



## Organo-bentonite for the adsorption of Pb(II) from aqueous solution: Temperature dependent parameters of several adsorption equations

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Received 10 January 2011; accepted 18 April 2011

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### ABSTRACT

The preparation of organo-bentonite was conducted using bentonite from Pacitan as the raw material. The modification of bentonite was conducted by microwave irradiation. The adsorption capability of natural and modified-bentonite was tested for the removal of lead metal from aqueous solution. The adsorption experiments were conducted isothermally in static mode at various temperatures. The temperature dependent forms of the Langmuir, Freundlich, Sips and Toth models were used to correlate equilibrium data. It was found that the temperature dependent forms of Sips model can correlate the experimental data better than other models. The pseudo-first-order and pseudo-second-order models were chosen to correlate the experimental kinetic data. The pseudo-second order correlated the experimental data fairly well.

**Keywords:** Adsorption; Bentonite; Organo-bentonite; Isotherm; Temperature dependent

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### 1. Introduction

The presence of heavy metals in air, soil and water are known to be harmful to living species. The presence of these substances in water such as Cr, Pb, Cd, Zn, Ni, As, Cu and Hg can affect human health because they are non-biodegradable, toxic and carcinogenic even at low concentration [1]. Among the heavy metals, lead is one of the most toxic metals due to its severe effects in human health. The presence of this metal in human body can cause several disorders and diseases such as diminishing IQ, anemia, chronic headache, high blood pressure, diarrhoea, poisoning and malfunction of reproductive and other organ systems such as liver, brain, kidney and central nerve [1,2]. Many kinds of technologies are available for the removal of lead from water or wastewater such as chemical precipitation,

ion exchange, biological treatment, electrochemical treatment, membrane filtration, and adsorption [3]. The main advantages of using adsorption process for sequestering of lead and other heavy metals is the efficiency, selectivity, simplicity in design, and low operational cost. This process can also remove heavy metals ions even at very low concentration. However, the main drawback of this technique is the high cost of commercially available adsorbents such as activated carbon, especially for industrial wastewater treatment purpose. Accordingly, alternative low-cost and abundantly available materials for wastewater treatment purpose are needed.

Clay has been developed as one of the potential low-cost materials in terms of high specific surface area, cation exchange capacity, chemical and mechanical stability [4,5]. The utilization of clays for the heavy metals removal from aqueous solutions has been studied [6–16] and strongly recommended due to their

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abundant and natural availability, technical feasibility, engineering applications and cost effectiveness. Bentonite is one of the clay materials found in many countries in the world. It is originated from the volcanic activities that contain montmorillonite, which is a 2:1 type aluminosilicates mineral [8]. Bentonite is composed of an Al-octahedral sheet and two Si-tetrahedral sheets. The tetrahedral sheet provide a substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  which gives a net negative charge on the clay surfaces. Moreover, montmorillonite has an amphoteric pH-dependent surface and high exchange capacity due to isomorphous substitution between  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$ . These surfaces provide suitable adsorption sites for cation species and make it as a potential alternative adsorbent for adsorption of heavy metals.

“Bentonite deposit in East Java, Indonesia, is mainly found as Ca or Mg-type bentonite. This type of bentonite is generally suitable as raw material for adsorbent and bleaching earth. In East Java, bentonite reserves can be found in several areas such as Pacitan, Ponorogo, Blitar, Trenggalek, etc, with total reserves more than 500 million tons” [17]. Recently, several studies about the utilization of bentonite clay for lead removal have been conducted [6,7,12], however, the utilization of Pacitan bentonite modified with linear alkylbenzene sulphonate (LAS) surfactant still not available in the literature. Therefore, by conducting this study, the potential application of Pacitan bentonite and its modified form for sequestering of Pb(II) from wastewater is obtained.

In most adsorption studies of heavy metals using clays, the equilibrium data were correlated with adsorption isotherm equations at single temperature. It is important that temperature dependence of adsorption isotherm equations should be presented in correlating equilibrium data at various temperatures. To the best of our knowledge, there is no information available about the use of temperature dependence forms of adsorption isotherm equations for correlation of heavy metals adsorption data. In this study, the temperature dependence forms of Langmuir, Freundlich, Sips and Toth models were employed and the physical meaning and validity of each parameter of the model also discussed.

