# Model for organic contaminant removal through the synthesis–adsorption one-step process of organobentonite

Luxiang Cai[a], Xinyu Zhang[b], Bingying Cui[b], Yu Mei[c],*

[a]Ningbo University of Finance & Economics, Ningbo 315175, China, email: 5464127@qq.com
[b]School of Environmental and Safety Engineering, Changzhou University, Jiangsu 213164, China,
email: 24069571@qq.com (X. Zhang), taojmy@163.com (B. Cui)
[c]College of Biological and Environmental Engineering, Zhejiang Shuren University, Hangzhou 310005,
China, email: imy1220@zjut.edu.cn

**ABSTRACT**

Organobentonite was applied in adsorption through a synthesis–adsorption one-step process. The influencing factors of the adsorption were discussed by the traditional partition theory. The one-step process showed very high removal efficiency for the PAHs (acenaphthene, β-naphthol, phenol, and naphthalene). The model of the treatment process was established based on the results of adsorption with the aid of different surfactants at various dosages. The model showed highly accurate and predicted results for the removal of phenanthrene and naphthalene, which were better than those for other contaminants. The maximum prediction error was only 6.7%, which confirmed that the adsorption mechanism of organobentonite is through partitioning.

*Keywords:* Model; Organobentonite; Synthesis–adsorption; Organic compound

## 1. Introduction

Bentonite is an aluminosilicate clay consisting mostly of montmorillonite type smectite. Its structure is strongly hydrophilic and involves the hydration of interlayer cations [1]. Therefore, the as-mined original bentonite exhibits extremely poor performance in the adsorption of organics, which greatly limits the adsorbent's application in organic wastewater treatment. Therefore, the unmodified bentonite is generally not an ideal material for adsorbing organics, especially some nonpolar organic pollutants. Modification or activation of bentonite to obtain various kinds of organobentonites for different applications is a common practice. To date, the adsorption properties of organobentonite have been extensively investigated [2–6]. Organobentonite refers to a kind of montmorillonite and organic composite consisting of montmorillonite and intercalated organic molecules, ions, and polymers,

which are held together by covalent bonds, ionic bonds, hydrogen bonds, dipoles, and/or van der Waals forces [7,8]. Various organic, cationic compounds can react with bentonite, such as alkyl ammonium ions, which contain carbon chains. These cationic compounds can exchange interlayer positive ions of montmorillonite to form ionic bonds [9,10].

The most widely used modification of cationic surfactants was done by the single-chain alkyl ammonium salt [11,12]. After applying bentonite, the surfactant combines with bentonite in two ways, namely, organic ion adsorption and physical adsorption. Moreover, the two adsorption forms can coexist and mainly combine through covalent bonds, ionic bonds, and van der Waals forces. The general adsorption performance of modified bentonite for organics is considerably improved relative to that of original bentonite. The former is several tens to hundreds of times more effective than the latter in removing organic molecules from water.

* Corresponding author.

The preparation for organobentonite is mainly divided into three methods: dry, pre-gel, and wet methods [13]. The dry preparation of organobentonite involves directly mixing an organic modifier, heating, and squeezing bentonite containing 20%–30% water. The pre-gel method is conducted by adding organic solvents (e.g., mineral oil) to clay and surfactant during this process followed by extracting the hydrophobic bentonite complex into the organic phase. The water phase is removed after evaporation, and the organobentonite pre-gel is retained. However, some problems exist in the first two methods, including high-energy consumption, product uniformity, and requirements for high bentonite quality and purity. Therefore, the wet modification technique is the most commonly used method currently.

The wet synthesis of organobentonite involves the dispersal of bentonite powder in water to make slurry. Then, an organic modifier is added for ion exchange under full mixing conditions to achieve the organic modified product [14–17]. The organobentonite prepared through the wet process is in suspension form, and the bentonite is sufficiently mixed with the surfactant. Under a sufficiently long reaction time, the interlayer metal cations of bentonite and the surfactant cations attain exchange equilibrium. After filtration, the bentonite is washed, dried, and ground to obtain stable organobentonite products with uniform particle morphology. The requirement for equipment and operation is lower in the wet method than in the dry method. Thus, the wet method is currently the most frequently applied preparation method for organobentonites.

To save energy and cut down cost, an organobentonite synthesis–adsorption one-step process was proposed by Zhu and Ma [18], which can utilize the surfactant existing in wastewater to synthesize organobentonite. In this process, the pollutants are adsorbed and the wastewater is treated at the same time to remove surfactant. The one-step process given above not only preserves the good adsorption properties of organobentonite but also overcomes the shortcomings (e.g., process complexity, separation difficulties, etc.) of traditional organobentonite in wastewater treatment [18–22]. The process is simple, the adsorption and removal efficiency of the pollutant are high, and a good separation effect is achieved. Currently, many more research studies are focused and progressed on the investigation of this one-step process [23–25]. Thus, the large-scale application of organobentonite in wastewater treatment can be realized.

However, no model for the application of this one-step process on organic wastewater treatment was established. In the present study, the effects of different surfactants and various dosages on the synthesis– adsorption of organobentonite were studied, and the model for the removal of the organic contaminants was established. The mathematical model will help predict the removal efficiency of the adsorption. The effects of three surfactants with different lengths of alkyl chains [i.e., cetyltrimethyl ammonium bromide (CTMAB), dodecyl trimethyl ammonium bromide (DTMAB), and octyltrimethyl ammonium bromide (OTMAB)], on the synthesis of organobentonite and the adsorption of acenaphthene, β-naphthol, phenol, and naphthalene were investigated. Various factors such as density as well as hydrophobicity of the bentonite layers, functions, and adsorption performance of bentonite, were adjusted by changing the category, composition, and surfactant loading. The relationship between the pollutants and their adsorption results in the presence of different surfactants was obtained by statistical regression.

## 2. Analysis of influencing factors

When bentonite was added to the wastewater containing non-ionic organic compound (NOCs), these NOCs were found to be present in the dissolved and bentonite-adsorbed states (or phases). When the cationic surfactants, such as CTMAB, were added to the system, the synthesis–adsorption one-step process was achieved. Three more states increased for the NOCs, namely, CTMAB monomer, dissolved state of CTMAB micelles, and adsorbed state of CTMAB (Fig. 1) on bentonite.

