methylene blue removal were also given in Table 6 [4,27–33].

3.5.4. Adsorption kinetics

Widely used equations such as Lagergren pseudo-first order [34] and pseudo-second order [35,36] were used to correlate our kinetic experimental data. The Lagergren pseudo-first order has the mathematic expression as follows

$$q_e - q_t \exp(-k't) = q_t \tag{6}$$

and the pseudo-second order can be written as:

$$q_t = k_s q_e^2 t / (1 + k_s q_e t) \tag{7}$$

where q_e (mg/g) and q_t (mg/g) are the amount of methylene blue adsorbed at equilibrium condition and at time t (min), respectively. k' (min⁻¹) and k_s (g mg⁻¹ min⁻¹) are the rate constant for pseudo-first order, and pseudo-second order kinetics, respectively.

Table 6
Langmuir based maximum adsorption capacity of several clay adsorbents for methylene blue removal.

Clay adsorbent	q_m (mg/g clay)	Reference
Pacitan bentonite	175–194	Present study
Organo-bentonite	231–256	Present study
Montmorillonite clay	289.12	Almeida et al. [4]
Bentonite	151–175	Hong et al. [27]
Clay	300	Bagane and Guiza [28]
Fibrous clay minerals	85	Hajjaji et al. [29]
Raw kaolin	13.99	Ghosh and Bhattacharyya [30]
Spent activated clay	127.5	Weng and Pan [31]
Clay	63	Gurses et al. [32]
Perlite	162.3	Dogan et al. [33]

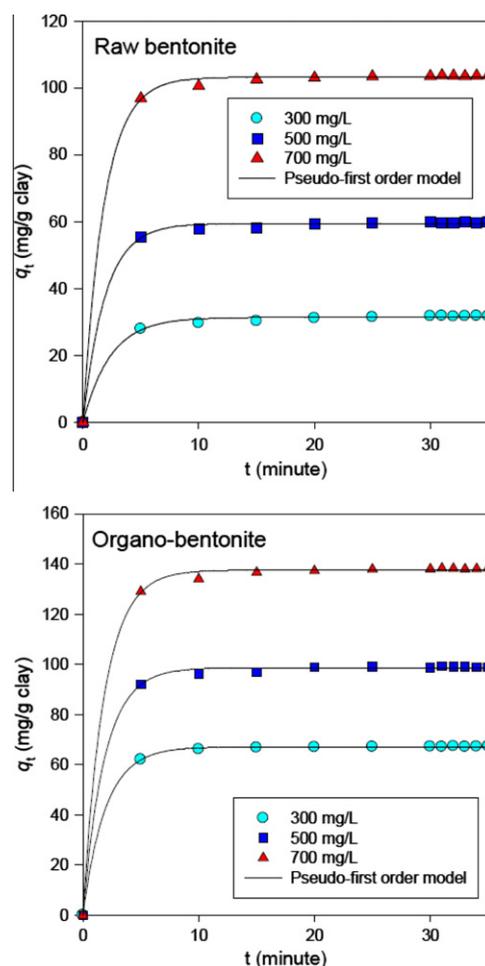


Fig. 12. The model fit of Lagergren pseudo-first order with kinetic experimental data at various initial concentration of methylene blue.

The plot of Lagergren pseudo-first order with the experimental data is shown in Fig. 12. From this figure it can be seen that the pseudo-first order describe the experimental data very well. The pseudo-second order model also can fit the experimental data very well as indicated in Fig. 13. The parameters of pseudo-first and pseudo-second order are given in Table 7.

The parameter k' in pseudo-first order is time scaling factor. Its value determines how fast the equilibrium in the system can be reached [37]. This parameter usually decreases with increasing of initial solute concentration in the bulk liquid phase [37–41]. Obviously, the higher the initial concentration of solute in bulk liquid phase, the longer time is needed for that system to reach equilibrium state [37]. The inconsistency of the parameter k' is observed in this experiment as shown in Table 7. The parameters k' increase with the increasing of initial solute concentration, hence the pseu-

