



Research paper

Preparation of cetyltrimethylammonium intercalated Indonesian montmorillonite for adsorption of toluene

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ABSTRACT

Organo-clays of cetyltrimethylammonium (CTMA)-intercalated montmorillonite from a naturally occurring Indonesian montmorillonite were prepared. Previous research showed that the insertion of surfactants into interlayer spaces in montmorillonite improved the adsorption of hydrophobic chemicals. The current research focused on the effects of preparation variables, the concentration of CTMA surfactant, the cation exchange capacity (CEC) of the montmorillonite clay and their ratio (CTMA/CEC) on the physicochemical characteristics of the organo-clays and adsorption of toluene. X-ray diffraction (XRD), surface area analysis, Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) were used to compare the physicochemical characteristics of the modified and unmodified montmorillonite clays. The adsorption of toluene was studied in kinetics and isotherm. It was found that the CTMA/CEC ratio strongly affected the physicochemical properties and adsorption capacities of the montmorillonite surfaces. Adsorption kinetics was evaluated by pseudo-first order, pseudo-second order and Elovich models. Adsorption isotherm was assessed with the Langmuir, Freundlich and Temkin isotherms. The data were best fit by the pseudo-second order model and the Langmuir model.

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1. Introduction

The applications of clay minerals in catalysis and adsorption are well known and widely reported. Montmorillonite within smectite group, with its high surface area, expandability and swellability, was reported to be a good adsorbent for the removal of cations and dyes (De Stefanis and Tomlinson, 2006; Lagaly et al., 2006). The adsorption capacity of montmorillonite is related to its structure and cation exchange capacity (CEC). The structure of montmorillonite clay makes it behave like a molecular sieve by interacting with cations and accommodating them in the spaces between layers. In many studies, clay surfaces were modified, and their hydrophobicity was altered to be functionalized solid materials in order to adsorb target molecules with high performance (Zhou, 2011). The native or normally occurring cations, such as Na⁺, K⁺ and Ca²⁺, were replaced by organophilic quaternary ammonium cations, which increased the “like dissolves like” interactions with organic contaminants and their uptake from a solution (dePaiva et al., 2008; Roberts et al., 2006). There is intensive interest in the modification of montmorillonite because of huge abundance of this mineral in Indonesia and the world and relatively cheaper to produce and use in industrial applications.

Much research has been attempted in the preparation of surfactant-modified clays (organo-clays) from various clay minerals and surfactant intercalation for applications in the recovery of hydrophobic organic contaminants. Organo-clays are usually prepared from the smectite group of clay minerals and utilized in wide applications due to their high cation exchange capacities, large surface areas, reactive surfaces and selective adsorption. A number of research papers reported a significant enhancement in the adsorption capacity of alkylamine-intercalated smectite mainly due to the attachment of long chain alkyl groups that would increase the number of non-polar sites for more effective interactions with organic molecules. Cetyltrimethylammonium (CTMA) cation is an interesting surfactant which contributes to the adsorption of not only dyes and other non-polar contaminants but also anionic contaminants (Atia, 2008; Beall, 2003; dePaiva et al., 2008). As a result, the organo-clays from CTMA and smectite clays are very effective adsorbents for the removal of poorly water-soluble organic compounds from aqueous solutions.

Previous investigations showed that the surface properties of an organo-clay depend on the type and size of the alkyl chains of intercalates and the characteristics of the unmodified or parent clay. High concentrations of impurities can interfere with the expansion of the clay layers and affect the specific surface area and adsorption (Patel et al., 2010; Roberts et al., 2006; Shabestary et al., 2007).

