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Production of low sulfur diesel fuel via adsorption: an equilibrium and kinetic study on the adsorption of dibenzothiophene onto NaY zeolite

Jianzhun Jiang · Flora T.T. Ng

Abstract The adsorption of dibenzothiophene (DBT) in hexadecane onto NaY zeolite has been studied by performing equilibrium and kinetic adsorption experiments. The influence of several variables such as contact time, initial concentration of DBT and temperature on the adsorption has been investigated. The results show that the isothermal equilibrium can be represented by the Langmuir equation. The maximum adsorption capacity at different temperatures and the corresponding Langmuir constant (K_L) have been deduced. The thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0) for the adsorption of DBT have also been calculated from the temperature dependence of K_L using the van't Hoff equation. The value of ΔH^0, ΔS^0 are found to be $-30.3\ \text{kJ mol}^{-1}$ and $-33.2\ \text{J mol}^{-1}\ \text{K}^{-1}$ respectively. The adsorption is spontaneous and exothermic. The kinetics for the adsorption process can be described by either the Langmuir model or a pseudo-second-order model. It is found that the adsorption capacity and the initial rate of adsorption are dependent on contact time, temperature and the initial DBT concentration. The low apparent activation energy ($12.4\ \text{kJ mol}^{-1}$) indicates that adsorption has a low potential barrier suggesting a mass transfer controlled process. In addition, the competitive adsorption between DBT, naphthalene and quinoline on NaY was also investigated.

J. Jiang
Beijing Research Institute of Chemical Industry, China Petroleum & Chemical Corporation (SINOPEC), Beijing 100013, China
e-mail: jiangjzh@brici.ac.cn

J. Jiang · F.T.T. Ng (✉)
Department of Chemical Engineering, Faculty of Engineering, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada
e-mail: fttng@cape.uwaterloo.ca

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Nomenclature

DBT	dibenzothiophene
t	contact time, min
c_0	initial concentration of adsorbate in the solution, mmol L^{-1}
c_t	the concentration of adsorbate at contact time t, mmol L^{-1}
c_e	equilibrium concentration of adsorbate in the solution, mmol L^{-1}
c_{DBT}	the concentration of DBT, mmol L^{-1}
k_0	temperature independent factor, $\text{g mmol}^{-1}\ \text{min}^{-1}$
k_2	pseudo-second-order rate constant, $\text{g mmol}^{-1}\ \text{min}^{-1}$
k_{ads}	adsorptive constant, $\text{L g}^{-1}\ \text{min}^{-1}$
k_d	desorptive constant, $\text{mmol g}^{-1}\ \text{min}^{-1}$
K_L	Langmuir constant, L mmol^{-1}
q_e	adsorptive amount of adsorbate after equilibrium, mmol g^{-1}
q_L	*a* solution of the second-order polynomial expression, mmol g^{-1}
q_m	adsorptive amount of adsorbate to its maximum, mmol g^{-1}
q_t	adsorptive amount of adsorbate at time t, mmol g^{-1}
θ	dimensionless ratio of coverage of the surface of adsorbent
v_0	initial adsorptive rate, $\text{mmol g}^{-1}\ \text{min}^{-1}$
v_{ads}	rate of adsorption, $\text{mmol g}^{-1}\ \text{min}^{-1}$
v_d	rate of desorption, $\text{mmol g}^{-1}\ \text{min}^{-1}$
v_t	rate of adsorption at time t, $\text{mmol g}^{-1}\ \text{min}^{-1}$
V	the volume of solution, L
W	the mass of adsorbent, g
R^2	regression coefficient
E_a	activation energy of adsorption, kJ mol^{-1}

R_g the universal gas constant, 8.314 J mol^{-1} K^{-1}
T temperature, °C
T_K temperature in Kelvin, K
ΔG^0 Gibbs free energy, kJ mol^{-1}
ΔH^0 enthalpy, kJ mol^{-1}
ΔS^0 entropy, J mol^{-1} K^{-1}

1 Introduction

In recent years, increasing attention has been focused on the desulfurization of transportation fuels due to regulations for environmental protection. The government agencies in various countries have implemented more stringent regulations of refineries to produce cleaner gasoline and diesel fuels with reduced sulfur content. Consequently, the U.S. Environmental Protection Agency (EPA) has issued a Tier II regulation that mandates refineries to reduce the sulfur content in gasoline and diesel from 300 and 500 ppmw to 30 and 15 ppmw, respectively since 2006. European legislation also restricts the sulfur level in gasoline and diesel to less than 50 ppmw by 2005 and 10 ppmw by 2010 (Song 2003). Moreover, the sulfur-containing compounds in the fuel are poisons to reforming and water gas shift catalysts. Thus, sulfur-free fuels will be required for the production of hydrogen for fuel cells since trace amount of sulfur compounds in the fuels will poison the catalysts (Song and Ma 2002; Ma et al. 2002; Velu et al. 2005a).

