Korean J. Chem. Eng., **27**(2), 602-608 (2010)
DOI: 10.1007/s11814-010-0084-z

Adsorption and desorption of m-xylene vapor on organically modified montmorillonite

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(*Received 10 April 2009 • accepted 2 September 2009*)

Abstract−m-Xylene vapor was adsorbed to organically modified montmorillonite (organoclay). Hexadecyltrimethylammonium (HDTMA) was used to modify the surface of the clay. In adsorption experiments, the organoclay, along with the non-modified (washed) clay, was used. m-Xylene was adsorbed from a gaseous phase by using a fixed adsorption bed. The adsorption breakthrough curves and the adsorption isotherms were determined at three different temperatures (24, 34, and 44 °C). The adsorption data were modeled with the BET isotherm equation. It was found that the adsorption isotherms of washed clay exhibited a favorable Type I behavior, which implies that the adsorption capacity is strongly dependent on vapor concentration at low concentration ranges. In regards to the organoclay, isotherms showed a marginally favorable Type II behavior with a reduced adsorption capacity at low concentrations, and exhibited a linear increase at elevated vapor concentrations. The adsorption capacity of both washed clay and organoclay obviously decreased with the temperature. The desorption of m-xylene from the clays was also performed by using pure nitrogen, and the desorption rate constant k was on the order of 10^{-5} min^{-1} for all types of clay.

Key words: Adsorption, HDTMA, Montmorillonite, Organoclay, m-Xylene

INTRODUCTION

Many technologies for emission control of volatile organic compounds (VOCs) have been developed to resolve air pollution problems. Among these technologies, adsorption is considered to be an effective method when the concentrations of VOCs are relatively low. So far, chlorinated hydrocarbons such as chlorobenzene, trichloroethylene and trichloroethane are most frequently treated VOCs by adsorption operations [1]. Besides chlorinated hydrocarbons, aromatic organic compounds belong to another category of VOC groups [2]. The wastes of aromatic compounds are generated by sources such as leakage from underground storage tanks, coal conversion plants, and oil and petroleum industries. The treatment of these aromatic compounds involves options such as bio-degradations and incineration. These technologies, however, are efficient only when the concentrations of aromatics are fairly high. In addition, high costs are usually associated with the application of these treatment methods [3,4]. Therefore, it is worth to investigate adsorption as a treatment technology of aromatic organic compounds when these compounds exist in the vapor phase at low concentrations.

Organically modified clay, which is called organoclay, is used as a natural adsorbent to prevent the underground leakage of hydrophobic compounds, and also to adsorb organic ingredients from waste water [5,6]. Clays such as smectite, modified with amine cations having an organophilic nature, provide enhanced immobilizing and adsorption capacity toward organic acids and various hydrocarbons. Among the various smectite clays, montmorillonite is popularly utilized for modification purposes because of its high adsorption capacity and favorable surface properties. Hexadecyltrimethylammonium (HDTMA), which has quaternary ammonium cations, is frequently used for the surface modification of clay particles. The adsorption sites of the organoclay consist of external surfaces and enlarged inter-lamellar spacing of the particles, which may provide selectivity due to the creation of a sorption zone into which hydrophobic contaminants can be partitioned [7,8]. Therefore, the adsorption capacity of organoclay may be proportional to the degree of HDTMA loading on the clay surface.

Researches on adsorption including organoclays have mainly focused on the investigation of adsorption behavior between clay matrices and aqueous environments [9,10]. The adsorption kinetics and equilibrium isotherms have been measured for hazardous organic materials. To date, however, research including adsorption from vapor phases is generally lacking, mainly because the adsorption capacity becomes fairly low when taking place from the vapor phase, which may attributed to the large mass transfer resistance formed at a gas-solid interface [11]. Indeed, natural soils and clays show weak affinity towards organic compounds and exhibit low adsorption capacity compared to synthetic adsorbents, such as activated carbon [12]. On the other hand, activated carbon has its drawbacks, including high prices and high energy cost for regeneration due to its high adsorption strength in regards to organic compounds. Therefore, soils and clays, which are inexpensive and regenerated easily, can be utilized for alternative adsorbents for the removal of hazardous compounds, even though these adsorbents have relatively low adsorption capacities toward organic compounds. In addition, the low adsorption capacity of clays can be overcome by means of proper surface modifications.

In this research, we investigated the adsorption behavior of m-xylene on montmorillonite organoclays which were modified by HDTMA. Organoclays along with the non-modified clay were used for adsorption, and the performance of different types of clay was compared. m-Xylene was adsorbed from a gaseous phase (nitrogen), and the adsorption isotherms were determined by using a dynamic response technique at three different temperatures. The desorption behavior was also investigated by using pure nitrogen, and desorption pro-

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files were fitted with a mathematical model.