The preparation of organo-clays from an Indonesian montmorillonite has been reported by Koswojo et al. (2010). The organo-clays were compared with raw montmorillonite in adsorption of acid

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green 25. Modification of the montmorillonite changed its surface profile and improved its adsorption. Kinetic studies of the acid green 25 adsorption demonstrated that the adsorption obeyed the Langmuir isotherm. Additional studies of the thermodynamics of the adsorption behavior indicated that there was a significant change in the heat of adsorption due to stronger interactions between the acid green 25 and the organo-clay surfaces. In the current work, toluene was selected as the target molecule for adsorption because this molecule is the subject of many other works on the abatement of organic pollutants. In a previous work, non-ionic molecular interactions were found to be important mechanistically for toluene adsorption (Hunger et al., 1998). Seliem et al. (2011) reported that an organo-clay was superior for adsorption of toluene in terms of the adsorption–desorption constant (K_d). Other investigations (He et al., 2006) found that the molar ratio of the CTMA to the CEC of montmorillonite was the most influential variable. Because the CTMA/CEC ratio affects the surface profile, the adsorption will be most effective at an optimum CTMA/CEC ratio. The present paper reported the preparation of alkylamine-intercalated smectite clay from naturally occurring Indonesian montmorillonite and cetyltrimethylammonium (CTMA). It was hypothesized that the C-16 alkyl carbon chains of the CTMA form an organic phase that covers most of the siloxane surfaces of the interlayers in the clay. The investigation focused on the physico-chemical characteristics of the organo-clays and the adsorption kinetics of toluene from aqueous solutions on the organo-clays as functions of the ratio of CTMA to the CEC of the clay.

2. Experimental

2.1. Materials

The primary material used in this research was a naturally occurring montmorillonite (PT. Tunas Inti Makmur, Semarang, Indonesia). This raw material has a cation exchange capacity of 69 meq/100 g and the chemical composition was reported previously (Fatimah et al., 2010). The montmorillonite was activated by refluxing with an acid before it was used to synthesize organo-clays with a similar procedure used in previous research (Fatimah et al., 2011). The chemicals included cetyltrimethylammonium bromide ($[\text{CH}_3(\text{CH}_2)_{15}] \text{NBr} (\text{CH}_3)_3$) (Sigma Aldrich), ethanol (E.Merck) and toluene (E.Merck), at pro-analytic grade.

2.2. Preparation and characterization of organo-clay

CTMA-intercalated montmorillonite samples were prepared by dropping a CTMA solution into a montmorillonite suspension (5% surfactant in water (w/w)) and stirring the mixture for 24 h at room temperature. In order to study the effects of the ratio of CTMA to CEC of montmorillonite, samples were prepared with CTMA/CEC ratios of 0.5, 1.0, 3.0 and 5.0, and the materials obtained at these ratios were designated as CT-0.5, CT-1.0, CT-2.0 and CT-3.0, respectively.

The organo-clays were compared to the raw montmorillonite with X-ray diffraction (XRD) using X-6000 Shimadzu, FTIR (Nicolet Avatar series), N_2 adsorption (NOVA 1200e Gas Sorption Analyzer) and SEM (Seiko). The XRD patterns of montmorillonite and CTMA-intercalated montmorillonite samples were recorded using Ni-filtered $\text{CuK}\alpha$ radiation with a step size of 0.2° and a scanning speed of $5^\circ/\text{min}$. The interlayer distance (d_{001}) was calculated from the measured value of the diffraction angle (2θ) using the Bragg equation.

2.3. Toluene adsorption

Toluene solutions were used in batch adsorption systems. A total of 0.2 g of adsorbents were added to 50 mL of toluene solutions at different concentrations in a range of 0.0125–0.25 mg/L. The solutions

were stirred for various specific time and then filtered. The concentration of toluene was determined by HPLC (HPLC Shimadzu, mobile phase of acetonitrile and water (50:50), a UV detector with detection limits of 5–10 mg/L). The percent of toluene removed by adsorption was calculated from equation (Eq. (1)):

$$\% \text{removal} = \frac{c_0 - c_t}{c_0} \times 100 \quad (1)$$

Where c_0 and c_t (mg/L) are the initial concentration and the concentration at the time of sampling, respectively. The toluene uptake (q) was determined by the following equation (Eq. (2)):

$$q = \left(\frac{c_0 - c_t}{m} \right) \cdot V \quad (2)$$

where V (L) is the volume of toluene solution and m (g) is mass of adsorbents.

3. Results and discussion

3.1. Material characterization

XRD spectra were interpreted with respect to the position of the first order basal reflection [001], which depends on the distance between sheets in smectite crystal lattice.