Hydrodesulfurization (HDS) is currently used to remove reactive sulfides, disulfides, mercaptans and light thiophenic sulfur compounds. However, hydrotreating processes normally result in a significant reduction of octane number due to the saturation of alkenes and arenes by hydrogenation reactions at high pressures and high temperatures (Song and Ma 2003). It is also difficult to remove refractory sulfur compounds such as dibenzothiophene (DBT) and their derivatives with one or two alkyl groups which are abundant in gasoline and especially in diesel. Thus, using the conventional hydrotreating processes, it is almost impossible to desulfurize to reach a total sulfur level of less than 15 ppmw without saturating some of the alkenes and arenes (Ma et al. 1994; Edwards 2000). Therefore, it is quite a challenge to develop a new process for the selective reduction of the sulfur compounds from petroleum fractions to less than 50 ppmw or lower without treating the whole fuel under high pressure and temperature. Compared to the conventional hydrodesulfurization process, the adsorptive removal technique is attractive in the removal of refractory sulfur compounds to produce ultra-clean fuels and has attracted the attention of many research groups since it can be accomplished at ambient pressure and temperature (Ng et al. 2005; Jiang and Ng 2006).

Finding a selective adsorbent with high capacity for the sulfur containing compounds is the key to develop an adsorptive technique. Various types of adsorbents such as reduced metals (Fukunaga et al. 2003; Ma and Velu 2005a, 2005b), mixed oxides (Watanabe et al. 2004), activated carbon (Haji and Erkey 2004; Kim et al. 2006; Wang and Yang 2007), zeolites-based materials (Velu et al. 2003, 2005a; Jiang and Ng 2006; Yang et al. 2003; Hernandez-Maldonado et al. 2003a, 2003b, 2004; Ng et al. 2005; Jiang et al. 2005) and some novel porous materials (Kim et al. 2006; Velu et al. 2005b; Ma et al. 2003) have been studied and the possible mechanisms have also been proposed. Recently, Song's group (Kim et al. 2006) has discussed in detail the ultra-deep desulfurization of diesel fuel by selective adsorption of six different species over three different adsorbents, namely, supported nickel adsorbent, activated alumina and activated carbon, of which activated carbon shows higher adsorptive capcacity and selectivity for sulfur, especially for the compounds with methyl groups, such as 4,6-dimethyldibenzothiophene (4,6-DMDBT).

Zeolites have been extensively used to catalyze some reactions in refinery and petrochemical processes according due to their pore structures and large specific surface areas. Moreover, zeolites have high chemical and hydrothermal stability. Therefore, zeolites are potential adsorbents for refractory sulfur-containing compounds and have attracted the most interest in recent years. Many publications have reported that zeolites are very effective for the removal of sulfur compounds (Jiang and Ng 2006; Hernandez-Maldonado et al. 2004, 2005; Hernandez-Maldonado and Yang 2003a, 2003b, 2004a, 2004b, 2004c, 2004d, 2004e; Velu et al. 2003; Ng et al. 2005; Jiang et al. 2005, Yang et al. 2001, 2003; Yu et al. 2002; Wang et al. 2009).

Yang and coworkers have extensively investigated the application of cation-exchanged Y zeolites, i.e., Cu(I)Y, AgY, NiY, ZnY and ZSM-5, USY, as adsorbents for the selective removal of sulfur compounds (Hernandez-Maldonado and Yang 2003b, 2004a, 2004b; Hernandez-Maldonado et al. 2005; Yang et al. 2001; Takahashi et al. 2002; Li et al. 2006; Ma and Yang 2007a, 2007b). Combined with the molecular orbital calculation, they confirmed that π-complexation between the sorbents and the organic sulfur molecules plays a key role on the selective adsorption of sulfur-containing compounds. Song reviewed the different approaches to deep desulfurization for the production of ultra-clean fuels and pointed out that the new approaches include adsorbents or reagents and methods for non-HDS-type processing schemes (Song 2003). Recently, they also reported that cation-exchanged Y zeolites (Cu, Ni, Zn, Pd and Ce) are effective for the adsorption of sulfur (Velu et al. 2003). Zeolites such as 13X have also been reported to be effective for the removal of sulfur compounds in fuels (Jiang et al. 2005; Ma and Yang 2007a; Salem and Hamid 1997).