## 2. Materials and methods

### 2.1. Materials

Bentonite used in this study was obtained from Pacitan, East Java, Indonesia. The type of bentonite from this location is Ca-bentonite. Prior to the use, the bentonite was treated using  $\text{H}_2\text{O}_2$  solution to remove its organic impurities. The complete procedure about

the purification of bentonite can be found elsewhere [18]. The cation exchange capacity (CEC) of bentonite was 57 meq/100 g of clay according to ASTM C837-99 procedure. The elemental analysis of bentonite was conducted using flame atomic absorption spectrophotometer (SHIMADZU AA-6200). The results are given as follow: Al 39.12%, Si 47.89%, Fe 3.44%, Ca 0.15%, Mg 0.45%, K 0.24%, Na 0.47%, Mn 0.03% and  $\text{H}_2\text{O}$  8.21%. The surfactant used as modifying agent was LAS purchased from Sigma Aldrich.

### 2.2. Preparation of organo-bentonite

The modification of bentonite was conducted by microwave heating irradiation method. The procedure was described as follow: 2 g of bentonite was added to 10 mL of surfactant solution with the concentration of LAS equal to the CEC of bentonite. The suspension was then irradiated for 5 min in a microwave oven (National NN-S327 WF) at heating power of 700 W. The selection of the microwave heating procedure is due to the time efficiency and energy-saving [19]. The sample was then washed by deionized water at least three times until the pH of the washing solution did not change significantly. Subsequently, the organo-bentonite was dried in an oven at 105°C for 24 h, crushed and sieved through 100/120 mesh screen.

### 2.3. Characterizations of materials

The characterizations of bentonite and organo-bentonite were conducted using X-ray diffraction (XRD) and FTIR technique. The XRD patterns of bentonite and organo-bentonite was recorded on a Rigaku Miniflex Powder Diffractometer at 30 kV and 15 mA with Cu  $K\alpha$  radiation at a step size of 0.01°. The infrared spectroscopy spectra of the materials was recorded using a FTIR SHIMADZU 8400S in order to identify the specific functional groups on the materials surface. The FTIR analysis was carried out by using KBr disk procedure in the wavenumber range of 500–4000  $\text{cm}^{-1}$ .

### 2.4. Adsorption experiments

Adsorption experiments were carried out in a static mode at different temperatures (30, 40 and 50°C). The adsorption isotherm study was conducted by adding various amounts of adsorbent (0.1–1.0 g) into a series of erlenmeyer flasks with glass stoppered containing 100 mL of metal solution at initial concentrations of 200 mg/L. The pH of solution was adjusted to 5 by adding an appropriate amount of 0.1 N HCl.

The solutions were then placed in a water-bath shaker (Memmert) and shaken at 100 rpm for 80 min at desired temperatures. After the process was

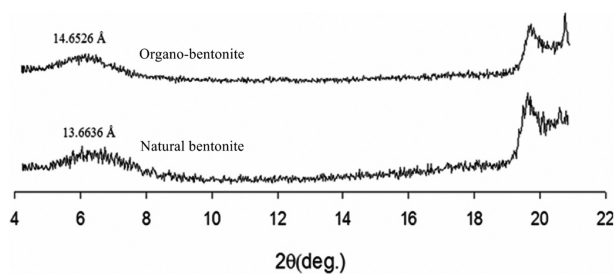


Fig. 1. The XRD patterns of natural and organo-bentonite.

completed, the flasks were removed from the bath and the mixtures were centrifuged at 3,500 rpm for 5 min to separate the solution from the adsorbent. The residual concentration of Pb(II) ions in the solution was analyzed by flame atomic absorption spectrophotometer at  $\lambda_{\max}$  of 283.3 nm. All adsorption experiments were performed in triplicate and the results were given as averages. The amount of Pb(II) ions adsorbed can be calculated by using the following equation:

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

where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of Pb(II) ions in liquid phase (mmol/L),  $q_e$  is the amount of metal adsorbed at equilibrium condition (mmol/g),  $V$  is the volume of solution (L) and  $m$  is the mass of the adsorbent (g).