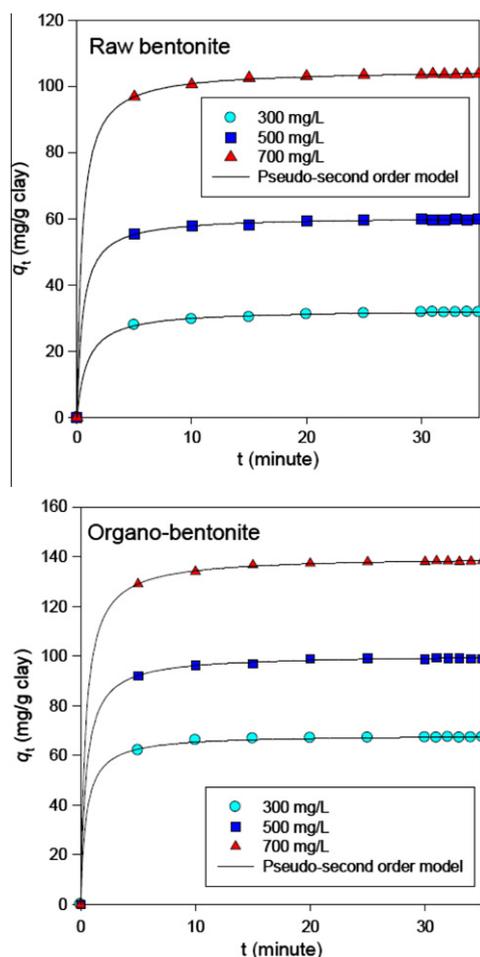


Fig. 13. The model fit of pseudo-second order with kinetic experimental data at various concentration of methylene blue.

Table 7
Parameter constant of Lagergren pseudo-first and pseudo-second order for methylene blue uptake onto raw bentonite and organo-bentonite.

Initial MB concentration (mg/L)	Pseudo-first order			Pseudo-second order		
	k' (min^{-1})	q_e (mg/g)	R^2	k_s ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$)	q_e (mg/g)	R^2
Raw bentonite						
300	0.4216	31.34	0.9957	0.0352	32.48	0.9995
500	0.5257	59.38	0.9987	0.0336	60.61	0.9998
700	0.5477	103.17	0.9993	0.0224	105.02	0.9999
Organo-bentonite						
300	0.5136	67.05	0.9998	0.0314	68.32	0.9997
500	0.5350	98.61	0.9991	0.0218	100.51	0.9998
700	0.5460	137.57	0.9993	0.0167	140.06	0.9999

do-first order model is not the correct choice for representing the adsorption kinetic data of methylene blue onto raw bentonite and organo-bentonite.

The parameter k_s of the pseudo-second order also strongly depend on the applied initial solute concentration. This parameter also is considered as a time scaling factor [37], therefore, this parameter will decrease with the increasing of initial concentration. The parameter k_s obtained from the fitting of our experimental data is in agreement with theory.

4. Conclusion

Parasaponin extracted from fruit pericarp of *S rarak DC* was used as natural surfactant for organo-bentonite preparation. In order to test and compare the adsorption capability, both of raw bentonite and organo-bentonite was used to remove methylene blue from aqueous solution. New reaction mechanism on the formation of organo-bentonite was proposed in this paper. The chemisorption mechanism of methylene blue onto organo-bentonite was also given. The adsorption studies were conducted in batch system at different operating condition. Freundlich isotherm model described the adsorption equilibrium data better than the Langmuir isotherm model. Based on the Langmuir isotherm constant (q_m), the highest adsorption capacity of organo-bentonite was 256 mg/g while for raw bentonite was 194 mg/g at 60 °C. While for the kinetic data, the pseudo-second order prevails over the pseudo-first order model.

Acknowledgement

The authors acknowledge the funding of this work through National Taiwan University of Science and Technology-Widya Mandala Surabaya Catholic University joint research project with contract no RP09-01 and Directorate General of Higher Education Republic of Indonesia through competitive grant for international publication with contract number 676/SP2H/PP/DP2M/VII/2009.