EXPERIMENTAL SECTION

1. Materials

Montmorillonite clay was purchased from Aldrich Chemical Co. (Lot 06016PN). Hexadecyltrimethylammonium (HDTMA, in the form of a 25 wt% solution in water) which forms quaternary amine cations $[(CH_3)_3NR]^+$ was also purchased from Aldrich Chemical Co. (Lot 0526JN). m-Xylene (99.5%) was obtained from Junsei Chemical Co. All chemicals were used as received.

2. Experimental Procedure

The clay was purified by repeated washing and digestion procedure using purified water and 35% H_2O_2 solutions, respectively. The washing and digestion process removed impurities and organics from the montmorillonite clay particles. Particle size of the washed clay was measured by scanning electron microscopy, and the image showed that the average size of washed montmorillonite particle was ca. 20 μm. The cation-exchange capacity (CEC) of the clay sample was measured by using calcium acetate $(Ca(CH_3COO)_2)$ solutions, and the CEC of washed clay was found to be 50.4 meq/100 g-clay, corresponding to 161 mg HDTMA/g-clay.

The washed clay was organically modified by HDTMA. First, a 5,000 ppm HDTMA solution in distilled water was prepared. Next, 30 g of washed clay was added to 1,000 ml of the HDTMA solution. The solution was agitated at 300 rpm for 24 hrs in order to allow the sorption of HDTMA onto the clay surface. The clay was separated from the solution by filtering and it was dried in an oven at 60 °C for 24 hrs. The HDTMA loading of this organoclay was measured by a total organic carbon analyzer (TOC, TOC-5000 Shimadzu), and the loading was found to be 152 mg HDTMA/g-clay. This amount of HDTMA loading was close to 94.4% of the CEC of washed clay (161 mg HDTMA/g-clay). For convenience, the modified clay sample was named as organoclay. In this study, two clay samples (washed clay and organoclay) were used in the adsorption experiments. Table 1 shows the properties of the used clays measured by the BET surface area measurement. It should be noted that the surface area and pore volume were reduced when the washed clay was modified by HDTMA.

Table 1. Properties of the clays used in this study

Clay type	Surface area (m^2/g)	Pore volume (cc/g)	Pore size (Å)
Washed clay	150.1	0.175	38.4
Organoclay	21.9	0.083	38.2

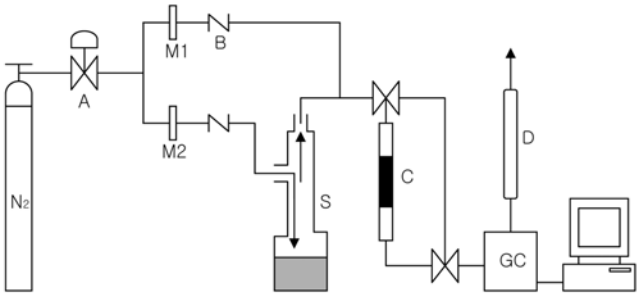

Fig. 1. Experimental apparatus for adsorption and desorption of m-xylene (A) gas regulator, (B) check valve, (C) adsorption bed, (D) soap bubble meter, (M1, M2) mass flow controller, (S) m-xylene saturator.

In this study, m-xylene vapor was adsorbed on two types of clays from the gas phase, and also desorbed from clays using pure nitrogen as a carrier gas. Fig. 1 shows the experimental apparatus used for adsorption and desorption. The unit consists of an m-xylene saturator, an adsorption bed, and a gas chromatograph. For adsorption experiments, the adsorption bed (7.75 mm ID, 9.5 mm OD, 310.0 mm length) was loaded with 14.5 g of clay. Nitrogen, in which the flow rate was controlled by a mass flow controller, was saturated with m-xylene by bubbling it through the saturator. Before the saturated nitrogen was introduced into the adsorption bed, the flow stream was mixed with pure nitrogen in which the flow rate was controlled by another mass flow controller. In this way, the inlet concentration of the gas stream was adjusted as desired. During the inlet concentration adjustment procedure, the gas stream passed through a bypass line in order to analyze the inlet concentration by a gas chromatograph. To begin the adsorption process, the stream was switched from the bypass to the adsorption bed, which generated the positive step change of inlet concentration. The effluent stream