The d_{001} value of raw montmorillonite is 17.75 Å; after the clay was intercalated with CTMA at a CTMA/CEC ratio of 0.5, the d_{001} value increased to 18.62 Å with a single reflection (Fig. 1). When the CTMA/CEC ratio is 1.0, there are double reflections that correspond to 26.59 and 18.9 Å, respectively. These reflections are most likely related to the transformation or the different conformations of the intercalated alkylamine molecules in the montmorillonite interlayers. Some investigations (He et al., 2006; 2010; Jianxi et al., 2003) showed that the increase in the d_{001} value is related to the conformation and length of the alkyl chains and is a function of the ratio of CTMA to CEC. At low surfactant loading, intercalated surfactant

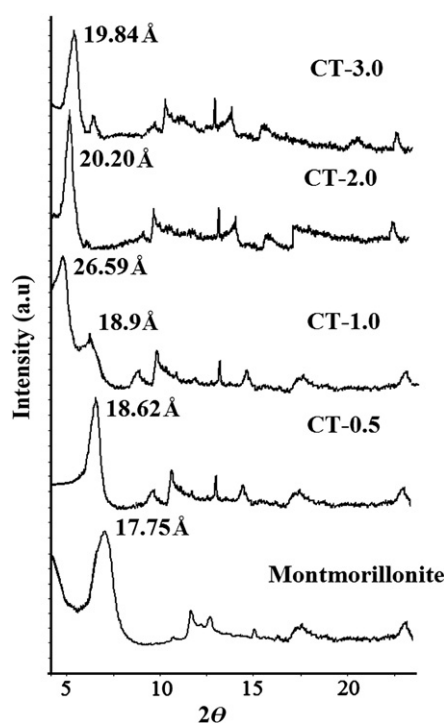


Fig. 1. XRD pattern of material (from top to down): montmorillonite, CT-0.5, CT-1.0, CT-2.0 and CT-3.0 respectively.

Table 1
Specific surface area and pore volume of montmorillonite and CTMA-montmorillonite.

Sample	Specific surface area (m ² /g)	Pore volume (cc/g)
Montmorillonite	55.98	6.24
CT-0.5	99.77	18.22
CT-1.0	39.45	4.25
CT-2.0	25.67	0.18
CT-3.0	18.96	0.18

molecules can be accommodated in the porous structure and exchangeable sites in the clay, and they arrange to form a lateral monolayer. This arrangement is usually identified by a single value of d_{001} . For higher surfactant loadings at specific conditions controlled by the cation exchange capacity and the type of surfactant, the surfactant molecules can form an irregular arrangement, most likely a combination of pseudo-trilayers and lateral bilayers (He et al., 2010; Zhu et al., 2007a, 2007b; Tiwari et al., 2008). In the case of CT-1.0, the main reflection shifts to 18.96 Å and the second reflection is at 25.96 Å, showing an interlayer distance with paraffin-type arrangement. At higher CTMA to CEC ratios, the d_{001} values at 20.20 and 19.86 Å for CT-2.0 and CT-3.0, respectively, also indicated that the alkyl chains were mostly intercalated in a paraffin-type arrangement. The larger layer-to-layer separation of intercalated clay particles on CT-1.0 (25.96 Å) compared to CT-2.0 and CT-3.0 is most likely related to the higher packing density and the greater tendency to form a non-homogeneous molecular distribution at a higher surfactant loading.

The reflection valued at 26.59 Å for CT-1.0 is slightly higher than the value reported by Koswojo et al. (2010), who prepared CTMA-intercalated montmorillonite from an Indonesian montmorillonite at a surfactant to CEC ratio of 130%. This difference might be due to different types of raw montmorillonite; Ca-montmorillonite was used by Koswojo et al. (2010), while Na-montmorillonite was used in this research. Additionally, different cation exchange capacities and

tendencies to be swollen by surfactant addition for the two unmodified clays might also be responsible for this difference.

