

p-Nitrophenol, phenol and aniline sorption by organo-clays

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Abstract

The aims of this study were to make use of organo-clays (i.e., Cloisite-10A, Cloisite-15A, Cloisite-30B and Cloisite-93A), to remove *p*-nitrophenol, phenol and aniline of organic pollutants. The organo-clays were characterized by X-ray diffraction (XRD). Sorption isotherm, kinetic and pH effect of *p*-nitrophenol, phenol and aniline sorbed by four organo-clays were evaluated. The *d*-spacings (0 0 1) of the XRD peak of Cloisite-10A, Cloisite-15A, Cloisite-30B and Cloisite-93A are 1.98, 2.76, 1.93 and 2.64 nm, respectively. The *d*(0 0 1)-spacings of XRD indicated that these *p*-nitrophenol, phenol and aniline could penetrate into the interlayer of clays and expand the *d*(0 0 1)-spacings. The linear sorption isotherm of constant partition was employed to describe the sorption isotherms of phenols sorbed by organo-clays through hydrophobic–hydrophobic chemical reactions. The parabolic diffusion and power-function of kinetic models were employed to describe properly the kinetic experiments. The rate limiting step of the *p*-nitrophenol sorption reactions on organo-clays were diffusion-controlled processes (i.e., 15A, 30B, 93A) and chemical-controlled process for 10A organo-clays. The pre-exponential factor of the *p*-nitrophenol sorbed by four organo-clays showed the trend as follows: 10A > 30B > 93A > 15A. The efficiency of these organo-clays in removing phenol compounds in water treatments merit further study.

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1. Introduction

Soil is known to function as a chemical as well as a biological filter that lessens the impact of organic chemicals on the environments through various processes [1]. The 2:1 layer silicates are important soil constituents in the preparation of organo-clays for polyphenols sorption. Montmorillonite, with its lower surface charge density, has substitution mostly in the octahedral sheet [2]. Inorganic cations in the clays can be exchanged with organic or inorganic chemicals. Hydrophilic clays can be changed to organophilic clays through organic chemicals [3]. Such modified organo-clays have various applications in paper, petroleum (oil-based drilling fluids for deep wells), catalytic, water treatment [4–6], and several other industries. It can also act as a sorbent for a great variety of organic pollutants, such as

chlorophenoxy propionic acids (CPA) [7–12], and some weakly acidic pesticides, which have been detected in surface waters [13–17]. These modified organo-clays have acted as a partition media in the sorption of organic pollutants [18–21].

p-Nitrophenol, phenol and aniline are common pollutants found particularly in the effluents from pesticides, pharmaceuticals, petrochemicals and other industries. Owing to their toxicity and reactivity, the presence of phenol compounds in the natural environment has been of great concern. In soil environments, the fate of pesticides is governed by the retention, transformation, and transport processes, and the interaction of these processes. Because of agricultural and industrial contamination of ground water by organic chemicals, increased attention has been paid to those factors influencing the reactivity and mobility of organic compounds through soils. Soils are a heterogeneous mixture of numerous components. Clays in soil environment often possess the ability to sorb organic species. The understanding of the reactivity of simple organic matters on clay surfaces can help prevent groundwater contamination [22–24].

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The organo-clay, modified by quaternary ammonium salts, often used to remove organic contaminants from water. However, the modified organo-clays were effect by their modifier polarity. These modified organo-clays were selected to act as sorbents for the sorption of *p*-nitrophenol, phenol and aniline of organic pollutants. The objective of this study was to evaluate the capabilities and mechanism of organo-clay for selective removal of organic pollutants from water. The *p*-nitrophenol, phenol, and aniline were used as representative organic pollutants in this research.