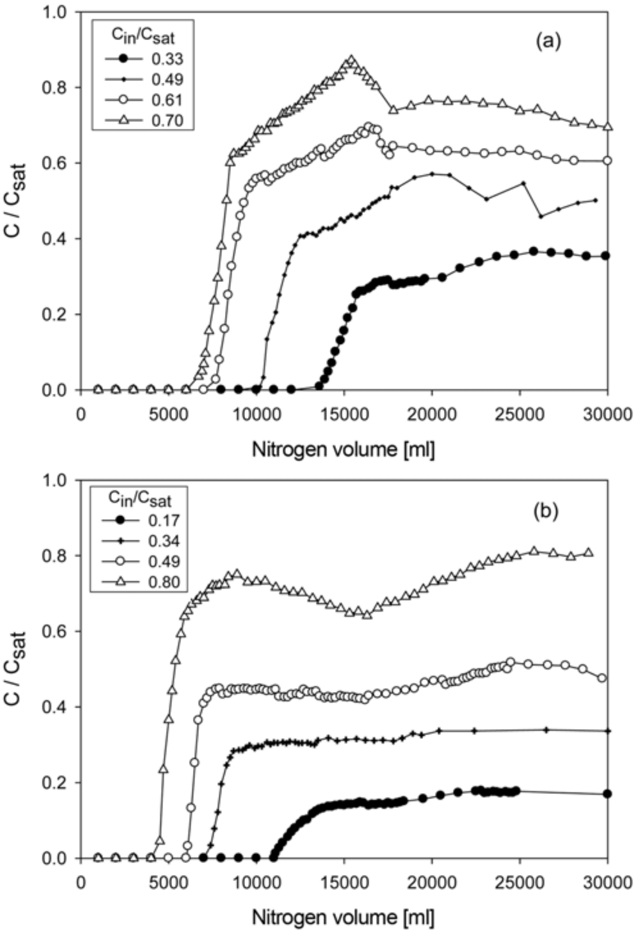

Fig. 2. Adsorption breakthrough curves of m-xylene for washed clay (a) and organoclay (b). The curves represent the effluent concentration responding to the various inlet concentration of m-xylene at 24 °C.

from the adsorption bed was analyzed by using an online sampling valve and a gas chromatograph equipped with a DB-1 (dimethylpolysiloxane) capillary column and an FID. The adsorption experiment was completed when the effluent concentration approached the inlet value.

When the adsorption experiment was completed, desorption was conducted by flowing pure nitrogen through the adsorption bed. The m-xylene concentration in the effluent stream was analyzed, and continued until reaching the detection limit of the gas chromatograph. The flow rate of nitrogen stream was measured by a soap bubble meter. The nitrogen flow rate was maintained at 1.2 ml/s for both the adsorption and desorption experiments. The adsorption and desorption were conducted at three different temperatures (24, 34 and 44 °C). The reason for using three different temperatures is to investigate the effect of temperature on the adsorption behavior of organoclay. In general, the adsorption capacity of normal clays decreases with increasing temperature. However, the temperature effect on the adsorption capacity of organoclay is not well known, so it is worth to perform the experiments at elevated temperatures.

RESULTS AND DISCUSSION

1. Adsorption Breakthrough Curves

Fig. 2 shows the adsorption breakthrough curves of m-xylene at 24 °C. The breakthrough curves were obtained at various inlet concentrations C_{in}. The concentration of m-xylene in the gas phase provided a step change from zero to a specific value at the entrance of the adsorption bed, and the responding effluent concentration was monitored as a function of time (or the volume of nitrogen used) at the bed exit. Washed clay (Fig. 2(a)) and organoclay (Fig. 2(b)) were used to obtain the curves. In these figures, the ordinate represents the ratio of effluent concentration C to the concentration of the m-xylene-saturated nitrogen stream C_{sat}. The abscissa is the volume of nitrogen passed through the adsorption bed. Various inlet concentrations were used in the range of 0.17- 0.80C_{sat} as illustrated in the figure legends.

Fig. 2 indicates that as the inlet concentration increased, the breakthrough points definitely shifted to the left. Moreover, the slope of the breakthrough curves consistently changed depending on the inlet concentration. In regards to both the washed clay and organoclay, the curves measured at low inlet concentrations have gentle slopes and the slopes became steeper as the inlet concentration increases. It is noteworthy that the breakthrough curves for washed clay (Fig. 2(a)), obtained at high inlet concentrations exhibited an interesting fluctuating pattern. For the curve obtained at inlet concentration of 0.70C_{sat}, the exit concentrations of m-xylene rapidly increased with a steep slope, immediately after the breakthrough took place. After that, the curve slope suddenly decreased with a discontinuity and