Table 1 presents data from the BET surface area measurements. The change in surfactant arrangement is also reflected by the change in specific surface area. The data listed in Table 1 suggest that the ionic surfactant molecules exchange with the native cations in montmorillonite when the CTMA/CEC ratio of 0.5 generated larger interlayer spaces between the silica sheets and increased the specific surface area from 56.0 to 99.8 m²/g. However, further addition of CTMA decreased the specific surface area, and the specific surface area of organo-clays increased in the order of CT-3.0 < CT-0.5 < CT-1.0. A comparison of the XRD pattern and the d_{001} values for CT-0.5 and CT-1.0 suggests that the cation exchange process in CT-0.5 was accommodated by the wider interlayer spaces. However, an increase in the CTMA/CEC ratio resulted in decreased specific surface area and pore volume. As discussed above, CT-1.0 has a lateral structure that may lead to interlayer stacking and increased density at higher ratios. This change could be observed on CT-0.5, CT-1.0 and CT-3.0 by SEM (Fig. 2). A rougher structure with more aggregates was observed for organo-clays, CT-0.5 and CT-1.0, compared to raw montmorillonite. CT-3.0 demonstrated a relatively compact surface with many layers homogeneously distributed on the surface. The profiles are similar to those reported by He et al. (2006) and Hong et al. (2008).

FTIR analysis was used to identify the changes of the functional groups present on the surfaces (Fig. 3). Compared to raw montmorillonite, there are some additional FTIR bands indicating the presence of the alkylammonium groups in the organo-clays at varying the CTMA/CEC ratios. The absorption bands around 2920 and 2820 cm⁻¹ corresponded to asymmetric and symmetric vibrations of CH₂ groups from the alkyl chains, respectively. The intense absorption band at around 1470 cm⁻¹ was referred to the C–H symmetric bending of (N⁺)–CH₃ groups from CTMA. These bands were commonly found in organo-clays containing alkylamine surfactants. The differences

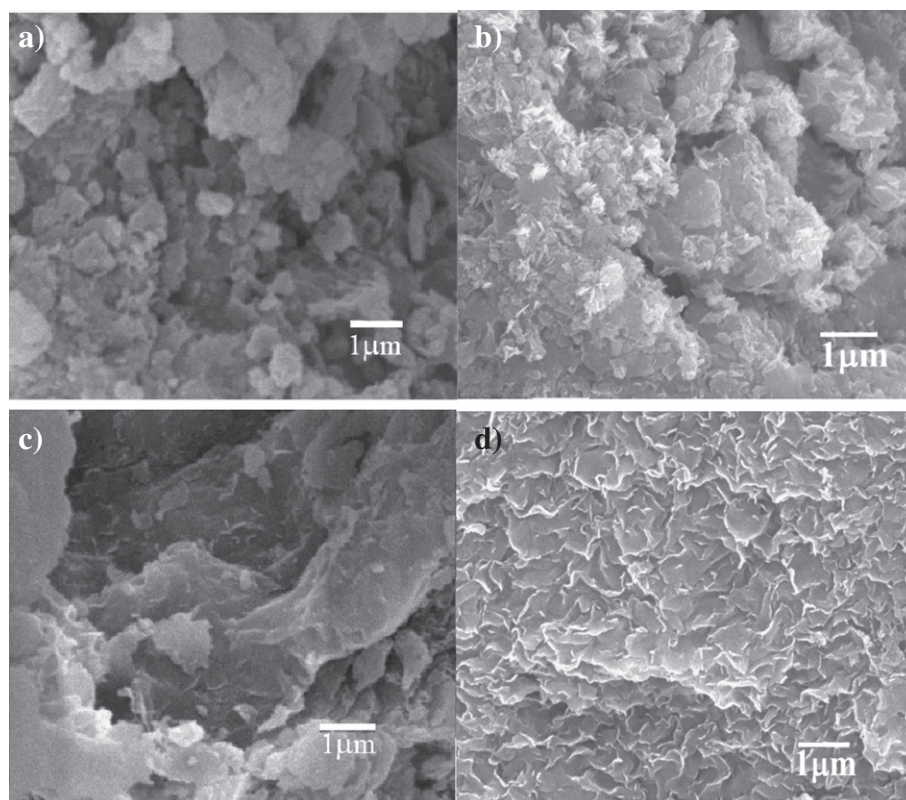


Fig. 2. SEM profile of (a) montmorillonite (b) CT-0.5 (c) CT-1.0 (d) CT-3.0.