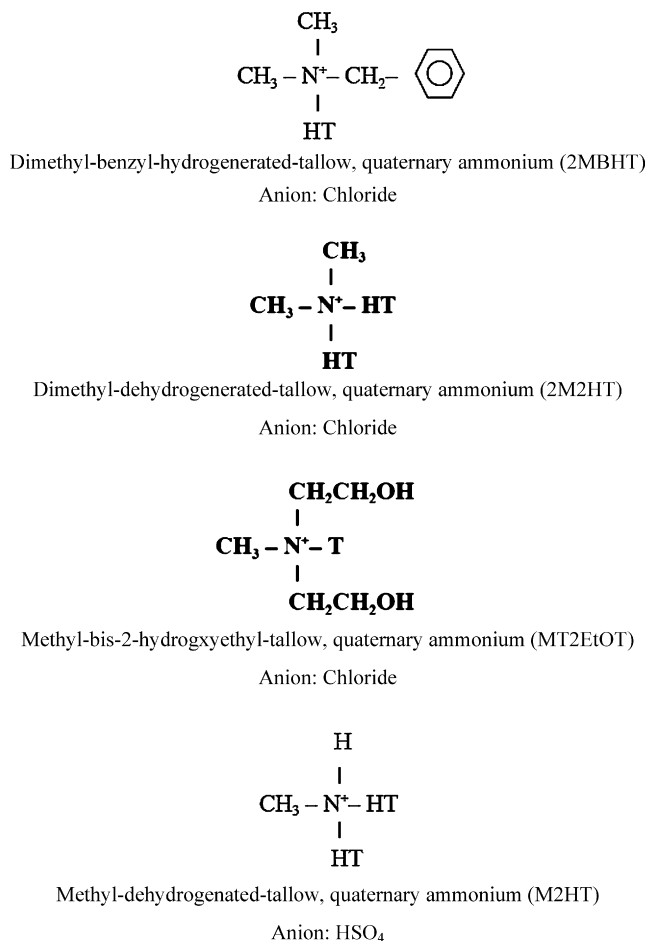
2. Materials and methods

2.1. Materials

The organo-clays, Cloisite-10A, Cloisite-15A, Cloisite-30B and Cloisite-93A, were prepared and supplied by Southern Clay Products, County of Gonzales, TX, USA. The Cloisite-10A, Cloisite-15A, Cloisite-30B and Cloisite-93A were the SWy-1 montmorillonite modified by 2MBHT (dimethyl-benzyl-hydrogenated-tallow, quaternary ammonium), 2M2HT (dimethyl-dehydrogenated-tallow, quaternary ammonium), MT2EtOT (methyl-bis-2-hydroxyethyl-tallow, quaternary ammonium), and M2HT (methyl-dehydrogenated-tallow, quaternary ammonium), respectively (Fig. 1). The modifier concentrations and specific gravity were 125, 95, 90 and 90 cmol kg⁻¹, and 1.90, 1.77, 1.98 and 1.88 g mL⁻¹, respectively. The hydrogenated tallow was mixed of ~65% of C18, ~30% of C16 and ~5% of C14. These data were adapted from commercial information of Southern Clay Products. The SWy-1 montmorillonite (CEC of 764 cmol kg⁻¹, surface area of 31.82 m² g⁻¹) (Crook County, Wyoming, USA) was the clay mineral used to prepare organo-clay complexes [25]. The size of these clays used for all experiments were less than 2 μm. The *p*-nitrophenol, phenol and aniline of analytical grade were obtained from Sigma Company, USA.

2.2. Physical and chemical properties of *p*-nitrophenol, phenol and aniline

p-nitrophenol is a colorless to yellowish solid. The chemical formula of *p*-nitrophenol is C₆H₅NO₃ and its molecular weight is 139.11. The solubility of *p*-nitrophenol is 1.6 g 100 mL⁻¹. The distribution constant between octanol and water, log *K*_{ow} is 1.91. Boiling and melting points, vapor pressure and density of *p*-nitrophenol are 279 °C, 60 °C, 2.2 mmHg and 1.27 kg L⁻¹, respectively. The LD₅₀ of *p*-nitrophenol is 620 mg kg⁻¹. Chemical formula and molecular weight of phenol are C₆H₅OH and 94.11, respectively [26]. Phenol is a colorless to pink-colored solid or dense liquid. The boiling and melting points and vapor pressure of phenol are 182 and 43 °C, and 3.24 mmHg, respectively. The solubility, density and log *K*_{ow} of phenol are 9.3, 1.06, and 1.46 g 100 mL⁻¹, respectively. The LD₅₀ of phenol is 317 mg kg⁻¹. The chemical formula and molecular weight of aniline are C₆H₅NH₂ and 93.13, respectively. Aniline is a colorless oil. Light radiation causes the browning effect of oil liquid with stun smelling. The solubility, density and log *K*_{ow} of aniline



Where HT is Hydrogenated Tallow (~65% C18, ~30% C16, ~5% C14)

Fig. 1. Chemical structure of quaternary alkylammonium salts used to prepare organoclays.

are 3.6, 1.02, and 0.90 g 100 mL⁻¹, respectively. The LD₅₀ of aniline is 250 mg kg⁻¹. The boiling and melting points, vapor pressure and vapor density of aniline are 184 °C and -6 °C, 0.7 mmHg and 3.22 kg L⁻¹, respectively [8,10,26–27].

2.2.1. Methods

2.2.1.1. Characterization of organo-clays. The organo-clays were prepared as slurries and dropped onto petrographic slides for X-ray diffraction (XRD) [28]. The oriented samples were examined by X-ray diffractometer, using a Rigaku Geigerflex with Cu Kα radiation with Ni filter generated at 35 kV and 15 mA. The XRD patterns were recorded in the range of 3 to 50° 2θ at a scanning speed of 1° 2θ min⁻¹. Small amounts of suspension after *p*-nitrophenol, phenol and aniline sorbed by organo-clays were also dropped onto petrographic slides for XRD analyses.

2.2.1.2. *p*-Nitrophenol, phenol and aniline sorbed by organo-clays. For the *p*-nitrophenol, phenol and aniline sorption isotherm studies, 50 mg of organo-clay were placed in 50 mL centrifuge tube and supplemented with 20 mL of 0.05, 0.075, 0.1, 0.125, 0.15, 0.175 and 0.2 mM concentrations of *p*-

nitrophenol, phenol and aniline sorption. The suspensions were shaken for 24 h. and centrifuged at $24,000 \times g$ and 25°C for 30 min. The phenol concentrations in supernatants were determined in supernatants. For the experiments of sorption isotherms, the constant partition (CP), Langmuir, and Freundlich equations were employed to fit the data of *p*-nitrophenol, phenol and aniline sorptions at the end of the 24 h reaction time.