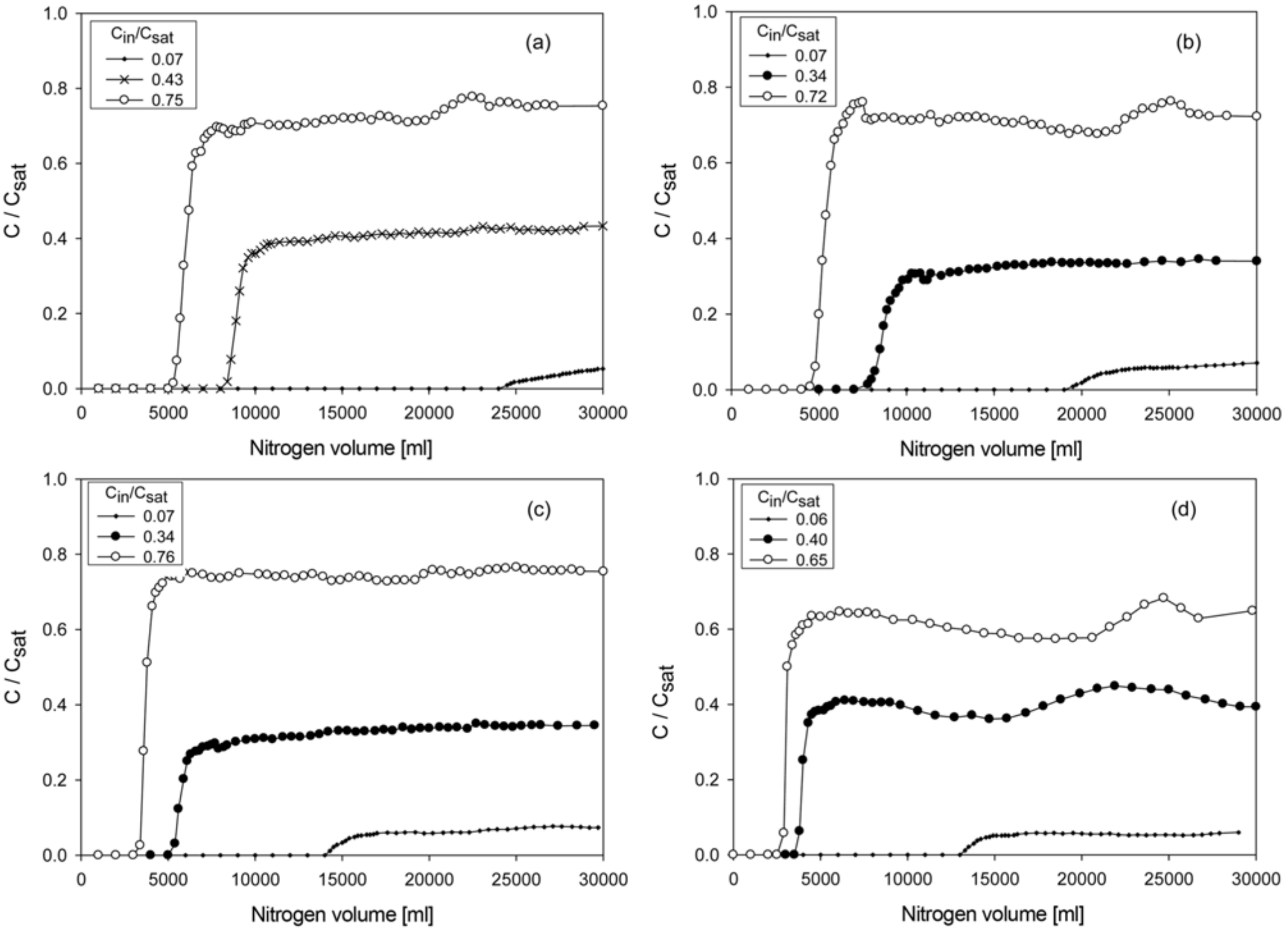

Fig. 3. Adsorption breakthrough curves of m-xylene for washed clay at 34 °C (a) and 44 °C (b), and the breakthrough curves for organoclay at 34 °C (c) and 44 °C (d).

the exit concentration steadily rose to a peak value. Then the exit concentration sharply dropped to a particular level and quickly stabilized. These fluctuating behaviors were also observed at inlet concentration of 0.61C_{sat}, and the fluctuation gradually disappeared as the inlet concentration decreased down to 0.49 and 0.33C_{sat}. In regards to the organoclay (Fig. 2(b)), however, the above-mentioned patterns slightly appeared only at inlet concentration of 0.80C_{sat} and the breakthrough curves became monotonic at other inlet concentrations.

The reduction of the fluctuating pattern in organoclay may be attributed to the formation of the surfactant sorption zone at the interface of the clay surface. Indeed, the adsorption of m-xylene on two types of clays takes place based on a different mechanism. When washed clay was used, the surface adsorption occurred, and when organoclay was used, multilayer sorption in the sorption zone took place. Therefore, the breakthrough curves for the organoclay showed less fluctuating behavior because of the damping action of the surfactant sorption zone.

Fig. 3 shows the breakthrough curves of washed clay and organoclay measured at different temperatures. Figs. 3(a) and 3(b) represent the curves for washed clay obtained at 34 and 44 °C, and Figs. 3(c) and 3(d) are those for organoclay measured at 34 and 44 °C, respectively. At high temperatures, the fluctuating behavior, that was observed at 24 °C curves, was not detected. In regards to the washed clay, the breakthrough points for the low inlet concentration curves shifted to the left as the temperature increased from 34 to 44 °C. However, the breakthrough points for the high inlet concentration curves were almost constant when the temperature was increased (Figs. 3(a) and 3(b)). Regarding the organoclay, on the other hand, the breakthrough points were rather insensitive to temperature change (Figs. 3(c) and 3(d)). These results indicate that in regards to the washed clay, the temperature effect on adsorption capacity was fairly high, but the temperature effect was lowered when the adsorption took place on organoclay.