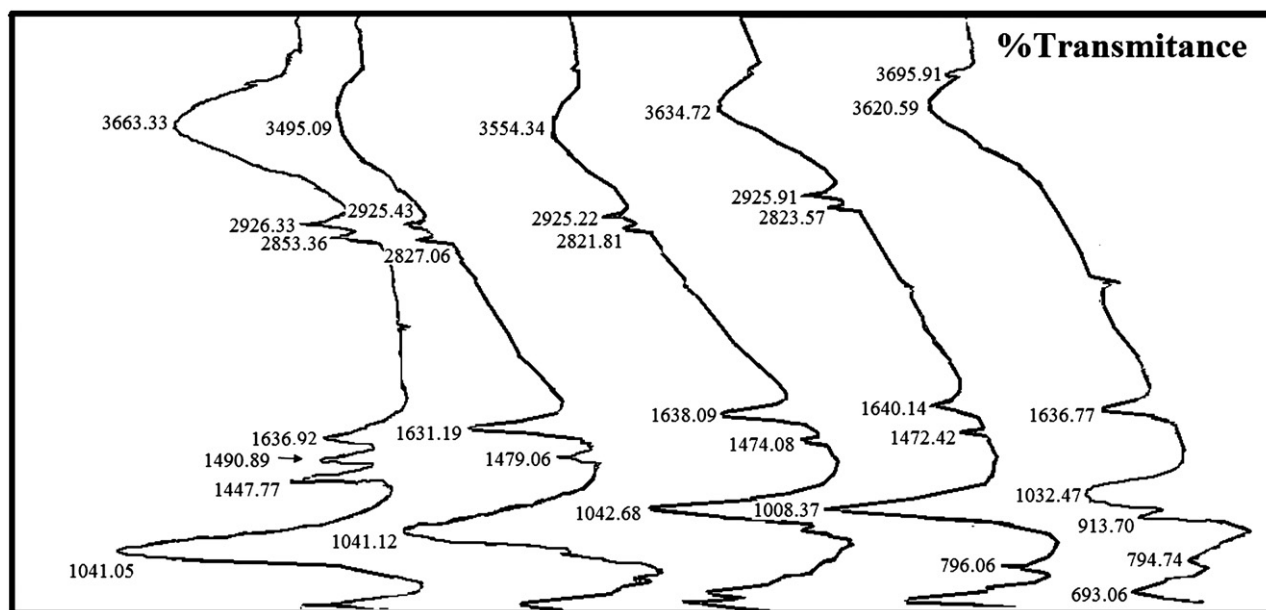


Fig. 3. FTIR spectra of material (from top to down): montmorillonite, CT-0.5, CT-1.0, CT-2.0 and CT-3.0 respectively.

occurring on the spectra of CT-0.5 and CT-1.0 are shifts of the band from 2926 cm^{-1} in CT-0.5 to 2925 cm^{-1} and the band from 2823 cm^{-1} to 2822 cm^{-1} . Li et al. (2008) attributed these shifts to the changes of the alkyl conformations within the silica sheets of montmorillonite. Furthermore, the shift of these bands to higher wavenumbers at increased CTMA/CEC ratio is possibly a result of stronger alkyl chain interactions in organo-clays compared to raw montmorillonite. More intense and sharper absorption bands at 1478 and 1491 cm^{-1} on CT-3.0 indicated that of the presence of free surfactant molecules not contributed from the silica sheets (He et al., 2006).

3.2. Adsorption kinetics of toluene

The use of these synthesized organo-clays in the adsorption of a model organic compound, toluene was investigated (Fig. 4). In general, there is a noticeable difference in the kinetic rate of adsorption of toluene by raw montmorillonite and CTMA-intercalated montmorillonite. The CTMA-intercalated montmorillonites demonstrated higher adsorption capabilities compared to the unmodified montmorillonite.