Traditionally, the constant partition sorption isotherm indicates that the sorbed-phase concentration (q_e) is directly proportional to the solution-phase concentration (C_i):

$$q_e = K_d C_i \quad (1)$$

where K_d is the distribution coefficient (L kg^{-1} organo-clay).

The Langmuir equation is shown in Eq. (2),

$$q_e = \frac{K_L B C_e}{1 + B C_e} \quad (2)$$

where q_e (mmol kg^{-1} soil) is the equilibrium sorption capacity, B (mmol kg^{-1} organo-clay) is the maximum monolayer sorption capacity, C_e (mmol L^{-1}) is the equilibrium solute concentration, and K_L is Langmuir affinity constant (L mmol^{-1}).

Another equilibrium-controlled sorption isotherm is the Freundlich sorption isotherm, which can be expressed in the following form:

$$q_e = K_F C_i^n \quad (3)$$

where K_F is the Freundlich sorption constant (L kg^{-1} organo-clay) and n is the Freundlich exponent.

2.3. Effects of kinetic reactions, pH and temperature effects

Sorption of 0.2 mM *p*-nitrophenol at different pH was prepared and shaken at 0, 5, 15, 30, 45, 60, 120, 240, 480, 720, 960, 1440 and 2880 min for kinetic sorption studies, using 50 mg of organo-clays and 20 mL of phenol solutions in 0.01 M CaCl_2 . The pH of suspensions were initially adjusted to 4, 7, and 9 with 0.1 M HCl or NaOH solutions by pH-stat (Radiometer TIM865) and the constant pH was maintained for one week. These suspensions were then shaken for 24 h and centrifuged under the same conditions as the sorption isotherm experiments in triplicates. The equilibrium pH and *p*-nitrophenol concentrations were then determined in supernatants. The experiment of *p*-nitrophenol sorption by organo-clays was conducted at phenol concentration of 0.2 mM and pH 7.0 at 288, 298, 308 and 318 K. The suspension was made by mixing 50 mg of organo-clays with 25 mL of *p*-nitrophenol, with pH adjusted to 7.0 using HCl or NaOH solutions by pH-stat and equilibrated at 288, 298, 308 and 318 K overnight.

The Arrhenius equation was employed to calculate the activation energy (E_a) and the pre-exponential factor [29]:

$$K = A e^{-E_a/RT} \quad (4)$$

where k is the rate coefficient, A is the pre-exponential factor (frequency factor), E_a is the Arrhenius activation energy, R is the universal gas constant, and T is the absolute temperature.

The amounts of *p*-nitrophenol sorption were calculated from the difference between the initial and equilibrium phenol concentrations in sorption isotherm studies. Triplicate kinetic runs were carried out for each treatment. Sorption data were fitted by the kinetic models, including zero-order, first-order, and second-order equations as well as empirical models including parabolic diffusion, power-function, and Elovich equations. These six selected models were the differential form of the general-rate equation [30].

2.4. Chemical analyses

The *p*-nitrophenol, phenol and aniline concentrations in supernatants (i.e., passed through $0.45 \mu\text{m}$ Millipore filter) were determined by UV spectroscopy at 317 nm for *p*-nitrophenol, 210 nm for phenol, and 230 nm for aniline [14,15,31,32]. A blank sample (50 mg of sample with 5 mL of 0.01 M CaCl_2) was used for background correction.

2.5. Statistical analysis

The linear forms of different kinetic equations were applied to the sorption and kinetic data and their goodness of fit was evaluated based on the R^2 , level of significance (*p*-value), and standard error (S.E.). The SAS version 8.0 was employed for statistical analysis. Statistical significance was defined as $p = 0.05$.

3. Results and discussion

The *d*-spacings (001) of the XRD peak of Cloisite-10A, Cloisite-15A, Cloisite-30B and Cloisite-93A from our observations are 1.98, 2.76, 1.93 and 2.64 nm, respectively (Fig. 2). Zhang et al. [33] reported that sorption of quaternary amines on clays involved at least three types of reactions, viz. a cation-exchange reaction, sorption of ion pairs and tail-tail interactions. The polarity of three organic sorbates showed following trend: phenol > aniline > *p*-nitrophenol. The hydrophobicity of four organo-clays showed the trend as follows: 15A > 93A > 10A > 30B. Because the modifier of the Cloisite-10A contained aromatic functional group, it would be shown higher hydrophobic properties than others.