For kinetic study, the adsorption process was carried out by adding a fixed amount natural or organo-bentonite (0.5 g) into a series of 250 mL iodine flasks that contained 100 mL of metal solution at initial concentrations of 200 mg/L. The flasks were then shaken in a thermostatic water-bath shaker at certain temperature (30, 40 and 50°C). During the experiments, at certain of time interval (every 10 min), the metal solution was taken from the flasks (10 mL using volumetric pipette), diluted with deionized water and centrifuged (3,500 rpm for 5 min). The residual concentration of Pb(II) ions in solution was analyzed using FAAS SHIMADZU AA-6200.

### 3. Results and discussion

#### 3.1. Characterizations of materials

The XRD analysis was used to determine the physical characteristic of the layer structure of the materials. The XRD patterns of natural and organo-bentonite are displayed in Fig. 1. In this figure, the basal spacing ( $d_{001}$ ) of natural and organo-bentonite is 13.6 Å ( $2\theta = 6.4634^\circ$ ) and 14.6 Å ( $2\theta = 6.0268^\circ$ ), respectively. The increase of basal spacing of organo-bentonite is

Table 1

FTIR analysis results of natural and organo-bentonite

Functional groups	Bentonite ( $\text{cm}^{-1}$ )	Organo-bentonite ( $\text{cm}^{-1}$ )
O–H stretch (Al–OH or Si–OH)	3630	3632
C–H stretch ( $(-\text{CH}_2)_n$ of LAS – structure)	–	–
Asymmetric vibration	–	2945
Symmetric vibration	–	2861
O–H bend (for adsorbed $\text{H}_2\text{O}$ )	1640	1644
Si–O stretch (in-plane for Si-tetrahedral layer)	1052	1054
Al–Al–OH bend	914	918
Si–O bend (quartz)	792	794
Si–O–Al bend	521	526
Si–O–Si bend	466	469

due to the intercalation of LAS molecule on the interlayer spacing of bentonite, causing an expansion of its interlamellar spacing.

The FTIR analysis results of natural and organo-bentonite are shown in Table 1. In this table, it can be shown that both natural and organo-bentonite had essentially the same surface groups, which are the characteristics of montmorillonite clay such as O–H stretch for Si–OH or Al–OH at around  $3,600 \text{ cm}^{-1}$ ; Si–O stretch (in-plane) for Si-tetrahedral layer at around  $1,050 \text{ cm}^{-1}$ ; Al–Al–OH bend at around  $910 \text{ cm}^{-1}$ ; Si–O bend for quartz at around  $790 \text{ cm}^{-1}$ ; Al–O–Si bend at around  $520 \text{ cm}^{-1}$  and Si–O–Si bend at around  $460 \text{ cm}^{-1}$ . After modification process with LAS surfactant, the existence of new absorption peaks at around 2,940 and 2,860  $\text{cm}^{-1}$  was noticed, these peaks attributed to the asymmetric and symmetric vibration of C–H stretch of methylene groups  $(-\text{CH}_2)_n$  in aliphatic carbon chain, respectively.

#### 3.2. Effect of temperature

The effect of temperature in the adsorption process was studied by varying the temperature of the process (30, 40 and 50°C). The experimental results (Figs. 2 and 3) indicate that the adsorption capacity of both adsorbents increases as the temperature increases, which are the characteristic of the chemisorption and endothermic process. This may be a result of the increase of the solute mobility in solution which enhanced the diffusion rate of adsorbate molecules onto the adsorbent pores. As the temperature increases, the viscosity of solution reduce hence diminishing the liquid phase mass-transfer resistance and facilitating solute penetration. Furthermore, bentonite