2. Adsorption Isotherms

Fig. 4 illustrates the adsorption isotherms of m-xylene on washed clay and organoclay, showing the m-xylene loading per unit mass of clay as a function of the inlet concentration. The two isotherm data were measured at 24 °C. In Fig. 4, the experimental data were fitted by an adsorption isotherm equation. The BET isotherm equation was adopted as follows [12].

$$\frac{X}{X_m}=\frac{cy}{1-y}\frac{1-(n+1)y^n+ny^{n+1}}{1+(c-1)y-cy^{n+1}} \tag{1}$$

where y is the relative vapor concentration (C/C_{sat}), X_m is the monolayer adsorption capacity, X is the uptake of m-xylene per unit mass of clay, c is the BET constant, and n is the theoretical number of adsorbed layers. The BET theory is a model isotherm accounting for multilayer adsorption, and this model is used to extract the monolayer adsorption capacity and specific surface area [13].

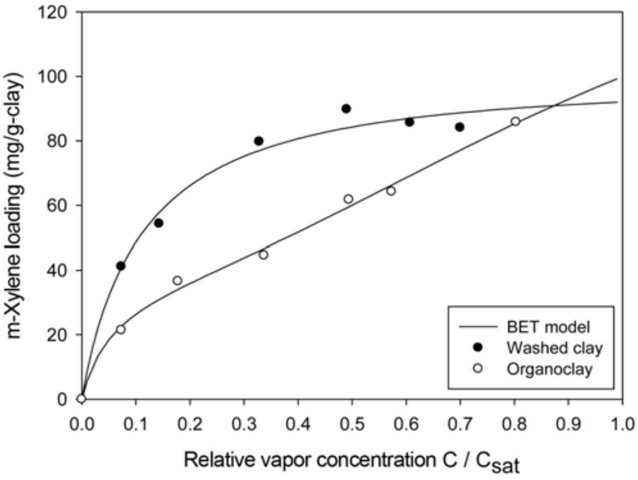

Fig. 4. Adsorption isotherms of m-xylene for washed clay and organoclays at 24 °C. The experimental data were fitted by BET equation.

Fig. 4 shows that the uptake of organoclay linearly increased with concentration, while that of washed clay rapidly increased at a low concentration range and then leveled off. Therefore, at a low concentration range, the m-xylene uptake of washed clay is higher than that of organoclays and the trend appears to be inversed at a high concentration range. These results indicate that the isotherm for washed clay exhibited a favorable Type I behavior [14] with a high initial slope, which implies that the adsorption capacity is strongly dependent on vapor concentrations at low concentration and became constant at high concentration levels. In regards to the organoclay, however, the isotherm showed a marginally favorable Type II behavior with reduced adsorption capacity at low concentrations, and exhibited a nearly linear increase at elevated vapor concentrations. As a result, the presentation of the two isotherm curves of the washed clay and organoclay at the same plot exhibit a crossover point, as shown in Fig. 4.

These results can be explained by the difference in the adsorption mechanism of the two types of clay. For washed clay, the adsorption capacity is proportional to the adsorption sites on clay surface, and the adsorption is completed when these sites are filled. Therefore, the m-xylene uptake rapidly increased at a low concentration range and then the uptake became almost constant as the concentration approached a saturated value. In the case of organoclay, however, a sorption zone was formed at the interface of the clay surface and the gas phase which was induced by the presence of surfactant molecules. The decreased uptake of m-xylene at a low concentration range is attributed to the reduced adsorption sites on the clay surface, which is preoccupied by the surfactant molecules.

Table 2. Adsorption isotherm constants for washed clay and organoclay used in the BET isotherm equation at 24, 34, and 44 °C

Clay	X_m (mg/g-clay)	n	c
	24 °C		
Washed clay	139.9	0.61	7.33
Organoclay	34.6	4.83	19.44
	34 °C		
Washed clay	45.6	2.88	21.79
Organoclay	29.2	2.81	1.85
	44 °C		
Washed clay	36.6	4.02	17.73
Organoclay	59.34	1.15	4.41