3.1. X-ray analyses of *p*-nitrophenol, phenol and aniline sorbed by organo-clays

The *d*(001)-spacings of *p*-nitrophenol, phenol and aniline sorbed by Cloisite-10A expanded to or remained at 1.81, 1.98 and 2.22 nm, respectively (Fig. 2). On the other hand, *p*-nitrophenol, phenol and aniline sorbed by Cloisite-15A, *d*(001)-spacings expanded to 2.85, 2.89 and 2.95 nm; Cloisite-30B samples expanded to or remained at 1.93, 1.95 and 1.98 nm, and Cloisite-93A samples expanded to 2.75, 2.76, and 2.77 nm, respectively. These results indicate that Cloisite-15A- and Cloisite-93A-sorbed *p*-nitrophenol, phenol and aniline expand the *d*(001)-spacings. Thus, these *p*-nitrophenol and phenol and aniline can penetrate into the interlayer of clays. The Cloisite-10A-sorbed *p*-nitrophenol and phenol, and Cloisite-30B-sorbed

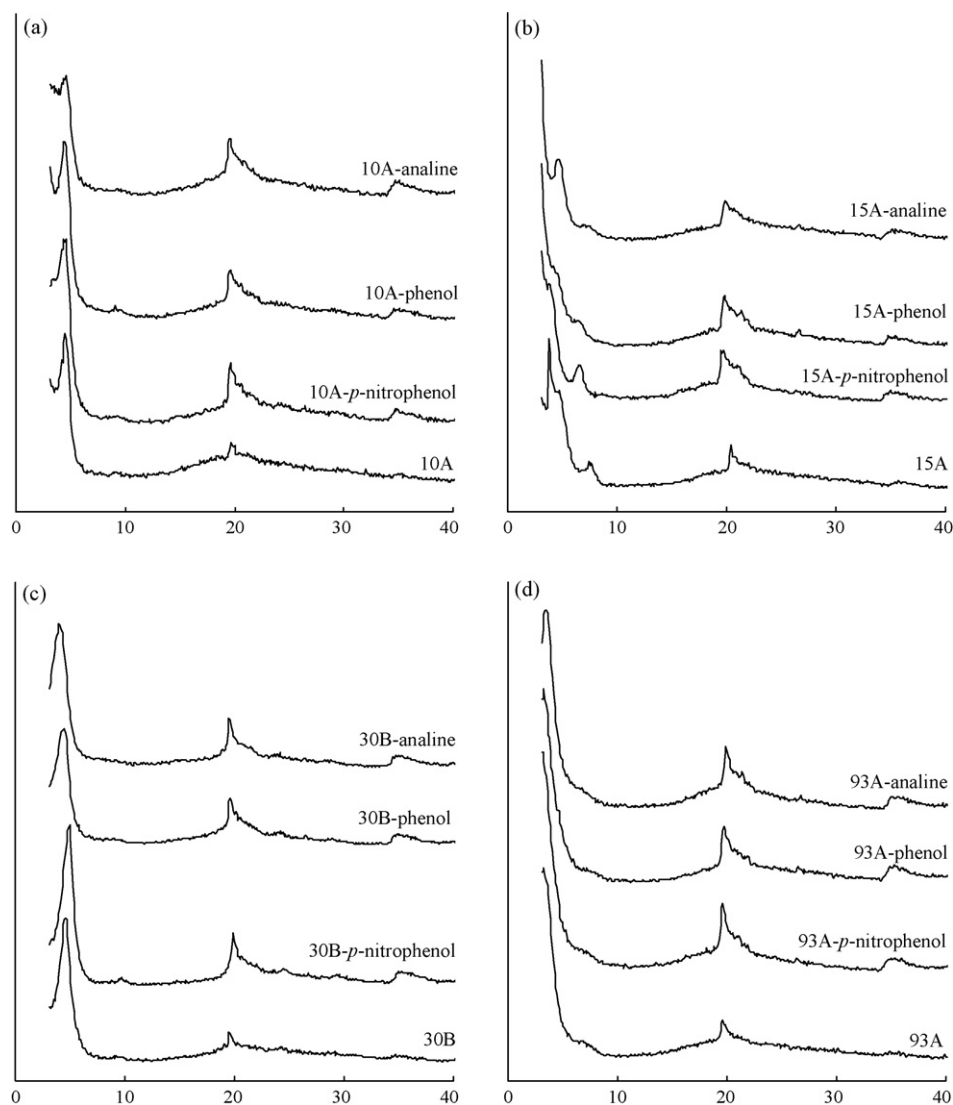


Fig. 2. X-ray diffraction patterns of (a) 10A, 10A-*p*-nitrophenol, 10A-phenol, and 10A-aniline, (b) 15A, 15A-*p*-nitrophenol, 15A-phenol, and 15A-aniline, (c) 30B, 30B-*p*-nitrophenol, 30B-phenol, and 30B-aniline and (d) 93A, 93A-*p*-nitrophenol, 93A-phenol, and 93A-aniline.

p-nitrophenol and aniline were the same $d(001)$ -spacings as original organo-clays, indicating that no *p*-nitrophenol penetrated into interlayers of clays. The Cloisite-10A-sorbed aniline and Cloisite-30B-sorbed phenols expand their $d(001)$ -spacings.

3.2. Sorption isotherms of *p*-nitrophenol, phenol and aniline by organo-clays

Sorption isotherms of *p*-nitrophenol, phenol and aniline sorbed by organo-clays revealed that the data fit well with linear, Langmuir and Freundlich sorption isotherm equations.