The equilibrium relation of NOCs existing in the synthesis–adsorption one-step process of organobentonite is complex, and the existing interface increases from 1 to 12 (Fig. 1). Four independent interface parameters were obtained as follows [26]: $K_d$, $K_{mn}$, $K_{mc}$, and $K_{sf}$ (Fig. 2). In the presence of surfactants, the migration behavior of NOCs in water/bentonite systems involves adsorption between the CTMAB alkyl chains exchanged by bentonite, partitioning in the monomer or micelles of the surfactant solution, and dissolution in the aqueous solution.

The apparent adsorption coefficient ($K_d$) of the adsorbed nature of organic matter in the soil–water–surfactant system is described as follows:

$$K_d = K'_d \times \frac{1 + f_{sf} K_{sf} / K'_d}{1 + X_{mn} K_{mn} + X_{mc} K_{mc}} \tag{1}$$

where $K_d$ is the apparent adsorption coefficient of NOCs on bentonite in the presence of surfactant, $K'_d$ is the adsorption coefficient of NOCs on bentonite in the absence of surfactant, and $K_{sf}$ is the adsorption coefficient of CTMAB for NOCs. Moreover, $f_{sf}$ is the amount of CTMAB adsorbed by bentonite, and $X_{mn}$ is the concentration of surfactant monomer in solution (when $X \le$ CMC, $X_{mn} = X$; when $X >$ CMC, $X_{mn} =$ CMC). $X_{mc}$ is the concentration of micelles in solution (when $X \le$ CMC, $X_{mc} = 0$; when $X >$ CMC, $X_{mc} = X -$ CMC), $X$ is the total amount of surfactant present in the solution, $K_{mn}$ is the solute partition coefficient between monomer and water, and $K_{mc}$ is the solute partition coefficient between micelle and water.

The results of Eq. (1) reveals that high $f_{sf}$ and $K_{sf}$ values must be obtained to achieve a high $K_d$, and $X_{mn}$, $X_{mc}$, $K_{mn}$, and $K_{mc}$ values should be relatively small. Based on the previous research results [10], in the presence of a certain CTMAB amount, the surfactant amount dissolved in the equilibrium solution of the one-step process is nearly 0, that is, $X_{mn} = X_{mc} = X = 0$. Thus, we can conclude that

$$K_d = f_{sf} K_{sf} \tag{2}$$

From Eq. (2) we can deduce that the amount of contaminant (NOCs) adsorbed is closely related to the amount of CTMAB adsorbed by bentonite and its adsorption coefficient for the NOCs. Meanwhile, the one-step process can be
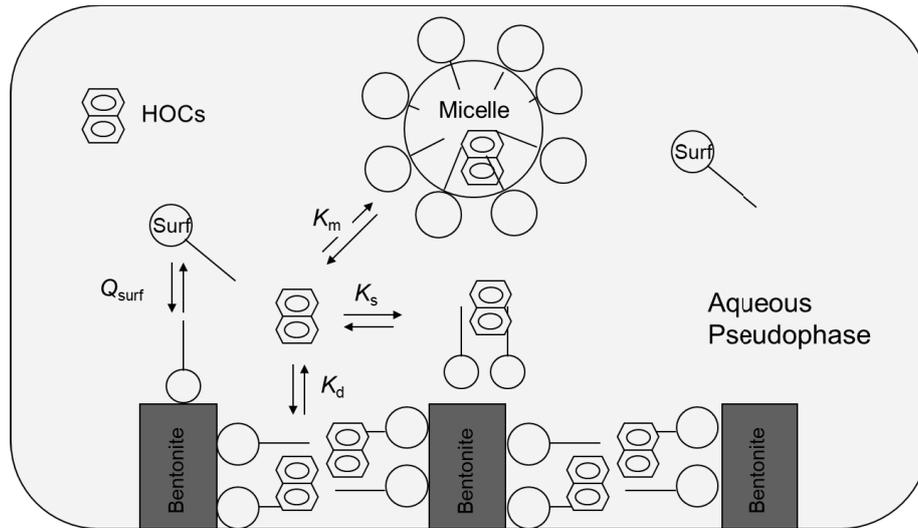
Fig. 1. Partition behavior of NOCs in the water/bentonite system containing CTMAB.



NOCs are dissolved in water, $m_{e(w)}$

NOCs are dissolved in CTMAB monomers, $m_{e(mn)}$

$K_{mn}$   $K_d$

$K_{mc}$   $K_{sf}$

NOCs are adsorbed by bentonite, $m_{a(s)}$

NOCs are dissolved in CTMAB micelles, $m_{e(mc)}$

NOCs are adsorbed by CTMAB, $m_{a(sf)}$

Adsorbed-phase NOCs: $m_a = m_{a(s)} + m_{a(sf)}$   Dissolved-phase NOCs: $m_e = m_{e(w)} + m_{e(mn)} + m_{e(mc)}$
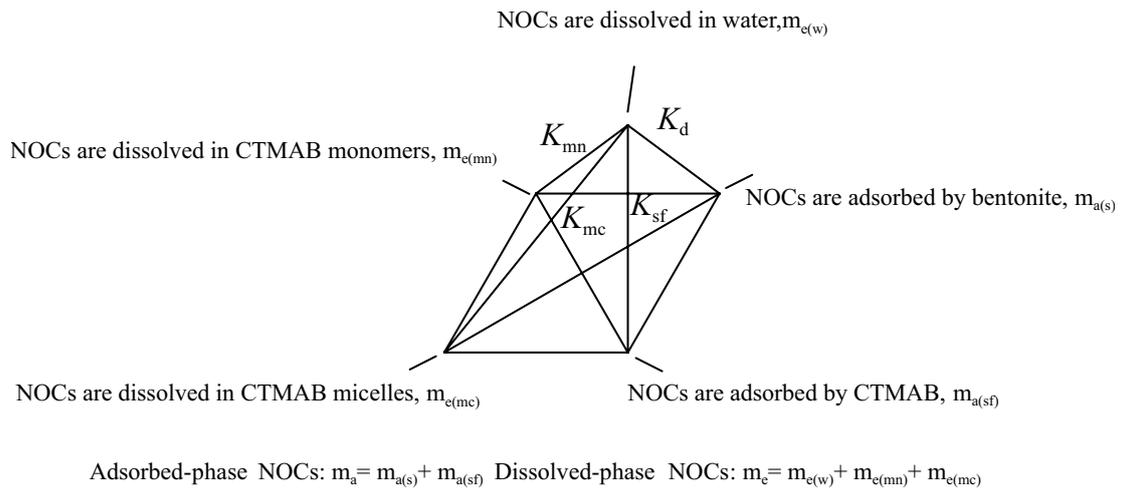
Fig. 2. Tetragonal partition of NOCs in the CTMAB–bentonite–water system.

simplified as the relationship between the amounts of bentonite and amounts of the bentonite-adsorbed surfactant, as well as the distributed adsorption performance of the contaminants. Given this viewpoint, we used this relationship to establish the synthesis–adsorption one-step mathematical model of organobentonite for predicting the removal efficiency of organobentonite for various pollutants [27,28].