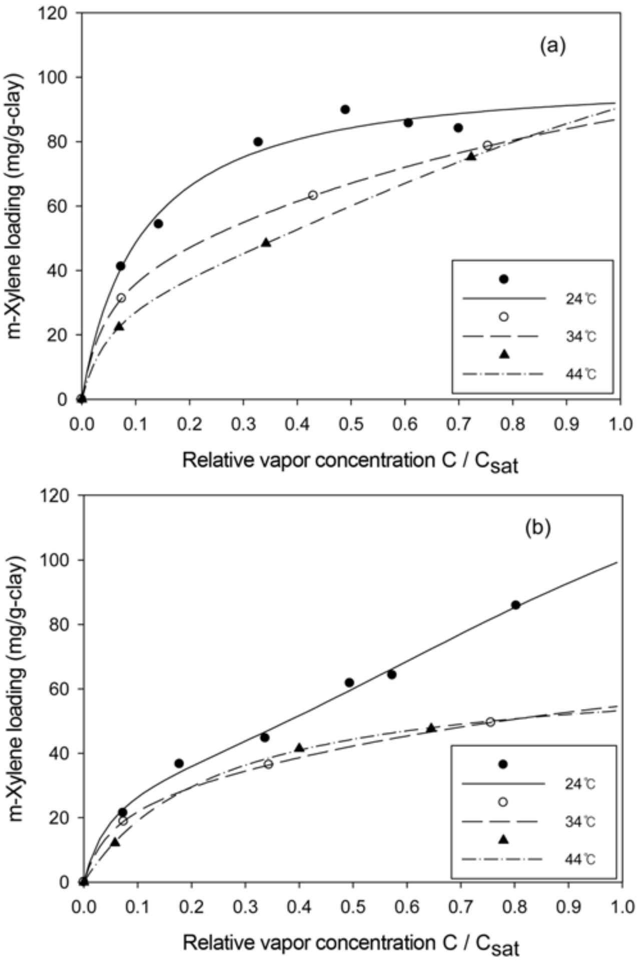

Fig. 5. Adsorption isotherms of m-xylene for washed clay (a) and organoclay (b) at 24, 34, and 44 °C. The experimental data were fitted by BET equation.

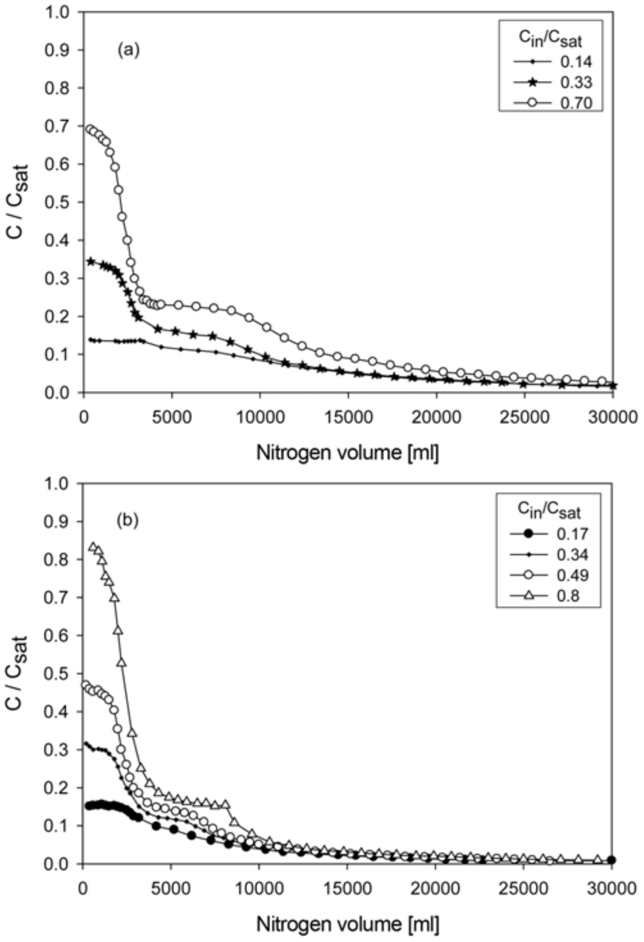

Fig. 6. Desorption profiles of m-xylene from washed clay (a) and organoclay (b) at 24 °C.

As the m-xylene concentration in the gas phase increased, however, the role of the sorption zone regarding the uptake of m-xylene became more crucial and hence, the adsorption capacity proportionally increased with m-xylene concentrations in the gas phase. At high concentrations, the large uptake of m-xylene on organoclay was achieved by the sorption mechanism rather than the surface adsorption phenomenon. Table 2 shows the BET isotherm constants for washed clay and organoclay used in Eq. (1), evaluated at three different temperatures.

Fig. 5 shows the adsorption isotherms of washed clay (Fig. 5(a)) and organoclay (Fig. 5(b)) measured at different temperatures (24, 34, and 44 °C). The BET isotherm model was used to obtain the curves in the figures. Fig. 5(a) shows that the isotherm curve patterns of the washed clay had not changed as the temperature increased from 24 to 44 °C. In other words, the washed clay consistently showed Type I adsorption behavior regardless of temperature. The isotherms indicated that the adsorption capacity decreased with the temperature at a constant gas phase concentration, and the three isotherms tended to merge to a single curve at a high concentration level. For organoclays, however, the temperature dependency of adsorption isotherms was obvious. Fig. 5(b) shows that the adsorption capacity of organoclay was not strongly affected by the temperature at a low concentration range. However, as the concentration increased, the adsorption capacity was significantly reduced when the temperature changed from 24 to 34 °C and further to 44 °C. These results imply that the sorption zone on the clay surface became inactive at high temperatures, which induced the reduction of the m-xylene uptake.