The K_d values of *p*-nitrophenol, phenol and aniline sorbed by organo-clays range from 2.49 to 34.39 L kg⁻¹ (Table 1). R^2 range from 0.57 to 0.99 with linear sorption isotherm. The constant determination values (R^2) of phenol sorbed by organo-clays are higher than those of *p*-nitrophenol and aniline sorbed by organo-clays. There are some unknown reasons that aniline sorbed by 30B organo-clay showed the lowest R^2 (Table 1). The maximum monolayer sorption capacity (B) showed higher

phenol sorption with Langmuir sorption isotherm than that of *p*-nitrophenol and aniline sorption by organo-clays. The n values of phenol sorbed by organo-clays were greater than those of *p*-nitrophenol and aniline when Freundlich isotherm equation was applied. The n value is an empirical constant in the Freundlich isotherm equation and range from 0.61 to 1.04 of phenol sorption. In general, three phenols sorbed by four types of organo-clays (10A, 15A, 30B, and 93A) show an obvious linear relationship with the Freundlich equation ($R^2 > 0.92$) except aniline sorbed by 30B organo-clay. The K_L values of phenol compounds sorbed by 10A and 15A organo-clays show the following trend: *p*-nitrophenol > phenol > aniline with Langmuir sorption isotherm. However, three phenol compounds sorbed by 30B and 93A show the reverse tendency. It is related to the polarity and solubility of *p*-nitrophenol (–NO₂, 1.6 g 100 mL⁻¹), phenol (–OH, 9.3 g 100 mL⁻¹) and aniline (–NH₂, 3.69 g 100 mL⁻¹). Furthermore, it is also related to the sorbents of organo-clays of Cloisite-10A, Cloisite-15A, Cloisite-30B and Cloisite-93A, which were modified by 2MBHT, 2M2HT,

Table 1
Linear, Langmuir and Freundlich sorption isotherm parameters of *p*-nitrophenol, phenol, and aniline sorption by organo-clays

| Clays | Linear sorption isotherm | | Langmuir sorption isotherm | | | Freundlich sorption isotherm | | |
|-----------------------|-----------------------------|-------|-------------------------------|------------------------------|-------|------------------------------|-------|-------|
| | K_d (L kg ⁻¹) | R^2 | K_L (L mmol ⁻¹) | B (mmol kg ⁻¹) | R^2 | K_F (L kg ⁻¹) | n | R^2 |
| <i>p</i> -Nitrophenol | | | | | | | | |
| 10A | 13.5 | 0.91 | 0.45 | 156 | 0.98 | 46.3 | 0.479 | 0.99 |
| 15A | 13.5 | 0.91 | 0.87 | 343 | 0.98 | 141.0 | 0.393 | 0.96 |
| 30B | 9.02 | 0.90 | 0.29 | 121 | 0.99 | 28.6 | 0.524 | 0.99 |
| 93A | 7.73 | 0.81 | 0.41 | 104 | 0.99 | 28.1 | 0.491 | 0.95 |
| Phenol | | | | | | | | |
| 10A | 2618 | 0.99 | 0.05 | 50708 | 0.99 | 3064 | 1.04 | 0.99 |
| 15A | 34.39 | 0.98 | 0.72 | 96.04 | 0.99 | 39.12 | 0.68 | 0.99 |
| 30B | 3.85 | 0.97 | 0.002 | 2001 | 0.96 | 4.31 | 0.86 | 0.97 |
| 93A | 19.27 | 0.88 | 1.40 | 43.45 | 0.92 | 24.20 | 0.61 | 0.92 |
| Aniline | | | | | | | | |
| 10A | 3.79 | 0.93 | 0.002 | 2005 | 0.93 | 4.17 | 0.84 | 0.93 |
| 15A | 12.82 | 0.97 | 0.003 | 3701 | 0.94 | 15.34 | 0.68 | 0.99 |
| 30B | 2.49 | 0.57 | 4.16 | 5.385 | 0.91 | 4.12 | 0.42 | 0.78 |
| 93A | 2.57 | 0.90 | 27.67 | 4.506 | 0.78 | 4.64 | 0.28 | 0.93 |

^a K_d : distribution coefficient; K_L : Langmuir affinity constant; B : maximum monolayer sorption capacity; K_F : Freundlich sorption constant; n : Freundlich exponent.

MT2EtOT, and M2HT, respectively. The hexadecyltrimethylammonium (HDTMA) molecules appear to combine to form an aggregate and reduce the surface area, and charge reversal occurs at more than 100% CEC of HDTMA [12,32], thus reducing the number of accessible sites [34,35]. Ghosh and Schnitzer [36], and Schnitzer [37] noted that the three parameters controlling the molecular characteristics of organics are the concentration of organic materials, pH of the system, and ionic strength of the medium.