Fig. 1 shows that the partition ratio of contaminants in the surfactant-solid micelles is as follows:

$$X_{adm} = \frac{C_0 - C_{eq}}{(C_0 - C_{eq}) + (S_0 - S_{eq})} \qquad (3)$$

where $C_0$ is the initial concentration of contaminants, $C_{eq}$ is the equilibrium concentration of contaminants, $S_0$ is the initial concentration of the surfactant, and $S_{eq}$ is the equilibrium concentration of surfactant.

The proportion of contaminants in the aqueous solution may be described as follows:

$$X_{aq} = \frac{C_{eq}}{C_{eq} + 55.55} \qquad (4)$$

where 55.55 is the water concentration. We propose that the equilibrium relationship between the pollutants in the solid-phase micelles and the solution is described by:

$$K_{ad} = \frac{X_{adm}}{X_{aq}} \qquad (5)$$

Eq. (5) shows that a large $K_{ad}$ value can be achieved through the following steps: (1) maximizing the pollutant amount in the solid-phase micelles and (2) reducing the pollutant concentration in the solution. The main influence

on the adsorption includes the residual surfactant amount in solution and the adsorbed surfactant amount in the bentonite, especially for the removal of the weakly soluble contaminants. The surfactant type in the adsorption may affect the adsorption amount and the mechanism during the one-step process of synthesis–adsorption. Therefore, this experiment focused on the type and amount of surfactant and the effect of these factors on the process. Then, an adsorption model was established.

## 3. Materials and methods

### 3.1. Materials

The natural bentonite composed primarily of $Ca^{2+}$-montmorillonite was obtained from Tianyu Co., Ltd., (Inner Mongolia, China). Its cation exchange capacity (CEC) is 1.084 mmol/g bentonite. The bentonite samples were gently ground to powder form. The surfactants (CTMAB, DTMAB, and OTMAB) and the adsorbates (acenaphthene, β-naphthol, phenol, and naphthalene) were all obtained from CR Co., Ltd., Shanghai (China). All the reagents were of analytical grade and used as received.

### 3.2. Adsorption experiments

For equilibrium measurements, a known amount of bentonite was added into a set of 22 mL centrifuge tubes, containing a known amount of surfactant and one of the adsorbates. The tubes were capped and placed on an orbital shaker at 180 rpm for 5 h to ensure apparent equilibrium. Preliminary kinetic investigations revealed that adsorption equilibrium was reached in less than 3 h. When the equilibrium was attained, the sorbent was separated by centrifugation at 3,000 rpm for 15 min. After the supernatant was analyzed for residual concentrations, the amount adsorbed was calculated. This procedure was used in all batch sorption experiments, which were carried out at ambient laboratory temperature (25°C ± 1°C).

The results of control experiment indicate the negligible evaporation and sorption on glass surface. All samples were run in triplicates under identical conditions.

### 3.3. Analyses

The concentrations of the adsorbate in solution were determined spectrophotometrically using UV/Vis Spectrophotometer Shimadzu UV-2450 (Shimadzu, Japan). Acenaphthene, β-naphthol, phenol, and naphthalene were measured at wavelength 234, 280, 287 and 223 nm, respectively.

The result of the control experiment showed that CTMAB at low concentration (<0.01 mol/L) had negligible effect on the examination of these adsorbates.

## 4. Model establishment

With the increase in pollutant $K_{ow}$, the $K_d$ in the isothermal adsorption curves increased accordingly [29]. The organic state formed by the alkyl chains in the bentonite layers is the key influence on the partitioning of organic contaminants. Boyd et al. [29] revealed that the adsorption

of benzene, trichlorobenzene, and 1,2-dichlorobenzene onto organobentonite is linearly related to the organic carbon content of organobentonite when 30%–100% CEC was used [29]. The related equation is as follows:

$$K_{oc} = \frac{K_d}{f_{oc}} \tag{6}$$

where $K_{oc}$ is a constant for a particular compound. The $f_{oc}$ under different conditions can be obtained through the amount of surfactant and the exchange capacity.

The relationship between $K_{oc}$ and $f_{oc}$ in Eq. (6) suggests that the partition coefficient $K_d$ of the pollutants in the surfactant-bentonite can be derived from the corresponding $K_{ow}$ and the linear relationship with $K_d$. At the same time, $K_{oc}$ can be obtained under the corresponding conditions of the $K_{ow}$ of different pollutants. The removal rates of different pollutants in the presence of different surfactants in the synthesis–adsorption process can be deduced based on the number of carbon atoms and surfactant molecular weight. The derivation process is as follows:

$$K_d = K_{oc} \cdot f_{oc} \tag{7}$$

where $f_{oc}$ is calculated using the following equation:

$$f_{oc} = \frac{A \times B \times W \times 12C / M}{W - 0.5 \times B \times W \times 40 \times A + (M - 80) \times A \times B \times W} \tag{8}$$

where $B$ is the CEC, $W$ is the amount of bentonite (g), $M$ is the molecular weight of the surfactant used, $C$ is the carbon content of the surfactant used, $A$ is the exchange capacity of bentonite (mmol/g), 40 is the atomic weight of the exchanged Ca, and 80 is the atomic weight of the bromide present in the surfactant.

$$f_{oc} = \frac{A \times B \times 12C / M}{1 - 20 \times B \times A + (M - 80) \times A \times B} \tag{9}$$

The above formula was then substituted in Eq. (7) to give:

$$K_d = K_{oc} \cdot f_{oc} = K_{oc} \cdot \frac{A \times B \times 12C / M}{1 - 20 \times B \times A + (M - 80) \times A \times B} \tag{10}$$

To maintain low cost, the surfactant amount was less than 120% CEC (i.e., $B < 1.2$) as obtained by previous studies [11]. The model can be simplified; particularly, the residual surfactant amount in the solution can be considered as 0, and the contaminants remain balanced between the aqueous solution and the solid-phase micelles [10].