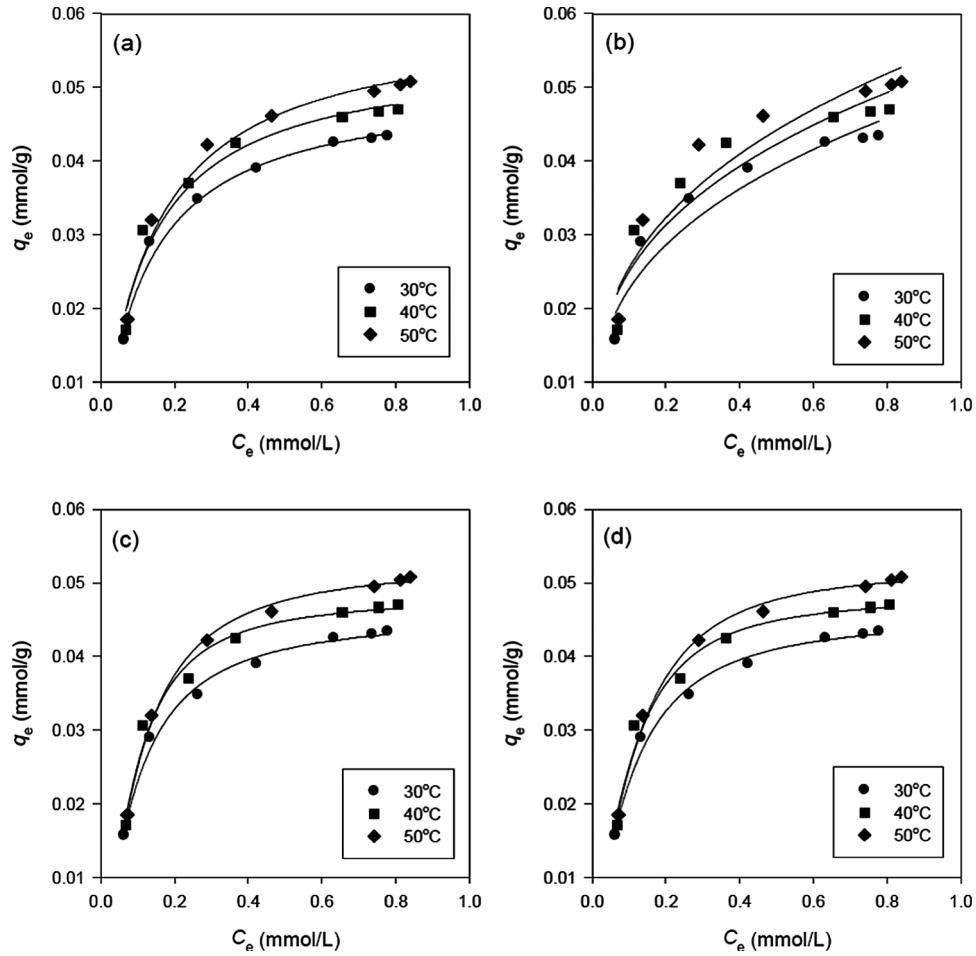


Fig. 2. Adsorption equilibrium data of Pb(II) onto natural bentonite and the model fit of (a) Langmuir, (b) Freundlich, (c) Sips and (d) Toth.

and organo-bentonite, which belong to montmorillonite clay has a lattice with thermal expansion coefficient so that any temperature increases in the system will promote the sorption capacity [18,20].

### 3.3. Adsorption isotherms

The adsorption equilibrium data of Pb(II) ions onto natural and organo-bentonite were correlated using several isotherm models (Langmuir, Freundlich, Sips and Toth) along with their temperature dependence forms. The Langmuir equation is a well-known isotherm model describing the monolayer adsorption on the homogeneous surface. In this model, the adsorbate can only occupy one site. The mathematical expression of Langmuir model is given as follow:

$$q_e = q_m \left( \frac{K_L C_e}{1 + K_L C_e} \right), \quad (2)$$

where  $q_e$  is the amount of solute adsorbed onto the adsorbent at equilibrium condition (mmol/g). The equilibrium concentration is symbolized by  $C_e$  (mmol/L) while  $q_m$  denotes the maximum adsorption capacity of the adsorbent, related to the monolayer coverage at solid surface (mmol/g). The  $K_L$  parameter is called as the adsorption affinity or Langmuir equilibrium constant (L/mmol). The temperature dependence forms of Langmuir model can be expressed as follows [21,22]:

$$q_m = q_0 \exp(\delta(T - T_0)), \quad (3)$$

$$K_L = K_{L_0} \exp\left(\frac{Q}{RT}\right). \quad (4)$$

Here  $q_0$  is the adsorption capacity (mmol/g) of adsorbent at a reference temperature  $T_0$  (taken as 298.15 K). The constant parameter relates to the expansion coefficient of the adsorbate is symbolized by  $\delta$ . The adsorption affinity at reference temperature  $T_0$  is