The Cloisite-15A- and Cloisite-93A-sorbed *p*-nitrophenol, phenol and aniline expand the $d(001)$ -spacings. Thus, these phenol compounds can penetrate into the interlayer of clays. The Cloisite-10A-sorbed *p*-nitrophenol and phenol, and Cloisite-30B-sorbed *p*-nitrophenol and aniline had the same $d(001)$ -spacings as original organo-clays, indicating that no *p*-nitrophenol has penetrated into interlayers of clays. The Cloisite-10A-sorbed aniline and Cloisite-30B-sorbed phenols also expand their $d(001)$ -spacings. The *p*-nitrophenol sorbed by organo-clay showed that the Cloisite-15A had the highest maximum monolayer sorption capacity, suggesting the *p*-nitrophenol sorbed on Cloisite-15A by nonionic interaction. The modifier of Cloisite-15A was more hydrophobic than other organo-clay, thus, the *p*-nitrophenol could easily interacted with Cloisite-15A by non-polar interaction. Boyd et al. [10] reported that *p*-nitrophenol should have been completely non-ionic ($\log K_{ow} = 1.91$) hydrophobic, it was sorbed strongly by the organo-clay complexes. The maximum monolayer sorption capacity of phenol sorbed on Cloisite-10A and -30B was 528–1167 and 21–46-folds higher than that on Cloisite-15A and -93A, respectively. The dramatic difference was affected by polarity. The Cloisite-10A and -30B showed more hydrophilic modifiers than others. Meanwhile, the solubility of phenol was higher than *p*-nitrophenol and aniline, thus, phenol could be dissociated easily in the water. Moreover, the $\log K_{ow}$ of the phenol and aniline are 1.49 and 0.90, respectively [26,27]. Thus, Westall et al. [26] and Lee et al. [27] suggested that not only

most of the sorption was non-coulombic and that hydrophobic or non-polar interaction between alkyl groups on the clays with phenol was possibly the major mechanism, but also dissociated phenol could be sorbed on organo-clay by hydrophilic interaction. The maximum monolayer sorption capacity of aniline sorbed on Cloisite-10A and -15A was 372–445 and 687–821-folds higher than that on Cloisite-30B and -93A, respectively. The polarity and solubility of aniline was between phenol and *p*-nitrophenol. In this experiment, the pH of suspension was higher than pK_a of aniline, indicating the lower H^+ concentration with the lower protonization. The modifiers of Cloisite-10A, -15A, and -30B contained the same anion (i.e., chloride), but the Cloisite-93A contained larger size of hydrosulfate. Therefore, the aniline tended to partition. Because of the large size of anion, the surface of Cloisite-93A formed steric shielding effect. Thus, the aniline sorption capacity of Cloisite-93A was lower than that of Cloisite-15A. Westall et al. [26] demonstrated that the distribution ratio of hydrophobic ionizable organic compounds, between aqueous and nonaqueous phases is shown to depend on the pH and ionic strength of the aqueous phase. For aqueous phases with high pH and ionic strengths, the dominant species of the phenol compounds in the octanol phase were the $-NO_3^-$, $-OH^-$, and NH_2^- phenolate ions in association with counter ions. Zhu et al. [38] suggested that sorption organic compounds to dual-cation organobentonite is affected by both adsorption and partition, with the relative effect being a function of the types and amounts of incorporated quaternary ammonium cations.

3.3. Kinetic studies

The kinetic and empirical equations, including the zero-, first-, and second-order rate equations, parabolic diffusion, power-function and Elovich equations were applied to the *p*-nitrophenol sorbed by organo-clays [30]. The goodness-of-fit of the equations to the data was evaluated using the constant of determination (R^2), probability (p), and standard error (S.E.) of

Table 2
Values of R^2 , p , and standard error (S.E.) for different kinetic models fitted to the p -nitrophenol sorption kinetics by organo-clays at 303 K

| Model | Clay | | | |
|---------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | 10A | 15A | 30B | 93A |
| R^2 | | | | |
| Zero-order | 0.764 | 0.724 | 0.807 | 0.829 |
| First-order | 0.788 | 0.825 | 0.812 | 0.856 |
| Second-order | 0.812 | 0.913 | 0.817 | 0.880 |
| Parabolic diffusion | 0.976 | 0.987 | 0.984 | 0.986 |
| Power-function | 0.968 | 0.946 | 0.982 | 0.985 |
| Elovich | 0.882 | 0.846 | 0.913 | 0.929 |
| p | | | | |
| Zero-order | 5.28×10^{-2} | 6.76×10^{-2} | 3.84×10^{-2} | 3.16×10^{-2} |
| First-order | 4.43×10^{-2} | 3.30×10^{-2} | 3.68×10^{-2} | 2.42×10^{-2} |
| Second-order | 3.69×10^{-2} | 1.11×10^{-2} | 3.52×10^{-2} | 1.84×10^{-2} |
| Parabolic diffusion | 1.50×10^{-3} | 6.00×10^{-4} | 9.00×10^{-4} | 7.00×10^{-4} |
| Power-function | 2.40×10^{-3} | 5.40×10^{-3} | 1.00×10^{-3} | 8.00×10^{-4} |
| Elovich | 1.78×10^{-2} | 2.71×10^{-2} | 1.12×10^{-2} | 8.20×10^{-3} |
| S.E. | | | | |
| Zero-order | 6.19×10^{-3} | 1.01×10^{-2} | 2.34×10^{-3} | 8.57×10^{-3} |
| First-order | 6.72×10^{-2} | 1.86×10^{-1} | 1.24×10^{-2} | 7.22×10^{-2} |
| Second-order | 7.33×10^{-1} | 3.30 | 6.56×10^{-2} | 6.15×10^{-1} |
| Parabolic diffusion | 1.50×10^{-3} | 6.00×10^{-4} | 9.00×10^{-4} | 7.00×10^{-4} |
| Power-function | 2.27×10^{-3} | 4.46×10^{-3} | 7.10×10^{-4} | 2.55×10^{-3} |
| Elovich | 4.37×10^{-3} | 7.53×10^{-3} | 1.57×10^{-3} | 5.53×10^{-3} |