3. Desorption Profiles

Desorption profiles were obtained by measuring m-xylene concentrations of a nitrogen effluent stream when pure nitrogen was introduced into the adsorption bed after a set of adsorption experiments was completed. Fig. 6 shows the typical desorption profiles for washed clay (Fig. 6(a)) and organoclay (Fig. 6(b)) at 24 °C, showing the variation of m-xylene concentration of effluent stream when nitrogen passes through. The ordinate represents the effluent concentration C normalized by saturation concentration C_{sat}. It was found that the desorption profile exhibited different types of behavior depending on the m-xylene initial loading. The profiles at high initial loadings exhibit two down steps. The first down step is sharp, followed by a plateau, and then by a second step exhibiting a tail. As the initial loading decreased, the two step behavior appears to be diminished and the desorption profiles became monotonic. This behavior was consistently observed in both the washed clay and organoclay as shown in Fig. 6. Fig. 7 shows the desorption profiles

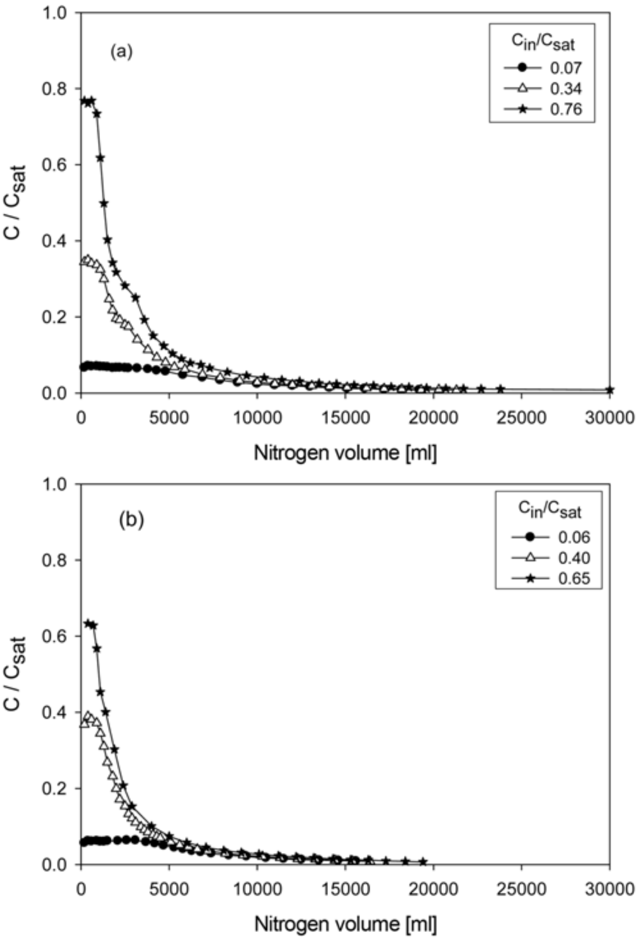

Fig. 7. Desorption profiles of m-xylene from organoclay at 34 °C (a) and 44 °C (b).

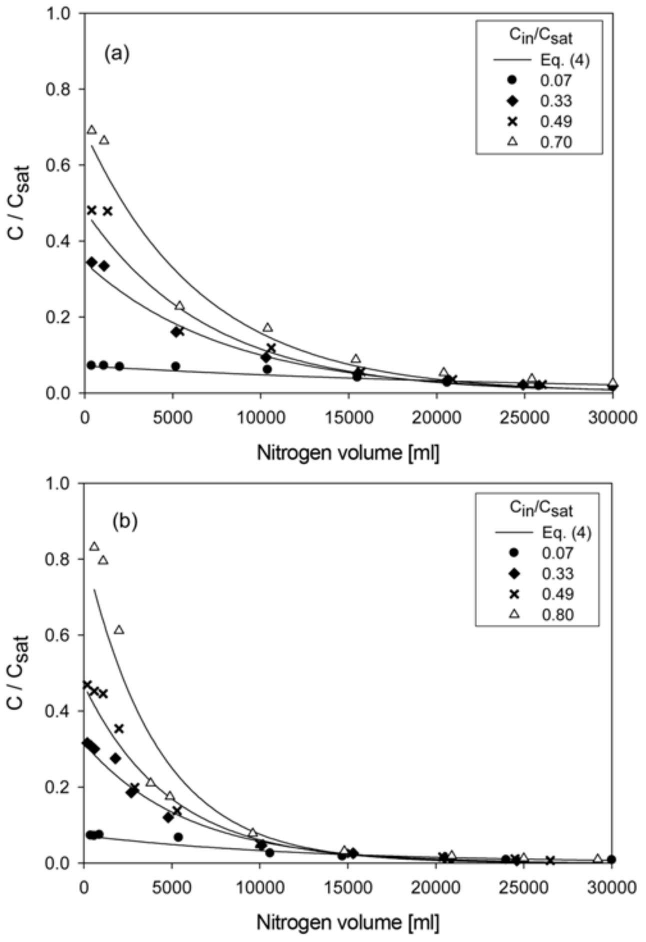

Fig. 8. Typical desorption profiles of m-xylene from washed clay (a) and organoclay (b) at 24 °C, with selected data points. The curves were obtained using Eq. (4).

of organoclay measured at high temperatures (34 and 44 °C). As temperature increased, the two down steps of desorption curves gradually disappeared and profiles of the effluent concentration monotonically decreased with the volume of nitrogen used, and the desorption profiles collapsed on almost a single curve.