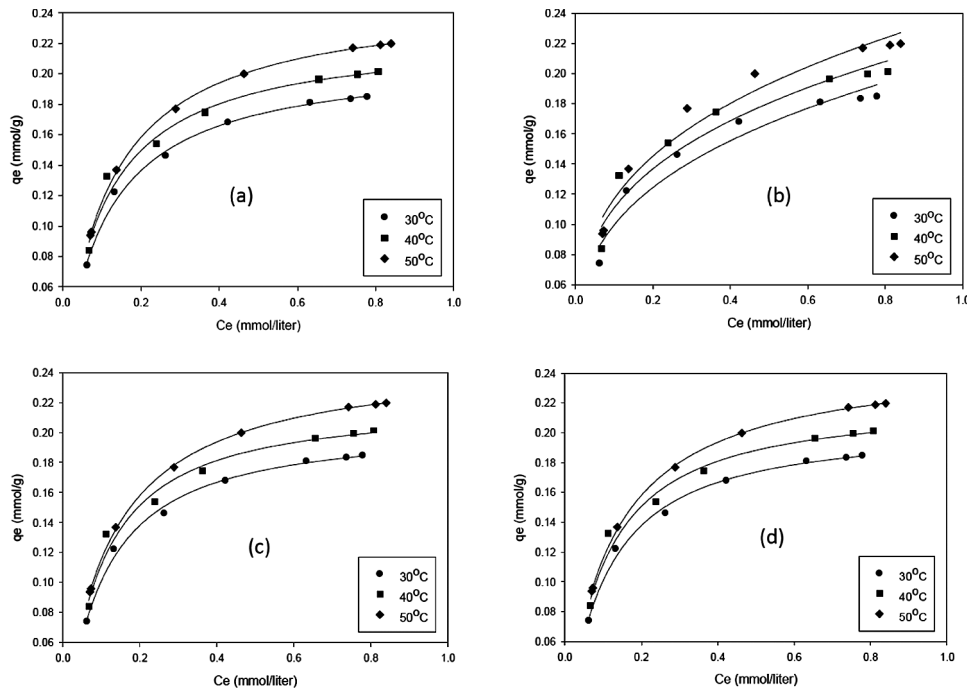


Fig. 3. Adsorption equilibrium data of Pb(II) onto organo-bentonite and the model fit of (a) Langmuir, (b) Freundlich, (c) Sips and (d) Toth.

symbolized by  $K_{L0}$ ,  $R$  is the gas constant (8.314 J/mol.K) and  $Q$  is the heat of adsorption (kJ/mol).

The Freundlich equation is also one of the most popular two-parameter isotherm models describing the adsorption behaviour in heterogeneous systems. The mathematical expression of Freundlich model is given as follows:

$$q_m = K_F C_e^{1/n_f}, \quad (5)$$

where  $1/n_f$  and  $K_F$  are Freundlich parameter characterizing the heterogeneity factor and adsorption intensity [(mmol/g)·(mmol/L) $^{1/n}$ ], also called as adsorption capacity when the value of  $n_f$  approaches infinite [23]. The temperature dependence forms of Freundlich model can be expressed below [21]:

$$\frac{1}{n_f} = \frac{RT}{A_0}, \quad (6)$$

$$K_F = K_{F0} \exp\left[\frac{-\alpha RT}{A_0}\right], \quad (7)$$

Here  $K_{F0}$  is the adsorption capacity at reference temperature  $T_0$  [(mmol/g)·(mmol/L) $^{1/n}$ ],  $\alpha$  is a constant parameter and  $A_0$  is the characteristic of adsorption potential (kJ/mol).

The Sips equation, which also known as Langmuir-Freundlich equation is a three-parameter models describing the adsorption phenomena in heterogeneous system. The Sips model has the following form [21]:

$$q_e = q_m \frac{(K_S C_e)^{1/n_s}}{1 + (K_S C_e)^{1/n_s}}. \quad (8)$$

The temperature dependence forms of Sips model are expressed as follow:

$$K_S = K_{S0} \exp\left[\frac{Q}{RT_0} \left(\frac{T_0}{T} - 1\right)\right], \quad (9)$$

$$n_s = \frac{1}{\frac{1}{n_0} + \eta \left(1 - \frac{T_0}{T}\right)}. \quad (10)$$

The temperature dependence form of adsorption capacity parameter ( $q_m$ ) is expressed in Eq. (3). The parameter  $K_{S0}$  is the adsorption affinity at  $T_0$  (L/mmol),  $n_0$  is the value of  $n_s$  at  $T_0$  and  $\eta$  is a constant parameter.