### 4.1. Model parameter estimation

The effect of different dosages and different types of surfactants on the adsorption was investigated, which will help estimate the parameters of the model. Three surfactants with alkyl chain lengths of 8, 12, and 16 were studied. The adsorption coefficients were studied under different organic carbon contents. Previous studies have shown

that when the alkyl chain carbon of a surfactant is greater than eight [30], the surfactant adsorbed by the bentonite can form solid-phase micelles, and the contaminants are fixed between the micelles because of hydrophobicity. The partition coefficients were obtained and were found to be similar under the same organic carbon content but with different surfactants.

The results showed that $f_{oc}$ exerts an important effect on pollutant adsorption (Figs. 3–6). A linear relationship between the amount of adsorbed contaminants and the surfactant amounts under different equilibrium concentrations can be achieved, which confirms that the role of the adsorption is mostly in partitioning. With the increased organic carbon content, the partition coefficient, $K_d$, increased. However, the adsorption coefficients of different pollutants were variable under different $f_{oc}$ values. The $K_{oc}$ can be obtained from the different $f_{oc}$ values of the pollutants. Here, the $K_{oc}$ was obtained from the adsorption results under various organic carbon contents, which

can achieve the accurate relationship between $\log K_{oc}$ and $\log K_{ow}$. The average values of $K_{oc}$ are listed in Tables 1–4.

The relationship between $K_{ow}$ and $K_{oc}$ was then obtained based on the results of $K_{oc}$ and $K_{ow}$ (Tables 1–4), as well as the effect of the organic carbon content of organobentonite on $K_d$. When the CTMAB amount was less than 120% of CEC, $K_{oc}$ appeared to be a constant, and the relationship between $f_{oc}$ and $K_d$ was linear as described by Eq. (7). Linear regression was used to derive the relationship of $K_{ow}$ and $K_{oc}$ with high correlation coefficient ($r^2 = 0.988$, as shown in Fig. 7):

$$\log K_{oc} = 1.1528 \log K_{ow} - 1.9848 \tag{11}$$

In the above relationship, the $K_{oc}$ values can be calculated under the known surfactant amounts in the process. Accordingly, the partition coefficient, $K_d$, obtained is:
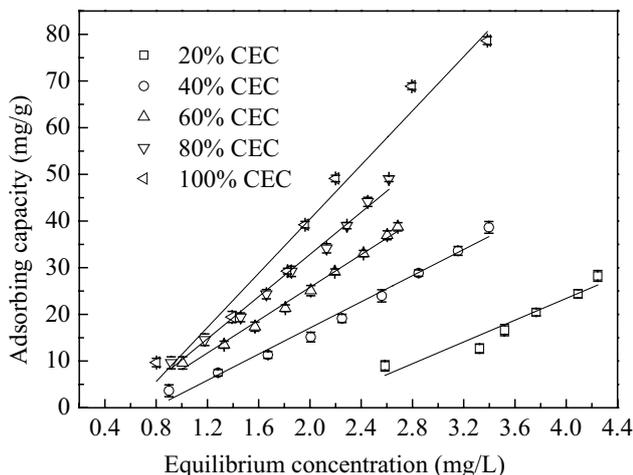


Fig. 3. Adsorption of acenaphthene onto organobentonite at various CTMAB amounts (180 rpm for 5 h, at 25°C).
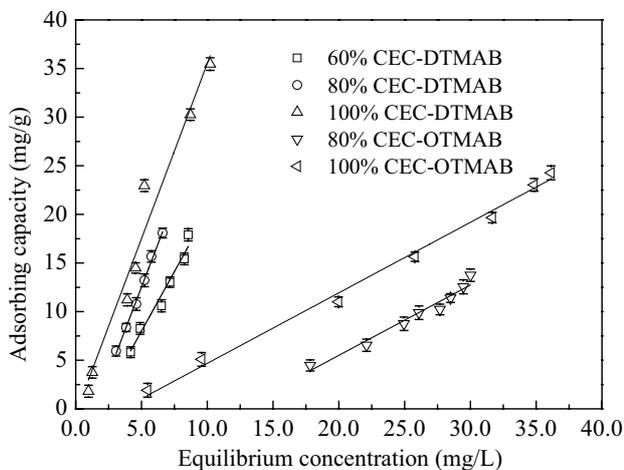


Fig. 5. Adsorption of phenol onto organobentonite at various surfactants and amounts (180 rpm for 5 h, at 25°C).
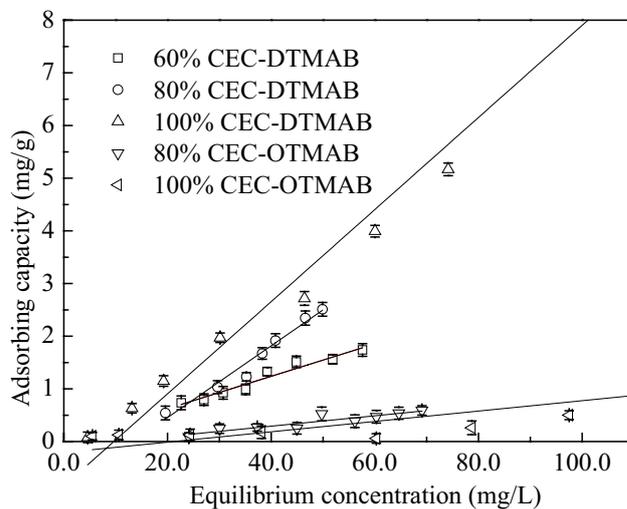


Fig. 4. Adsorption of β-naphthol onto organobentonite at various surfactants and amounts (180 rpm for 5 h, at 25°C).
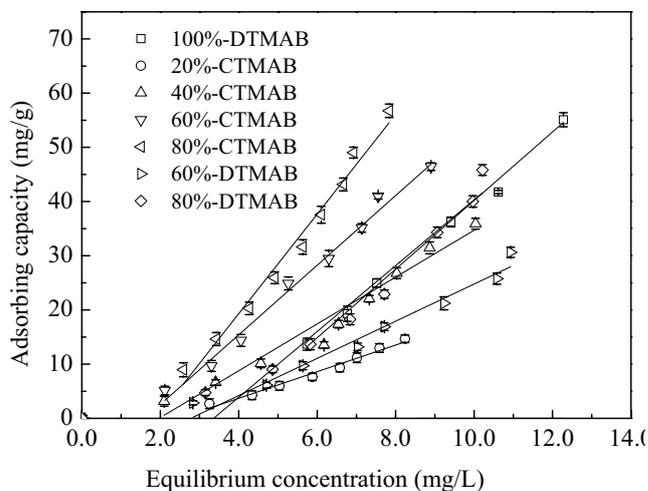


Fig. 6. Adsorption of naphthalene onto organobentonite at various surfactants and amounts (180 rpm for 5 h, at 25°C).