References

- [1] M. Dogan, M. Alkan, O. Demirbaş, Y. Özdemir, C. Özmetin, Chem. Eng. J. 124 (2006) 89–101.
- [2] M. Arami, N. Yousefi Limaee, N.M. Mahmoodi, Chemosphere 65 (2006) 1999–2008.
- [3] T. Akar, T.A. Demir, I. Kiran, A. Ozcan, A.S. Ozcan, S. Tunali, J. Chem. Technol. Biotechnol. 81 (2006) 1100–1106.
- [4] C.A.P. Almeida, N.A. Debacher, A.J. Downs, L. Cottet, C.A.D. Mello, J. Colloid Interf. Sci. 332 (2009) 46–53.
- [5] V.K. Gupta, I. Ali, V.K. Saini, T. Van Gerven, B.D. Van Bruggen, C. Vandecasteele, Ind. Eng. Chem. Res. 44 (2005) 3655–3664.
- [6] V.K. Gupta, I. Ali, V.K. Saini, J. Colloid Interf. Sci. 315 (2007) 87–93.
- [7] A.K. Jain, V.K. Gupta, A. Bhatnagar, N. Suhas, J. Hazard. Mater. 101 (2003) 31–42.
- [8] S.P. Dubey, K. Gopal, J.L. Bersillon, J. Environ. Biol. 30 (2009) 327–332.
- [9] V.K. Gupta, N. Suhas, J. Environ. Manage. 90 (2009) 2313–2342.
- [10] P. Liu, L. Zhang, Sep. Purif. Technol. 58 (2007) 32–39.
- [11] J.J.M. Órfão, A.L.M. Silva, J.C.V. Pereira, S.A. Barata, I.M. Fonseca, P.C.C. Faria, M.F.R. Pereira, J. Colloid Interf. Sci. 296 (2006) 480–489.
- [12] Y. Asao, T. Morikawa, X.I.E. Yuanyuan, M. Okamoto, M. Hamao, H. Matsuda, O. Muraoka, D. Yuan, M. Yoshikawa, Chem. Pharma. Bull. 57 (2009) 198–203.
- [13] R. Koswojo, R.P. Utomo, Y.H. Ju, A. Ayucitra, F.E. Soetaredjo, J. Sunarso, S. Ismadji, Appl. Clay Sci. 48 (2010) 81–86.
- [14] E.K. Putra, R. Pranowo, J. Sunarso, N. Indraswati, S. Ismadji, Water Res. 43 (2009) 2419–2430.
- [15] S. Kubilay, R. Gurkan, A. Savran, T. Sahan, Adsorption 13 (2007) 41–51.
- [16] J. Madejová, J. Bujdák, M. Janek, P. Komadel, Spectrochim. Acta, Part A 54 (1998) 1397–1406.
- [17] P. Komadel, J. Madejová, J.W. Stucki, Appl. Clay Sci. 34 (2006) 88–94.
- [18] M.A. Vicente, Langmuir 12 (1996) 566–572.
- [19] Z. Khalid, Studies of the photochemical kinetics of methylene blue with reductants Department of Chemistry, University of Karachi, Karachi, 2001.
- [20] A.S. Ozcan, B. Erdem, A. Ozcan, Colloids Surf. A 266 (2005) 73–81.
- [21] I. Langmuir, J. Am. Chem. Soc. 38 (1916) 2221–2295.
- [22] H. Freundlich, Trans. Faraday Soc. 28 (1932) 195–201.
- [23] D.D. Do, Adsorption Analysis: Equilibria and Kinetics, Imperial College Press, London, UK, 1998.
- [24] Z. Boubberka, A. Khenifi, N. Benderdouche, Z. Derriche, J. Hazard. Mater. 133 (2006) 154–161.
- [25] O. Hamdaoui, J. Hazard. Mater. 138 (2006) 293–303.
- [26] G. Rytwo, R. Huterer-Harari, S. Dultz, Y. Gonen, J. Therm. Anal. Calorim. 84 (2006) 225–231.
- [27] S. Hong, C. Wen, J. He, F. Gan, Y.S. Ho, J. Hazard. Mater. 167 (2009) 630–633.
- [28] M. Bagane, S. Guiza, Ann. Chim. 25 (2000) 615–626.
- [29] M. Hajjaji, A. Alami, A. El Bouadili, J. Hazard. Mater. B135 (2006) 188–192.
- [30] D. Ghosh, K.G. Bhattacharyya, Appl. Clay Sci. 20 (2002) 295–300.
- [31] C.H. Weng, Y.F. Pan, J. Hazard. Mater. 144 (2007) 355–362.

- [32] A. Gurses, S. Karaca, C. Dogar, R. Bayrak, M. Acikyildiz, M. Yalcin, J. Colloid Interf. Sci. 269 (2004) 310–314.
- [33] M. Dogan, M. Alkan, Y. Onager, *Water Air Soil Pollut.* 120 (2000) 229–248.
- [34] S. Lagergren, *Kungliga Svenska Vetenskapsakademiens Handlingar* 24 (1898) 1–39.
- [35] G. Blanchard, M. Maunay, G. Martin, *Water Res.* 18 (1984) 1501–1507.
- [36] Y.S. Ho, *J. Hazard. Mater.* 136 (2006) 681–689.
- [37] W. Plazinski, W. Rudzinski, A. Plazinska, *Adv. Colloid Interface Sci.* 152 (2009) 2–13.
- [38] J. Febrianto, A.N. Kosasih, J. Sunarso, Y.H. Ju, N. Indraswati, S. Ismadji, *J. Hazard. Mater.* 162 (2009) 616–645.
- [39] S.J. Allen, Q. Gan, R. Matthews, P.A. Johnson, *J. Colloid Interf. Sci.* 286 (2005) 101–109.
- [40] G. Crini, *Bioresour. Technol.* 97 (2006) 1061–1085.
- [41] C. Namasivayam, D. Sangeetha, *Desalination* 219 (2008) 1–13.