The experimental data of desorption profiles such as data shown in Figs. 6 and 7 were correlated by using a mathematical model suggested by Tan and Liou [15]. A material balance in the bed (without considering the axial dispersion) can be written as

$$\varepsilon\frac{\partial C}{\partial t}+u\frac{\partial C}{\partial z}=-(1-\varepsilon)\frac{\partial S}{\partial t} \tag{2}$$

where ε is the bed porosity, u is the superficial velocity of gas stream, and S is the m-xylene concentration per unit volume of clay. The initial and boundary conditions are at t=0, C=0 and z=0, C = 0. The linear desorption kinetics used is as follows.

$$\frac{\partial S}{\partial t}=-kS \tag{3}$$

where k is the desorption rate constant. The initial condition is at t= 0, $S=S_o$. The solution of Eqs. (2) and (3) with the initial and boundary conditions provides the expression for the concentration at the exit of adsorption bed C_e.

$$C_e=\frac{1-\varepsilon}{\varepsilon}S_0\left\{\exp\left[-k\left(t-\frac{\varepsilon L}{u}\right)\right]-\exp(-kt)\right\} \tag{4}$$

where L is the bed length. The amount of desorption can be calculated by integrating C_e with respect to time. The desorption rate constant k is determined by the regression of Eq. (4) with the experimental data.

Fig. 8 shows the typical desorption profile curves that were calculated based on Eq. (4) at 24 °C. The data points used in Fig. 8 are the selected experimental data from desorption profiles as shown in Fig. 6. Correlation was performed by using an evaluated desorption rate constant k used in Eq. (4). Table 3 summarizes the values of desorption rate constant k calculated at 24, 34, and 44 °C. It was found that k values were in the order of 10^{-5} min^{-1} and the values had not largely varied when the clay type changed from washed clay to organoclay. In addition, the k values evaluated at 34 and 44 °C were in the similar range. At all temperatures, the k value increased with inlet concentration of m-xylene. Considering these results and Eq. (4), the desorption rate of m-xylene primarily depended on the initial loading of m-xylene on clays.

This may be attributed to the relatively high vapor pressure of m-xylene. Due to its high volatility, the adsorbed m-xylene was readily stripped to the gas phase as the nitrogen passed through the bed.

Table 3. Desorption rate constant k used for Tan and Liou model, Eq. (4) at 24, 34, and 44 °C

Clay	Temperature (°C)	C_{in}/C_{sat}	k (min^{-1})
Washed clay	24	0.07	0.0000132
	24	0.14	0.0000209
	24	0.33	0.0000412
	24	0.49	0.0000475
	24	0.60	0.0000518
	24	0.70	0.0000493
	34	0.07	0.0000129
	34	0.43	0.0000611
	34	0.75	0.0000821
	44	0.06	0.0000281
	44	0.34	0.0000618
	44	0.72	0.0000101
Organoclay	24	0.07	0.0000263
	24	0.17	0.0000339
	24	0.33	0.0000572
	24	0.49	0.0000681
	24	0.57	0.0000738
	24	0.80	0.0000799
	34	0.07	0.0000278
	34	0.34	0.0000844
	34	0.76	0.0000109
	44	0.06	0.0000253
	44	0.40	0.0000988
	44	0.65	0.000126

These results reflect the relatively weak affinity between the clays and m-xylene molecules, suggesting that the adsorption strength of m-xylene on washed clay and on organoclay is not significantly different.

CONCLUSIONS

m-Xylene vapor was adsorbed on HDTMA-modified montmorillonite, as well as on non-modified washed clay. The pattern of the breakthrough curves changed depending on both the type of clay and the inlet concentration of m-xylene. In regards to the washed clay, the temperature effect on adsorption was fairly high, but the effect of temperature was reduced when the adsorption took place on organoclay. Adsorption data were well represented by the BET isotherm equation. The isotherms for washed clay exhibited a favorable Type I behavior with a high initial slope, which implies that the adsorption capacity was a strong function of vapor concentrations at a low concentration range, and the adsorption capacity became constant at a high concentration level. For the organoclays, however, isotherms show a marginally favorable Type II behavior with the reduced adsorption capacity at low concentrations, and exhibited a linear increase at elevated vapor concentration levels. The desorption profiles of m-xylene exhibited different types of behavior depending on the m-xylene initial loading. The profiles at high initial loadings exhibited two down steps, and these behaviors were consistently observed in both the washed clay and organoclay. As temperature increased, the two down steps of desorption curves gradually disappeared and profiles of the effluent concentration monotonically decreased with time and the desorption profiles collapsed on almost a single curve. The rate of m-xylene desorption from both washed clay and organoclays depended on the initial loading of m-xylene on clays.

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