Reaction time (5–60 min)

linear regression analysis. The R^2 , p , and S.E. values of these three parameters obtained by applying different models to the kinetic data obtained in the reactions of p -nitrophenol sorbed by four organo-clays are given in Table 2. All six rate equations fit satisfactorily the p -nitrophenol sorption data. Among the six models tested, the R^2 values in parabolic diffusion and power-function equations of p -nitrophenol sorbed by four organo-clays, and p -nitrophenol sorbed by 10A, 15A, 30B and 93A organo-clays fit to the parabolic diffusion equation are all above 0.984, and those to the power-function are >0.946 . The R^2 values of the second-order kinetic model are greater than 0.812. The p and S.E. values of p -nitrophenol sorbed by four organo-clays showed lower parabolic diffusion and power-function of kinetic models than that of the second-order model. According to all these observations, the parabolic diffusion and power-function equations were chosen as the common kinetic models in this study but those two kinetic equations are empirical models. However, in order to determine the rate constants, the second-order kinetic model was recommended. Fig. 3 shows the p -nitrophenol sorbed by organo-clays and fitted by the second-order kinetic model. The R^2 values are greater than 0.811. The kinetic rate of p -nitrophenol sorbed by organo-clays with the second-order kinetic model showed the following trend: $15A > 10A \approx 93A > 30B$ at pH 4, 7 and

9 (Table 3). However, the pH had no significant influence on the phenols sorbed by the same organo-clays of hydrophobic-hydrophobic chemical reactions.

3.4. Activation energy and pre-exponential factor of p -nitrophenol sorption

Temperature dependence of the rate constant of p -nitrophenol sorption on organo-clays was illustrated in Fig. 4 and Table 4. The rate constant decreases with increasing temperature. This demonstrates that the rate constant of p -nitrophenol sorption reactions on organo-clays were of Arrhenius temperature dependence. The activation energy and pre-exponential factor were calculated from the slope and intercept of the plotting of $\ln K$ versus $1/T$. The activation energies of p -nitrophenol sorption data fitted to Arrhenius equation were 84.15, 28.78, 37.05 and $-0.66 \text{ kJ mol}^{-1}$ with respect to 10A, 15A, 30B and 93A organo-clays (Table 5). Low E_a values ($<42 \text{ kJ mol}^{-1}$) indicate diffusion-controlled processes, whereas high E_a values ($>42 \text{ kJ mol}^{-1}$) (i.e., 10A) indicate chemically-controlled processes [30]. Therefore, the rate limiting step of the p -nitrophenol sorption reactions on organo-clays were diffusion-controlled processes (i.e., 15A, 30B, 93A). Diffusion processes, which

Table 3
Second-order rate constants for p -nitrophenol sorption by organo-clays

| | Clay | | | |
|---|----------------------|----------------------|----------------------|----------------------|
| | 10A | 15A | 30B | 93A |
| Rate constant ($\text{mM}^{-1} \text{ min}^{-1}$) | 5.9×10^{-2} | 4.1×10^{-1} | 5.4×10^{-3} | 6.4×10^{-2} |
| Standard error | 1.6×10^{-2} | 7.4×10^{-2} | 1.4×10^{-3} | 1.3×10^{-2} |

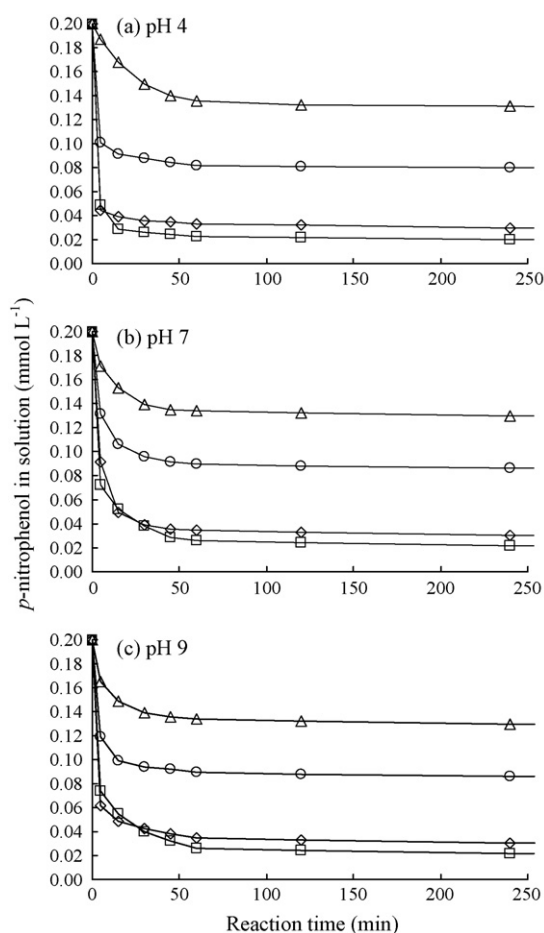


Fig. 3. pH effects on the kinetics of *p*-nitrophenol sorption on clays. Experiments were conducted with clay concentration, 2.0 g L^{-1} ; initial pH 7.0; initial concentration of *p*-nitrophenol 0.2 mM.