Table 1
Adsorption of acenaphthene onto organobentonite under various surfactant types and amounts in the one-step process

| Surfactant amount (CEC) | $K_d$ (L/g) | $f_{oc}$ (%) | $K_{oc}$ (L/g) | $\log K_{oc}$ (L/g) |
|---|---|---|---|---|
| 20% CTMAB | 11.66 | 4.62 | 252.38 | 2.40 |
| 40% CTMAB | 14.06 | 8.67 | 162.17 | 2.21 |
| 60% CTMAB | 17.79 | 12.26 | 145.11 | 2.16 |
| 80% CTMAB | 22.99 | 15.44 | 148.90 | 2.17 |
| 100% CTMAB | 29.107 | 18.3 | 159.05 | 2.20 |

Table 2
Adsorption of β-naphthol onto organobentonite under various surfactant types and amounts in the one-step process

| Surfactant amount (CEC) | $K_d$ (L/g) | $f_{oc}$ (%) | $K_{oc}$ (L/g) | $\log K_{oc}$ (L/g) |
|---|---|---|---|---|
| 60% DTMAB | 2.50 | 9.98 | 25.05 | 1.40 |
| 80% DTMAB | 3.54 | 12.67 | 27.94 | 1.45 |
| 100% DTMAB | 3.65 | 15.13 | 24.12 | 1.38 |
| 80% OTMAB | 0.93 | 9.68 | 9.61 | 0.98 |
| 100% OTMAB | 0.71 | 11.64 | 6.10 | 0.79 |

Table 3
Adsorption of phenol onto organobentonite at various surfactant types and amounts in the one-step process

| Surfactant amount (CEC) | $K_d$ (L/g) | $f_{oc}$ (%) | $K_{oc}$ (L/g) | $\log K_{oc}$ (L/g) |
|---|---|---|---|---|
| 60% DTMAB | 0.031 | 9.98 | 0.31 | −0.51 |
| 80% DTMAB | 0.069 | 12.67 | 0.54 | −0.27 |
| 100% DTMAB | 0.087 | 15.13 | 0.57 | −0.24 |
| 80% OTMAB | 0.0099 | 9.68 | 0.10 | −0.99 |
| 100% OTMAB | 0.0089 | 11.64 | 0.08 | −1.11 |

Table 4
Adsorption of naphthalene onto organobentonite under various surfactant types and amounts in the one-step process

| Surfactant amount (CEC) | $K_d$ (L/g) | $f_{oc}$ (%) | $K_{oc}$ (L/g) | $\log K_{oc}$ (L/g) |
|---|---|---|---|---|
| 100% DTMAB | 4.469 | 15.13 | 0.30 | −0.529 |
| 20% CTMAB | 1.833 | 4.62 | 0.40 | −0.401 |
| 40% CTMAB | 3.738 | 8.67 | 0.43 | −0.365 |
| 60% CTMAB | 5.672 | 12.26 | 0.46 | −0.334 |
| 80% CTMAB | 7.529 | 15.44 | 0.49 | −0.312 |
| 60% DTMAB | 2.797 | 9.98 | 0.28 | −0.552 |
| 80% DTMAB | 4.520 | 12.67 | 0.36 | −0.448 |

$$K_d = K_{oc} \cdot f_{oc} = K_{oc} \cdot \frac{A \times B \times 12C / M}{1 - 20 \times B \times A + (M - 80) \times A \times B} = K_{oc} \cdot \frac{12ABC}{M + ABM^2 - 100ABM} = \frac{12ABCK_{ow}^{1.1528}}{M + ABM^2 - 100ABM} \cdot \frac{1}{10^{1.9848}} \quad (12)$$

Correspondingly, the removal rate is given by:

$$\eta = 1 - \frac{C_e}{C_0} = \frac{rK_d}{rK_d + 1} = \frac{rK_{oc}f_{oc}}{rK_{oc}f_{oc} + 1} = \frac{r\dfrac{12ABCK_{ow}^{1.1528}}{M + ABM^2 - 100ABM} \cdot \dfrac{1}{10^{1.9848}}}{r\dfrac{12ABCK_{ow}^{1.1528}}{M + ABM^2 - 100ABM} \cdot \dfrac{1}{10^{1.9848}} + 1} = \frac{r\dfrac{0.12 \times ABCK_{ow}^{1.1528}}{M + ABM^2 - 100ABM}}{r\dfrac{1.2 \times 10^{-3} ABCK_{ow}^{1.1528}}{M + ABM^2 - 100ABM} + 1} \quad (13)$$

*4.2. Model validation*

The obtained model was validated by adsorption of phenanthrene, naphthalene, and nitrobenzene. CTMAB, DTMAB, and OTMAB were applied as surfactants in the process. The surfactant dosage is 40%–100% CEC of the bentonite. The experimental and model values were compared under the same temperature.

Fig. 8 shows that no differences were observed between the model and experimental values of the phenanthrene. For the 40% CEC CTMAB and 100% CEC OTMAB, the $K_d$ values were 348.5 and 185.8 L/g, respectively, in the experiments, but 333.6 and 184.4 L/g, respectively, for the model predictions; the error values are approximately 4.2% and 0.7%, respectively, which are very low.

The model results are very close to the experimental findings, which confirmed that the mechanism of phenanthrene adsorption onto the organobentonite layer is due to

partition. The prediction model based on such mechanism provided accurate results, which is beneficial for guiding actual wastewater treatment. However, given the complexity of wastewater, the synergistic effect between organic molecules in the adsorption process also promotes the adsorption, which will lead to an inevitable error of prediction. Moreover, the deviation caused by high salinity in the wastewater requires further study.