Most recently, Wang et al. (2009) studied the adsorption of DBT over Ce/NiY zeolites with the emphasis on the effect of Ce^{3+} as a co-cation. They found that NiCeY exhibits higher adsorptive selectivity for DBT than NiY and CeY, indicating that NiCeY is a more effective adsorbent to remove sulfur-containing compounds from transportation fuels.

The heat of adsorption is a critical parameter in estimating the performance of an adsorptive separation process. We have pioneered the use of flow calorimetric technique to investigate the adsorptive capacity and the heat flow during the adsorption of thiophenic sulfur compounds dissolved in normal hexadecane to mimic sulfur in diesel fuel on different types of commercial zeolites, such as NaY, USY, HY, and 13X (Ng et al. 2005; Jiang et al. 2005; Jiang and Ng 2006). We found that NaY has the highest saturation sorption capacity among the four zeolites that we used for the adsorption of the sulfur-containing compounds (Ng et al. 2005). The measured heat of adsorption for sulfur-containing compounds includes the heat of the displacement of the adsorbed solvent molecules by sulfur-containing compounds and is much lower than that obtained by gas phase adsorption of sulfur-containing compounds in the zeolites. Moreover, the measured heat of adsorption per gram of sorbent is also influenced by the molecular size of the sulfur compounds and decreases in the order: thiophene > benzothiophene > dibenzothiophene due to the higher sorbent capacity for the smaller sulfur compounds (Jiang et al. 2005). Also, we found that transition metal ion exchanged zeolites exhibit excellent properties for the adsorption of the sulfur-containing compounds and the measured adsorption strength for each mole sulfur adsorbed on Y zeolites is in the order of CuY > NiY > NaY because of the formation of the π-complexes (Jiang and Ng 2006). Recently, our results on the heat of adsorption are further confirmed by Yang and coworkers based on the calculation by using the Clausius-Clapeyron equation and according to the measurement of the heats of adsorption both from liquid solutions and from pure vapor phase (Ma and Yang 2007b).

As mentioned above, much attention has been focused on finding a suitable adsorbent. However, to our knowledge there is no comprehensive report on the equilibrium and kinetic studies on the removal of the sulfur-containing compounds. In this paper, we selected a commercial NaY zeolite as an adsorbent, investigated the equilibrium and kinetic adsorption of dibenzothiophene (DBT) using hexadecane as the solvent to model the adsorption of sulfur-containing compounds from diesel fuel. We also studied competitive adsorption of DBT in the presence of aromatic and nitrogen-containing compound such as naphthalene and quinoline. Analysis of the equilibrium and kinetic adsorption and the heat of the adsorption of DBT in hexadecane calculated from the van't Hoff equation are described in this paper.

2 Materials and methods

2.1 Materials

Zeolite NaY powder with a porous volume of 0.6 ($\mathrm{mL\,g^{-1}}$) and Langmuir surface area of 677 ($\mathrm{m^2\,g^{-1}}$) as determined by N_2 adsorption at 77 K was obtained from Strem Chemicals. It was pressed, crushed and sieved into the size range of 250–500 µm. Prior to the experiments, the zeolite was dehydrated by heating in air at a rate of 2 °C per min up to 400 °C and kept at 400 °C for two hours.

Dibenzothiophene (DBT), naphthalene, quinoline and hexadecane, all of A.R. grade, were obtained from Aldrich and were used without further purification. Hexadecane was used as solvent in experiment.

2.2 Equilibrium isothermal adsorption

The equilibrium isothermal adsorption was carried out by placing 60 mg of the zeolite into 5.0 g of the solution containing a certain amount of adsorbate in a 20 mL vial, of which the concentrations typically range from 1 to 30 ($\mathrm{mmol\,L^{-1}}$). The vials were sealed and shaken at 150 rpm in a thermostated bath maintained at certain temperature (typically 45 °C) for 20 h. In each case, a control vial containing the same amount of solution but without any adsorbent was also placed in the same batch.