include diffusion of sorbate occluded in micropores (pore diffusion) and along pore-wall surfaces (surface diffusion) and diffusion processes in the bulk of the solid may dominate the kinetics of the overall processes and they are also extremely important in controlling the rates of sorption and desorption of *p*-nitrophenol from surface coordination sites of sorbents [39]. The pre-exponential factor of the *p*-nitrophenol sorbed by four organo-clays showed the trend as follows: $10\text{A} > 30\text{B} > 93\text{A} > 15\text{A}$. The lower activation energy and higher pre-exponential factor corresponded to the higher coefficient rate.

Table 4
Second-order rate constants for *p*-nitrophenol sorption by clays at different temperatures

| Clay | Rate constant ($\text{mM}^{-1} \text{ min}^{-1}$) | | | |
|------|---|------------------|------------------|------------------|
| | 278 ^a | 288 ^a | 298 ^a | 308 ^a |
| 10A | 0.111 | 0.298 | 0.059 | 0.036 |
| 15A | 0.687 | 0.458 | 0.418 | 0.199 |
| 30B | 0.007 | 0.029 | 0.005 | 0.011 |
| 93A | 0.006 | 0.059 | 0.065 | 0.060 |

^a Temperature (K).

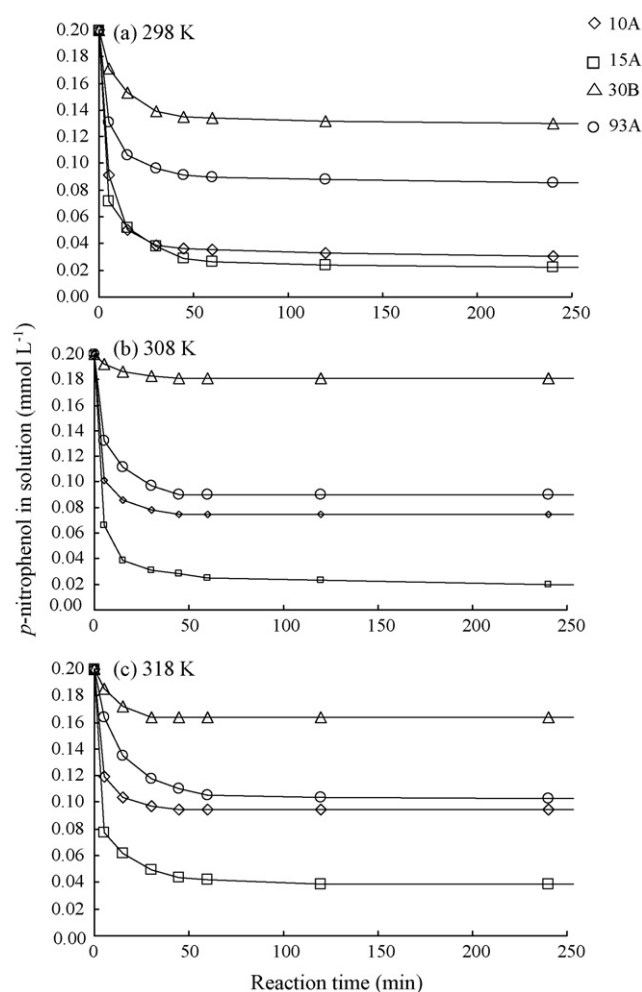


Fig. 4. Temperature effects on the kinetics of *p*-nitrophenol sorption on clays. Experiments were conducted with clay concentration, 2.0 g L^{-1} ; initial pH 7.0; initial concentration of *p*-nitrophenol 0.2 mM.

Table 5
Activation energy and pre-exponential factor of *p*-nitrophenol sorption on the organo-clays

| Clay | Activation energy (kJ mol^{-1}) | Pre-exponential factor ($\text{M}^{-1} \text{ h}^{-1}$) |
|------|--|---|
| 10A | 84.15 | 3.72×10^{10} |
| 15A | 28.78 | 3.85 |
| 30B | 37.05 | 1.60×10^8 |
| 93A | -0.66 | 12.6 |

4. Conclusions

Sorption of phenol compounds by organo-clays was affected by the concentration, solubility and $\log K_{ow}$ of sorbates, temperature, kinetic reaction time, and steric contour of organics. The suspension pH had no significant influence the sorption of phenol compounds by organo-clays through hydrophobic–hydrophobic chemical reaction. The rate limiting step of the *p*-nitrophenol sorption reactions on organo-clays were diffusion-controlled processes (i.e., 15A, 30B, 93A), however, *p*-nitrophenol sorbed by 10A showed the activation energy of $84.15 \text{ kJ mol}^{-1}$, indicating chemically-controlled processes.

The efficiency of these organo-clays in removing phenol compounds in water treatments will be further explored in future studies. Development of innovative organo-nanoparticles of layered silicated and silica nanocomposites with large surface area merits more in-depth research.

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