Figs. 9 and 10 show the comparison between the model and experimental $K_d$ values obtained for the adsorption of naphthalene and nitrobenzene onto organobentonite in the presence of CTMAB in 100% CEC. The $K_d$ values are listed in Table 5. The model exhibited good correlation with the experimental results, with only a small variation, for the high $K_{ow}$ compound adsorption, such as phenanthrene and naphthalene. However, for compounds, such as nitrobenzene, which have small $K_{ow}$, the adsorption prediction was biased. The achieved results were due to the fact
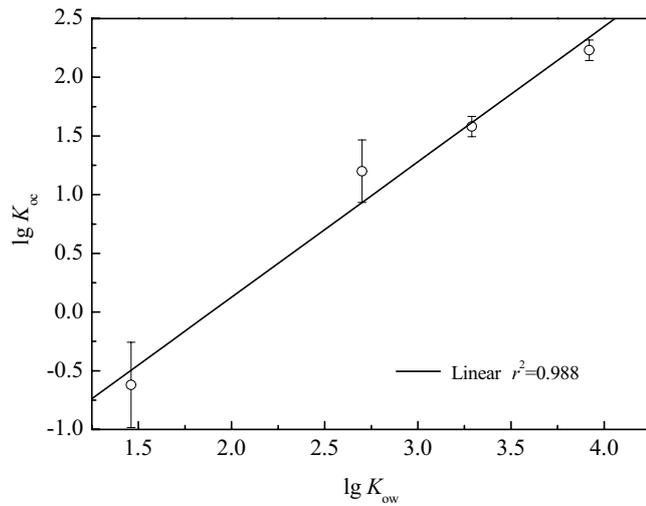
Fig. 7. Linear relation between $K_{ow}$ and $K_{oc}$.



Fig. 9. Comparison between the model and experimental values of naphthalene sorption.



Fig. 8. Comparison between the experimental and model values of $K_d$ under various surfactant types and amounts (180 rpm for 5 h, at 25°C).
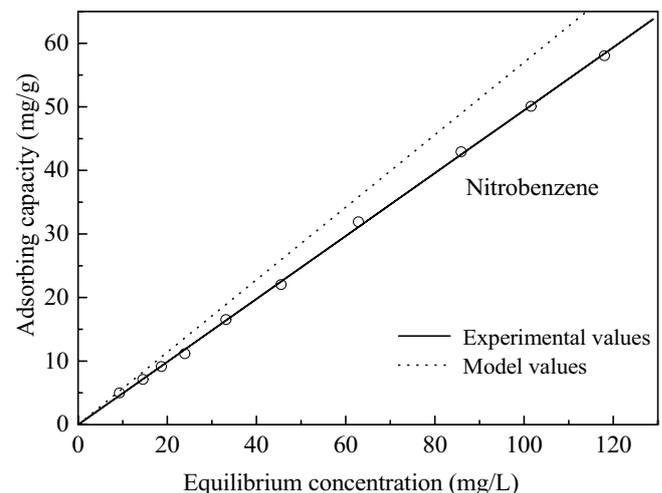


Fig. 10. Comparison of the model and experimental values of nitrobenzene sorption.

that partition plays a dominant role in the adsorption of organic pollutants. The compounds with large $K_{ow}$ values are partitioned in the organic phase, whereas the hydrophilic substances exhibit more dissolution than partition or compete with water during the adsorption. Hence, the prediction of the model for the substances with low $K_{ow}$ leads to deviation.

### 4.3. Model application

When the adsorbent and water ratios of phenanthrene, naphthalene, and nitrobenzene were 2.5, 1.25, and 10 g/L, respectively, in the water treatment, the wastewater treatment results can be obtained using Eq. (12).

We substituted $A$, $B$, $C$, $M$, $K_{ow}$, and $r$ into Eq. (12) to obtain the respective removal rates for several kinds of treated effluents. In the calculation, the exchange capacity of calcium-based bentonite remained at 1.084 mmol/g,

and the surfactant amounts used were 40% CTMAB and 100% of CEC. The experimental and model values were compared under the same temperature, and the results are shown in Figs. 11 and 12, respectively. As the results of removal rate, the prediction model can accurately calculate the removal rate of phenanthrene and naphthalene through the one-step process of organobentonite. In particular, the maximum error was 6.7%. However, nitrobenzene achieved the highest error for the removal of these four contaminants, with a maximum error of 30.5%. The experimental removal rates are lower than those of predicted values by model, which can be explained by the relatively low $K_{ow}$ and weak partitioning in the organobentonite. The pollutants with low $K_{ow}$ values are easily dissolved in water. The accuracy of the model reduced by the hydrophilic group (e.g., –OH) at the edges of bentonite layers, which easily forms H-bond with the low $K_{ow}$ pollutants. Thus, the mechanism is changed, and the model does not

Table 5
Model and experimental $K_d$ values in the one-step process

| Organics | $K_{ow}$ | $\log K_{ow}$ | Model values $K_d$ (L/g) | $K_d$ (L/g) | Deviation (%) |
|---|---|---|---|---|---|
| Phenanthrene–CTMAB 40% CEC | 37,153 | 4.57 | 333.6 | 348.5 | 4.2 |
| Phenanthrene–OTMAB 100% CEC | 37,153 | 4.57 | 184.44 | 185.78 | 0.7 |
| Naphthalene–CTMAB 100% CEC | 1950 | 3.29 | 16.75 | 18.286 | 8.4 |
| Nitrobenzene–CTMAB 100% CEC | 31 | 1.85 | 0.57 | 0.495 | 19.7 |
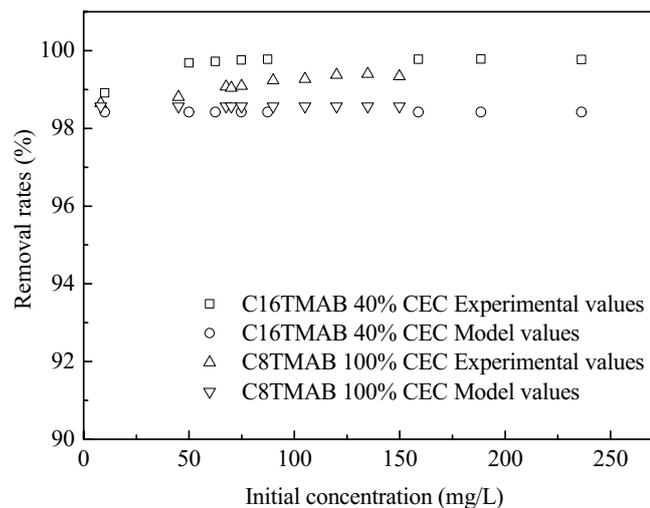