The Toth equation, which is generally used for describing adsorption system in heterogeneous system with sub-monolayer coverage, has the following form [21]:

Table 2  
The fitted temperature dependent parameters of several isotherm models

Isotherm	Parameters	Natural	
		bentonite	Organo-bentonite
Langmuir	$q_0$ (mmol/g)	0.047	0.193
	$K_{L0}$ (L/mmol)	$1.23 \times 10^{-4}$	$1.45 \times 10^{-5}$
	$Q$ (Kj/mol)	27.71	33.49
	$\delta$ (1/K)	0.0017	0.0189
Freundlich	$K_{F0}$	0.0034	0.0081
	$\alpha/A_0$	-1.065	-1.295
	$A_0$	0.318	0.413
Sips	$Q_0$ (mmol/g)	0.047	0.204
	$K_{S0}$ (L/mmol)	8.574	9.528
	$Q$ (kj/mol)	13.57	19.37
	$\delta$ (1/K)	0.0096	0.0011
	$n_{S0}$	1.044	1.117
	$H$	4.868	5.720
Toth	$q_0$ (mmol/g)	0.049	0.207
	$K_{T0}$ (L/mmol)	8.66	11.39
	$Q$ (kj/mol)	29.14	38.92
	$\delta$ (1/K)	0.0079	0.0082
	$H$	8.453	10.771

$$q_e = q_m \frac{C_e \cdot K_T}{(1 + (K_T \cdot C_e)^{n_T})^{1/n_T}} \quad (11)$$

Here  $K_T$  and  $n_T$  are Toth parameters which are specific for adsorbate–adsorbent pairs. The heterogeneity factor is given by parameter  $1/n_T$  and if the value of this parameter is unity, Eq. (11) reduces to Langmuir equation. At very low concentrations, Toth equation also reduces to Henry's law. The mathematical expression of Toth temperature dependence parameters are given below:

$$K_T = K_{T_0} \exp \left[ \frac{Q}{RT_0} \left( \frac{T_0}{T} - 1 \right) \right], \quad (12)$$

$$n_T = n_{T_0} + \eta \left( 1 - \frac{T_0}{T} \right), \quad (13)$$

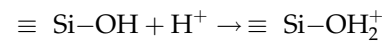
where  $K_{T_0}$  is the adsorption affinity at  $T_0$ ,  $n_{T_0}$  is the parameter  $n_T$  at  $T_0$  and  $\eta$  is a constant parameter. The temperature dependence parameters of the Langmuir, Freundlich, Sips and Toth model were obtained by non-linear least square fit method. The following error function was used as objective function to be minimized:

$$SSE = \left( \frac{(\sum q_{e(\text{exp})} - q_{e(\text{cal})})^2}{N} \right)^{1/2} \quad (14)$$

Here  $q_{e(\text{exp})}$  is the actual amount of Pb(II) ions adsorbed,  $q_{e(\text{cal})}$  is the calculated amount of Pb(II) adsorbed and  $N$  is the number of experimental data.

The adsorption equilibrium data of Pb(II) and the fitting of models are depicted in Figs. 2 and 3. The calculated temperature dependence parameters of the Langmuir, Freundlich, Sips and Toth models are listed in Table 2. It is obvious that Freundlich model fails to represent the equilibrium data of Pb(II) onto natural and organo-bentonite (Figs. 2 and 3). Other models seem can still correlate the experimental data fairly well. However, the judgement of the validity of the model to represent the experimental data should not be based on the graphical representation only and  $R^2$  value but the most important thing should be based on the physical meaning of the parameters. Subsequently, we discuss the physical meaning of each isotherm parameter in Langmuir, Sips and Toth model. We excluded the Freundlich model in further discussion since this equation failed to represent the experimental data.

First, we begin our examination in the adsorption capacity parameter ( $q_0$ ) at  $T_0$  (298.15 K). The values of parameter  $q_0$  in Langmuir, Sips and Toth are reasonable and comparable to the values reported by other studies [10–12,16,24,25]. Based on the experimental data, it is obvious that organo-bentonite had higher adsorption capacity than the natural one. At an acid pH (5.0), the silanol groups of bentonite were protonated due to the presence of excess  $H^+$  ions in the solution:



The electrostatic repulsion force between protonated silanol groups with Pb(II) ions occurred and it retarded the sorption process. The sorption process of Pb(II) occurred due to the physical interaction such as Van der Waals between the surface of bentonite and Pb(II) ions. In organo-bentonite, the presence of linear alkyl benzene sulfonate ions in the bentonite interlayer caused the formation of negative charge in the adsorbent surface. Accordingly, electrostatic interactions between the negatively charged organo-bentonite and Pb(II) cations was taken place which enhanced the sorption capacity. The values of parameter  $q_0$  in the Langmuir, Sips and Toth model are consistent with these adsorption phenomena.