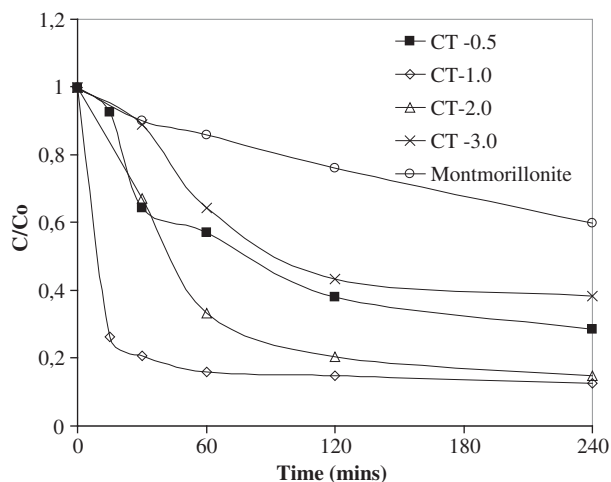


Fig. 4. Kinetics curve of toluene adsorption by using varied CTMA-montmorillonite and montmorillonite.

The rate of toluene uptake increased in the following order: CT 2.0 < CT-0.5 < CT 3.0 < CT-1.0. The adsorption kinetics was evaluated by the Elovich, pseudo-first order and second order equations. The results are presented in Table 1.

Pseudo-first order equation:

$$\log(q_e - q_t) = \log(q_e) - \frac{k}{2.303} t \quad (3)$$

Pseudo-second order equation:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (4)$$

where q_e and q_t (mg/g) are the toluene uptake at equilibrium and at a specific time, t , respectively, and k is the constant of adsorption kinetics.

The Elovich model equation is as follows:

$$qt = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (5)$$

where α (mg/g.min) and β (g/mg) are the initial adsorption rate and the desorption constant, respectively (Azizian, 2004; Ho and McKay, 1999).

The relationship between the CTMA/CEC ratio and the adsorption constant is not linear. The relationship is not linear with respect to the

Table 2
Coefficient of determination data from simulated kinetics model: pseudo-first order, pseudo-second order and Elovich model.

Sample	Coefficient of determination (R^2) of the simulated model		
	Pseudo first order	Pseudo second order	Elovich model
Montmorillonite	0.1093	0.9779 ($k = 1.17 \times 10^{-6}/\% \cdot \text{min}$)	0.9328
CT-0.5	0.9761 ($k = 0.12/\text{min}$)	0.9294 ($k = 2.40 \times 10^{-2}/\% \cdot \text{min}$)	0.9515
CT-1.0	0.9206	0.9467 ($k = 1.77 \times 10^{-1}/\% \cdot \text{min}$)	0.9197
CT-2.0	0.6775	0.9756 ($k = 4.6 \times 10^{-2}/\% \cdot \text{min}$)	0.8748
CT-3.0	0.7977	0.9783 ($5.08 \times 10^{-3}/\% \cdot \text{min}$)	0.9352

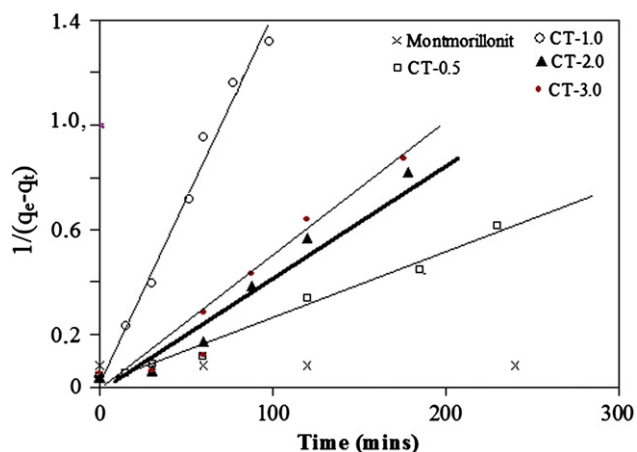


Fig. 5. Pseudo-second order plot for kinetics data of toluene adsorption by montmorillonite and CTMA-montmorillonite samples.