Fig. 11. Comparison of the experimental and model results of phenanthrene adsorption (180 rpm for 5 h, at 25°C).
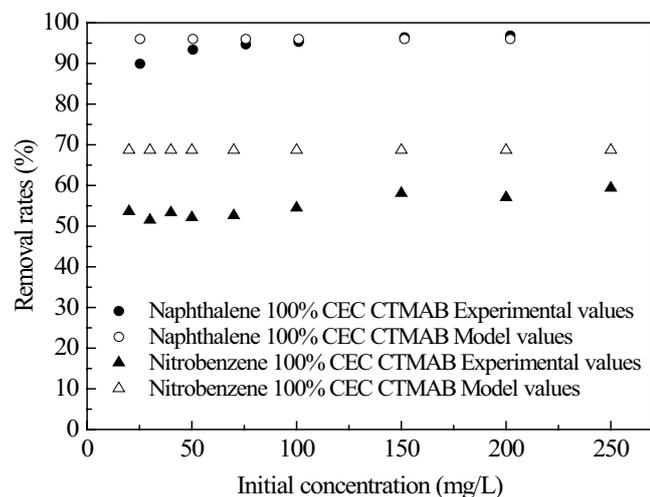


Fig. 12. Comparison of the experimental and model results of sorption of naphthalene and nitrobenzene in the one-step process (180 rpm for 5 h, at 25°C).

fit the condition. On the other hand, increased surfactant density can promote pollutant partitioning, but an exceedingly high density can decrease the adsorption by steric hindrance [31], which also introduces a deviation from prediction.
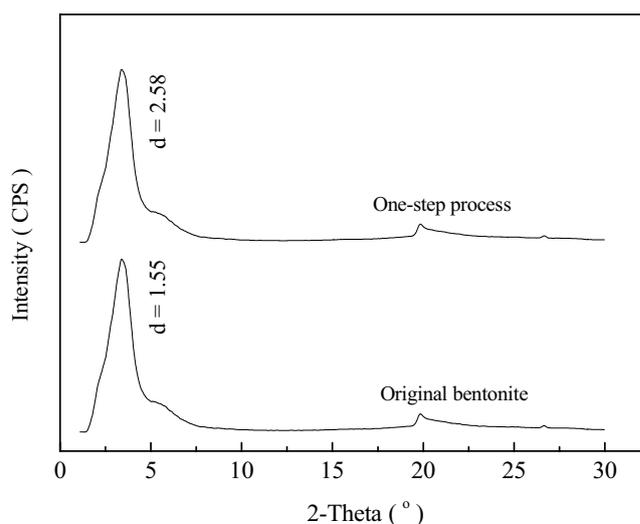


Fig. 13. X-ray diffraction patters of original bentonite and one-step organobentonite adsorbed nitrobenzene.

The X-ray diffraction analysis of original bentonite and the bentonite with adsorbed amount of nitrobenzene by one-step process of synthesis–adsorption is shown in Fig. 13. The layer spacing of original bentonite is 1.55 nm. When nitrobenzene was adsorbed by organobentonite in the one-step process, the interlayer spacing reached 2.58 nm, which is increased by 1.03 nm compared with the original bentonite. The layer spacing of CTMAB modified/exchanged (100% CEC) organic bentonite is 1.85 nm [32]. The results proved that the adsorbed nitrobenzene expanded the spacing by about 0.73 nm, which inferred that the nitrobenzene was adsorbed into the interlayers.

5. Conclusion

The adsorptions of various organic compounds under different surfactants and bentonite dosages were studied. When the relationship between $K_{ow}$ and $K_{oc}$ was fitted, a quantitative relationship between $K_{ow}$ and bentonite was established to obtain another quantitative relationship between the removal efficiency and the surfactant exchange capacity. The following results were achieved:

• On the basis of the experimental results and literature findings, a prediction model of the adsorption for removal of various compounds by the organobentonite using the synthesis–adsorption one-step process was

established. The model can predict the removal efficiencies in the adsorption process.

- The prediction results for the adsorption of phenanthrene and naphthalene were better than those for others, and the maximum prediction error was only 6.7%. For water-soluble contaminants, the predictive accuracy was reduced because of the competitive adsorption between the micellar partition and presence in aqueous phases.

## Acknowledgements

## Data availability statement

All relevant data are included in the paper or its Supplementary Information.

## Variables

| | | |
|---|---|---|
| $K_d$ | — | Apparent adsorption coefficient |
| $K_d'$ | — | Adsorption coefficient |
| $K_{sf}$ | — | Adsorption coefficient |
| $f_{sf}$ | — | Adsorbed amount, mol/L |
| $X_{mn}$ | — | Concentration of surfactant monomer in solution, mg/kg |
| $X_{mc}$ | — | Concentration of micelles in solution, mg/kg |
| $X$ | — | Total amount of surfactant in solution, mg/kg |
| $K_{mn}$ | — | Solute partition coefficient between monomer and water |
| $K_{mc}$ | — | Solute partition coefficient between micelle and water |
| $C_0$ | — | Initial concentration of contaminants, mg/L |
| $C_{eq}$ | — | Equilibrium concentration of contaminants, mg/L |
| $S_0$ | — | Initial concentration of the surfactant, mol/L |
| $S_{eq}$ | — | Equilibrium concentration of surfactant, mol/L |
| $X_{aq}$ | — | Proportion of contaminants in the aqueous solution |
| $K_{oc}$ | — | Constant for a particular compound |
| $f_{oc}$ | — | Raction of organic carbon contents, % |
| $B$ | — | Cation exchange capacity, mmol/g |
| $W$ | — | Amount of bentonite, g |
| $M$ | — | Molecular weight of the surfactant |
| $C$ | — | Carbon content of the surfactant |
| $A$ | — | Exchange capacity of bentonite, mmol/g |

## References

[1] V. Masindi, W.M. Gitari, K.G. Pindihama, Synthesis of cryptocrystalline magnesite/bentonite clay composite and its application for removal of phosphate from municipal wastewaters, Environ. Technol., 37 (2016) 603–612.

[2] J.A. Smith, A. Galan, Sorption of nonionic organic comtaminants to single and dual organic cation bentonites from water, Environ. Sci. Technol., 29 (1995) 685–692.

[3] R.W. Miller, S.D. Faust, Sorption from aqueous solution by organo-clay: III. Effect of pH on sorption of various phenols, Environ. Lett., 4 (1973) 211–223.

[4] A.Z. Redding, S.E. Burns, Compressibility and index properties of organic exchanged bentonite, Geotech. Special Publ., 105 (2000) 142–150.

[5] Y. Seki, K. Yurdakoc, Paraquat adsorption onto clays and organoclays from aqueous solution, J. Colloid Interface Sci., 287 (2005) 1–5.

[6] L.Z. Zhu, Y.H. Su, Benzene vapor sorption by organobentonites from ambient air, Clays Clay Miner., 50 (2002) 421–427.