The adsorbate–adsorbent interaction strength in adsorption can be represented by affinity parameter. When the value of this parameter is high, the surface

is covered with more solute molecules as a result of stronger affinity towards the solid surface. Since the adsorption mechanism of Pb(II) ions onto organo-bentonite also involved electrostatic interaction hence the adsorbate molecules has stronger affinity towards the solid surface. The fitting results of adsorption affinity parameter of Toth ( $K_{T0}$ ) and Sips ( $K_{S0}$ ) model are consistent with experimental data. However, the  $K_{L0}$  parameter in the Langmuir model gives contrary results, the affinity of Pb(II) ions toward natural bentonite surface is higher than modified-bentonite. Additionally, the value of  $K_{L0}$  of both natural and organo-bentonite are considerably low compared with other values in most adsorption systems. Accordingly, in the subsequent discussion, we only discuss the validity of the temperature dependence form of Sips and Toth model.

The heat of adsorption provides important insights in the mechanism of adsorption. It is also a crucial thermodynamic properties for the design of adsorption system to estimate the heat released (or consumed) during adsorption or desorption process. The values of the heat of adsorption ( $Q$ ) can be determined either by varying the temperatures during adsorption process or by direct calorimetric measurements [26]. The parameter  $Q$  in Sips and Toth model is only the measure of the adsorption heat [21]. As mentioned in previous paragraph, electrostatic interactions also occurred during the adsorption of Pb(II) ions onto organo-bentonite thus higher value of the adsorption heat is expected. The fitting results of  $Q$  parameter in Sips and Toth model is in agreement, in which the heat of adsorption of Pb(II) onto organo-bentonite is higher than natural one.

The temperature coefficient of the expansion of adsorbate is represented by  $\delta$ , in which this parameter essentially independent of the type of adsorbent and the value is usually in the order of  $10^{-3} \text{ K}^{-1}$ . The results in Table 2 show that the fitting value of  $\delta$  parameter in Toth and Sips model is consistent with the  $\delta$  values of many solutes [22].

The last examination was carried out in the parameter characterizing the system heterogeneity. This parameter is symbolized by  $n_{T0}$  in Toth and  $n_{S0}$  in Sips model. The value of this parameter is usually greater than unity, the larger value of  $n$  indicates the more heterogeneous is the system. The presence of LAS molecules in the bentonite interlayer caused the adsorbent more heterogeneous thus higher value of  $n$  is expected in the adsorption system using organo-bentonite. In Table 2, it can be seen that the fitting values of  $n_{S0}$  parameter in Sips model is consistent while Toth model fails to give the correct value of  $n_{T0}$  parameter. Based on the analysis of the physical meaning of each isotherm parameters above, it is obvious

that the adsorption equilibrium data of Pb(II) fitted best with the Sips model.

### 3.4. Adsorption kinetics

The kinetics data provide fundamental and complete description of the transport mechanisms of adsorbate into adsorbent. In order to achieve the proper design of the sorption system, the adsorption equilibrium data need to be supported with adsorption kinetics. Several kinetic models are available, among them the pseudo-first-order and pseudo-second-order model are widely used to correlate experimental data [27]. Since the natural bentonite had lower adsorption capacity than the modified one, in this section, the kinetic study was only conducted for organo-bentonite.

The earliest known equation to describe the sorption rate in the liquid phase was proposed by Lagergren [28] and known as Lagergren pseudo-first-order equation. The expression of this equation in terms of pseudo-first order was employed by Sharma