specific surface area and pore volume either. He et al. (2006) proposed that the change in clay structure during surfactant loading occurred because an organo-clay has the low surfactant packing density and the greatest tendency to form a lateral monolayer structure. This occurred in CT-0.5, where the interaction between toluene and the adsorbent was strongly influenced by the interaction of the silica-alumina sheets in montmorillonite in spite of hydrophobic sites created by the intercalated CTMA. When the CTMA/CEC ratio was increased to 1.0, there was an intense increase in the interaction between the montmorillonite clay surface and the CTMA, which trapped a high amount of toluene. Accordingly, when CTMA was added, the role of alkyl chains on clay surface is dominant and the interactions among the hydrocarbon chains were relatively strong. Conversely, the interaction of the adsorbate with the silicate surface was weaker. However, at further addition of alkylamine, the contribution of hydrocarbon chains on surface is not significant towards porous structure of montmorillonite. This was inferred by the adsorption capacities of CT-2.0 and CT-3.0 that were lower compared to CT-0.5 and CT-1.0. The confirmation can also be obtained from XRD profile and FTIR analysis. The XRD reflections showed that the CT-3.0 organo-clay has a lower d_{001} value than CT-2.0, suggesting that CTMA addition within this range did not increase the distance between the silica layers and CTMA adsorbed on the external surfaces of the montmorillonite.

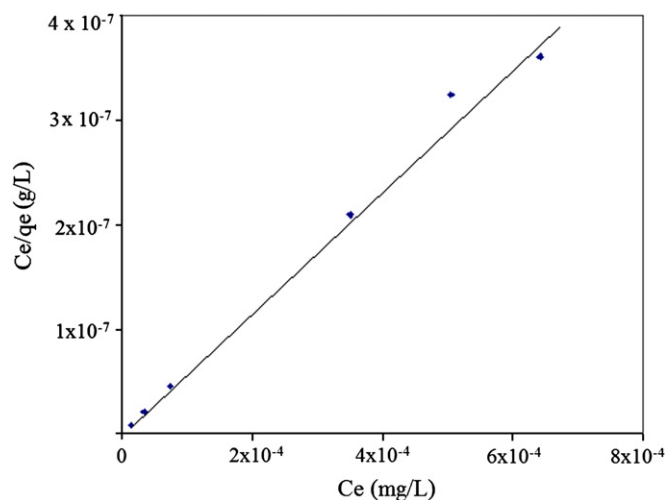


Fig. 6. Langmuir isotherm plot of toluene adsorption kinetics by CT-1.0.

Table 3

Coefficient of determination data from simulated adsorption isotherm: Langmuir, Freundlich and Temkin isotherm.

Sample	Coefficient of correlation		
	Langmuir	Temkin	Freundlich
Montmorillonite	0.9503	0.6066	0.9470
CT-0.5	0.9999	0.9257	0.9987
CT-1.0	0.9999	0.8962	0.8935
CT-2.0	0.8556	0.0022	0.1273
CT-3.0	0.9998	0.8961	0.9366

From the evaluation of coefficient of determination (R^2) for each kinetic model with respect to experimental data, the pseudo-second order fit to the data with the highest values of the coefficients for almost all adsorbents, suggesting that the pseudo-second order is the most appropriate model for montmorillonite and CTMA-intercalated montmorillonite (Table 2). Similar results were reported by Tong et al. (2010) in acid red G adsorption on octadecyltrimethylammonium-montmorillonite, Park et al. (2011) for the recalcitrant organic molecules adsorption from aqueous media and Gök et al. (2008) in the adsorption of naphthalene on organo-sepiolite. Plots of the pseudo-second order model are presented in Fig. 5.