[7] H. Favre, G. Lagaly, Organo-bentonites with quaternary alkylammonium ions, Clay Miner., 26 (1991) 19–32.

[8] J.M. Brixie, S.A. Boyd, Treatment of contaminated soils with organoclays to reduce leachable pentachlorophenol, J. Environ. Qual., 23 (1994) 1283–1290.

[9] A. Jacobo-Azuara, R. Leyva-Ramos, E. Padilla-Ortega, A. Aragón-Piña, R.M. Guerrero-Coronado, J. Mendoza-Barron, Removal of toxic pollutants from aqueous solutions by adsorption onto an organobentonite, Adsorpt. Sci. Technol., 24 (2006) 687–799.

[10] J. Ma, B. Cui, J. Dai, D. Li, Mechanism of adsorption of anionic dye from aqueous solutions onto organobentonite, J. Hazard. Mater., 186 (2011) 1758–1765.

[11] K.J. Shailesh, A.S. Najam, D. Anirban, K. Jitendra, K.S. Mukesh, Sorption kinetics and isotherm modelling of imidacloprid on bentonite and organobentonites, J. Environ. Sci. Health., Part B, 52 (2017) 326–337.

[12] S. Marinovic, M. Ajdukovic, N. Jovic-Jovicic, P. Bankovic, Z. Mojovic, A. Milutinovic-Nikolic, D. Jovanovic, Organo-bentonite: characterization and adsorptive properties towards phenol and its derivatives, Sci. Sintering, 48 (2016) 167–176.

[13] H.P. Toledo-Jaldin, A. Blanco-Flores, V. Sánchez-Mendieta, O. Martín-Hernández, Influence of the chain length of surfactant in the modification of zeolites and clays. Removal of atrazine from water solutions, Environ. Technol., 39 (2017) 2679–2690.

[14] S.H. Lin, M.J. Cheng, Adsorption of phenol and m-chlorophenol on organobentonites and repeated thermal regeneration, Waste Manage., 22 (2002) 595–603.

[15] R. Gönülşen, N. Yıldız, A. Çalımlı, Adsorption of organic compounds on to bentonites modified with single or dual quaternary ammonium cations, Adsorpt. Sci. Technol., 21 (2003) 135–148.

[16] H. Sayilkan, S. Erdemoğlu, S. Sener, F. Sayilkan, M. Akarsu, M. Erdemoglu, Surface modification of pyrophyllite with amino silane coupling agent for the removal of 4-nitrophenol from aqueous solutions, J. Colloid Interface Sci., 275 (2004) 530–538.

[17] X. Peng, Z. Luan, H. Zhang, B.H. Tian, Zirconia pillared montmorillonite for removal of arsenate from water, Environ. Lett., 40 (2005) 1055–1067.

[18] L. Zhu, J. Ma, Simultaneous removal of acid dye and cationic surfactant from water by bentonite in one-step process, Chem. Eng. J., 139 (2008) 503–509.

[19] Z. Li, M. Yao, J. Lin, B. Yang, X. Zhang, L. Lei, Pentachlorophenol sorption in the cetyltrimethylammonium bromide/bentonite one-step process in single and multiple solute systems, J. Chem. Eng. Data, 58 (2013) 2610–2615.

[20] Q. Li, Z.S. Chen, H.H. Wang, H. Yang, T. Wen, S.Q. Wang, B.W. Hu, X.K. Wang, Removal of organic compounds by nanoscale zero-valent iron and its composites, Sci. Total Environ., 792 (2021) 148546, doi: 10.1016/j.scitotenv.2021. 148546.

[21] M.J. Hao, M.Q. Qiu, H. Yang, B.W. Hu, X.X. Wang, Recent advances on preparation and environmental applications of MOF-derived carbons in catalysis, Sci. Total Environ., 760 (2021) 143333, doi: 10.1016/j.scitotenv.2020.143333.

[22] L. Yao, H.Yang, Z.S. Chen, M.Q. Qiu, B.W. Hu, X.X. Wang, Bismuth oxychloride-based materials for the removal of organic pollutants in wastewater, Chemosphere, 273 (2021) 128576, doi: 10.1016/j.chemosphere.2020.128576.

[23] Y. Liu, L. Zhu, Enhanced treatment of dispersed dye-production wastewater by self-assembled organobentonite in

a one-step process with poly-aluminium chloride, Sci. Rep., 7 (2017) 6843, doi: 10.1038/s41598-017-07333-2.

[24] S. Peng, Z. Tang, W. Jiang, D. Wu, S. Hong, B. Xing, Mechanism and performance for adsorption of 2-chlorophenol onto zeolite with surfactant by one-step process from aqueous phase, Sci. Total Environ., 581 (2017) 550–558.

[25] M. Yao, X. Zhang L. Lei, Removal of Reactive Blue 13 from dyeing wastewater by self-assembled organobentonite in a one-step process, J. Chem. Eng. Data, 57 (2012) 1915–1922.

[26] L.Z. Zhu, B.L. Chen, S. Tao, Sorption behavior of polycyclic aromatic hydrocarbons in soil-water system containing nonionic surfactant, Environ. Eng. Sci., 21 (2004) 263–272.

[27] P.S. Ghosal, A.K. Gupta, Development of a generalized adsorption isotherm model at solid-liquid interface: a novel approach, J. Mol. Liq., 240 (2017) 21–24.

[28] W.Y. Pang, Y.Q. He, C.H. Yan, Z.H. Jin, Tackling the challenges in the estimation of methane absolute adsorption in kerogen nanoporous media from molecular and analytical approaches, Fuel, 243 (2019) 687–698.

[29] S.A. Boyd, M.M. Mortland, C.T. Chiou, Sorption characteristics of organic compounds on hexadecyltrimethylammonium-smectite, Soil Sci. Soc. Am. J., 52 (1988) 652–657.

[30] J.L. Bonczek, W.G. Harris, P.N. Kizza, Monolayer to bilayer transitional arrangements of hexadecyltrimethylammonium cations on na-montmorillonite, Clays Clay Miner., 50 (2002) 11–17.

[31] S.L. Bartelt-Hunt, S.E. Burns, J.A. Smith, Nonionic organic solute sorption onto two organobentonites as a function of organic-carbon content, J. Colloid Interface Sci., 266 (2003) 251–258.

[32] J.X. Zhu, L.Z. Zhu, R.L. Zhu, B.L. Chen, Microstructure of organo-bentonites in water and the effect of steric hindrance on the uptake of organic compounds, Clays Clay Miner., 56 (2008) 144–154.