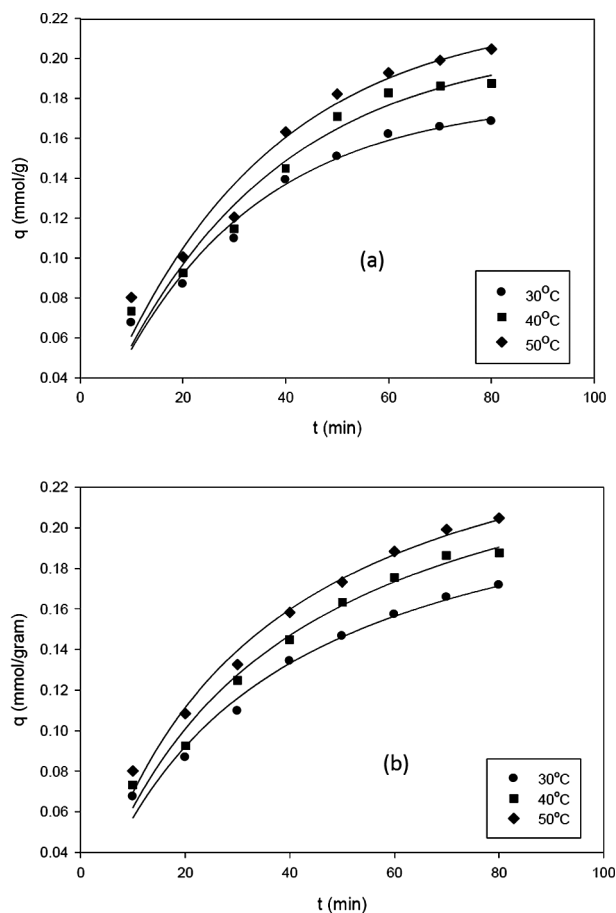


Fig. 4. The kinetic plots of (a) pseudo-first order and (b) pseudo-second order model for the adsorption of Pb(II) onto organo-bentonite.

Table 3  
The fitted kinetic parameters for the adsorption of Pb(II) onto organo-bentonite

T (K)	$q_{e,exp}$	Pseudo-first order			Pseudo-second order		
		$q_{e,cal}$ (mmol/g)	$k'$ ( $\text{min}^{-1}$ )	$R^2$	$q_{e,cal}$ (mmol/g)	$k_s$ (g/mmol min)	$R^2$
313.15	0.2421	0.1801	0.0357	0.9716	0.2402	0.1097	0.9972
323.15	0.2532	0.2091	0.0310	0.9599	0.2706	0.1153	0.9971
333.15	0.2642	0.2238	0.0316	0.9568	0.2824	0.1293	0.9985

et al. [29] to correlate the sorption kinetic data of Ni(II) ions into wollastonite. The Lagergren pseudo-first order has mathematic expression as follows:

$$q_e - q_e \exp(-k't) = q_t, \quad (15)$$

where  $q_e$  and  $q_t$  are the amount of Pb(II) ions adsorbed at equilibrium condition and at time  $t$  (min), respectively. The  $k'$  ( $\text{min}^{-1}$ ) parameter is the rate constant for pseudo-first order.

The pseudo-second-order model is commonly associated with the situation when the rate of direct adsorption/desorption process controls the overall sorption kinetics [30]. The first mathematical expression of the pseudo-second-order model was proposed by Blanchard et al. [31], which has the form as follows:

$$q_t = k_s q_e^2 t / (1 + k_s q_e t), \quad (16)$$

where  $k_s$  ( $\text{g mmol}^{-1} \text{min}^{-1}$ ) is the rate constant for pseudo-second-order model.

The kinetic data and the model fitted are given in Fig. 4. The fitted parameters of the kinetic models are summarized in Table 3. By comparing the fitting results of pseudo-first and pseudo-second-order parameter, both of them seem to give well correlation. However, the calculated values of  $q_e$  from pseudo-first order deviate quite large from experimental data while pseudo-second order gave reasonable values. The potential advantages of the pseudo-second-order model as an expression to estimate the  $q_e$  value is its small sensitivity for the influence of the random experimental error. Moreover, the  $q_e$  value can also be determined from the plot independently of the kinetic mechanism which controls the sorption process [30,32].

#### 4. Conclusions

Organo-bentonite synthesized from Pacitan bentonite using LAS as modifying agent has potential application for Pb(II) ions removal. The characterizations of materials were conducted using FTIR and XRD techniques. The temperature dependent form of several adsorption isotherm equations (Langmuir, Freundlich,

Sips and Toth) was employed to correlate the equilibrium data. The Sips model gave best representation to the experimental data with reasonable fitted parameters results. The kinetic data for the adsorption of Pb(II) ions onto organo-bentonite was best represented by the pseudo-second order model.

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