In addition, the second-order kinetics was found to apply in the adsorption of acid green 25 by CTMA-intercalated montmorillonite by Koswojo et al. (2010), the adsorption of reactive red MF-3B by surfactant-modified attapulgite (Huang et al., 2007), erythrosine B and 2,4,5-trichlorophenol adsorption (Rytwo and Gonen, 2006) and acid dye adsorption (Baskaralingam et al., 2006). Ho and McKay (1999) proposed that the good fit of the pseudo-second order model indicated that the rate-limiting step in the adsorption process may be chemical sorption or chemisorption that involves valency forces through sharing or exchanging electrons between the adsorbent and the sorbate. In the case of the organo-clay adsorbents, the chemical interactions most likely involve the alkyl groups as active surface sites to bind with toluene molecules, and the cations within the clay layers provide electrostatic forces.

For CT-0.5, the kinetics seems to be a first order, with a higher coefficient, rather than a pseudo-second order. The difference in the kinetic order of the adsorption kinetics was most likely caused by the number of surfactant sites on the clay surface where there was the lowest probability of chemical interactions between the alkyl groups and toluene. Another possible explanation is that the interlayer distance in CT-0.5 was the lowest among the CTMA-intercalated montmorillonite organo-clays as indicated by the value of d_{001} and the pore radius. In similar experiments reported by Sekrane et al. (2011), the rate of adsorption was affected by intra-particle diffusion. Because chemical interactions can dominate the mechanism of adsorption, the smaller pore radius most likely affected the adsorption by molecular sieving processes such that the rate of adsorption was lower even though the specific surface area of adsorbent was higher. From adsorption kinetic constant (k), the adsorption capabilities were in the following order: montmorillonite < CT-0.5 < CT-3.0 < CT-2.0 < CT-1.0.

Table 4

Langmuir parameters of montmorillonite and CTMA-montmorillonite.

Sample	Langmuir parameter	
	K_L (L/g)	q_{max} (mg/g)
Montmorillonite	85.45	8.41
CT-0.5	112.97	33.68
CT-1.0	310.84	58.63
CT-2.0	284.96	21.11
CT-3.0	279.99	18.64

3.3. Adsorption isotherms

Isotherms of adsorption data were fitted with linearized forms of the Langmuir, Freundlich and Temkin models, which are expressed in the following Eqs. (6–8).

$$\frac{c_e}{q_e} = \frac{c_e}{q_{max}} + \frac{1}{K_L q_{max}} \quad (6)$$

$$\log(q_e) = \log K_f + \frac{1}{n} \log c_e \quad (7)$$

$$q_e = \left(\frac{RT}{bT} \right) \ln(Ac_e) \quad (8)$$

Where c_e (mg/L) is the toluene concentration in the filtrate, q_{max} (mg/g) is the adsorption capacity at the monolayer surface, K_L (L/g) is the Langmuir constant, K_f (mg/g) is the Freundlich constant for adsorption capacity and n is the Freundlich constant for adsorption intensity. From Eq. (8), RT/bT (J/mol) is the Temkin constant that is related to the heat of sorption, and A (l/g) is the equilibrium binding constant related to the maximum binding energy, whereas R (8.314 J/mol K) is the universal gas constant, and T (K) is the absolute temperature of the solution. The fit of the Temkin model was determined by a plot of q_e versus $\ln c_e$ (Ahmad and Rahman, 2011; Azizian, 2004).

Refer to the highest value of coefficient of determination (R^2) and plot of the Langmuir isotherm (Fig. 6 and Table 3), it can be concluded that the isotherm is fit for the Langmuir model than the Temkin and Freundlich isotherms. Similar results were obtained for the adsorption of toluene by organo-mica (Seliem et al., 2011). From a comparison of the parameters, the surfactant modification of montmorillonite significantly enhanced its capability to adsorb toluene (Table 4). The q_{max} values found in these experiments are slightly higher than the values reported by Seliem et al. (2011) in similar experiments using an organo-mica.

4. Conclusion

Cetyltrimethylammonium-intercalated Indonesian montmorillonite showed significantly better adsorption of toluene than raw montmorillonite. The CTMA/CEC ratio influenced the adsorption kinetics showing strong correlations with physicochemical characteristics such as the d_{001} value, specific surface area, functional groups and structure. Kinetic and isotherm studies revealed that toluene adsorption obeyed pseudo-second order model and the Langmuir isotherm.

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