The concentrations of the adsorbate in the solutions both in the sample and in the control were determined by a Varian CP3800 gas chromatograph using a DB1701 column and a FID detector (Jiang et al. 2005; Ng et al. 2005).

The adsorptive amount of adsorbate (q_e) was calculated by comparing the adsorbate contents in the solution with that in the corresponding control vial using the following equation:

$$q_e = V\frac{c_0 - c_e}{W} \tag{1}$$

where V (L) is the volume of solution and W (g) is the mass of a given dry adsorbent; c_0 and c_e ($\mathrm{mmol\,L^{-1}}$) denote the initial and equilibrium concentration of adsorbate in the solution.

2.3 Adsorption kinetics

The kinetics of the adsorption was determined by adding a certain amount (typically 60 mg) of the zeolite into a series of solutions (typically 8.00 g) contained in 20 mL vials placed inside the shaking bath for different contact time. A timer was used to determine the contact time between the zeolite and the solution. The vial was immediately removed from the bath after the contact time was reached and typically a 1 mL of clear solution was taken for GC analysis after the phase separation. The influence of several variables, such as the initial adsorbate concentrations and temperature were investigated.

The adsorptive amount of adsorbate at different contact time was calculated by comparing the concentration of the adsorbate in the solution with the initial adsorbate concentration.

3 Results and discussion

3.1 Equilibrium isothermal adsorption

Ma and Yang (2007a, 2007b) recently reported that the rate of adsorption of four sulfur compounds from their binary solutions in n-octane on metal modified Y zeolite and active carbon were fairy rapid and in all case, 7 h was adequate for reaching equilibrium. In this study, the equilibrium isothermal adsorption was conducted with a contact time of 20 h at 30 °C, 45 °C and 60 °C with hexadecane as the solvent and hence the equilibrium adsorption should be reached. Figure 1 shows the relationship of the adsorptive amount of DBT per gram of NaY zeolite (q_e, (mmol g^{-1})) against the equilibrium concentration of DBT in the binary solution (c_e, (mmol L^{-1})). As seen from Fig. 1, initially, with an increase of c_e, q_e value increases sharply. When c_e is higher than 10.00 (mmol L^{-1}), q_e does not change much and reaches a plateau. This indicates that when the initial concentration of DBT is lower than a certain value, almost all DBT is adsorbed onto NaY zeolite. When the concentration of DBT is high enough, the adsorption reaches its saturation and q_e is close to the maximum adsorption (q_m). From Fig. 1, one can estimate q_m to be around 1.30, 1.45 and 1.60 (mmol g^{-1}) at 30 °C, 45 °C and 60 °C respectively.

In general, the interaction between the adsorbent and the adsorbates in the solution contains two processes, namely, adsorption and desorption. The rate of adsorption (v_{ads}) and desorption (v_d) can be described as follows:

$$v_{\text{ads}} = k_{\text{ads}} c_t (1 - \theta), \tag{2}$$

$$v_d = k_d \theta \tag{3}$$

where k_{ads} and k_d are the adsorptive and desorptive constants; c_t is the concentration of adsorbate at time t; θ is the dimensionless ratio of coverage of the surface of adsorbent, which can be expressed by the division of adsorptive amount of adsorbate at time t (q_t) to its maximum (q_m), i.e., q_t/q_m.

When the adsorption reaches its equilibrium, the values of v_{ads} and v_d are equal and the concentration of adsorbate (c_t) and the adsorption amount (q_t) can be written as c_e and q_e. Thus, one can obtain the Langmuir isothermal model as below:

$$q_e = \frac{K_L q_m c_e}{1 + K_L c_e} \tag{4}$$

where K_L is Langmuir constant and $K_L = \frac{k_{\text{ads}}}{k_d}$.

Linear regression is frequently used to determine the best-fitting isotherm and the method of least squares has been used for finding the parameters of the isotherm. With further rearrangement, (4) has a linear form as shown in (5):

$$\frac{c_e}{q_e} = \frac{1}{q_m} c_e + \frac{1}{K_L q_m}. \tag{5}$$

Therefore, one can obtain the Langmuir constant K_L and the maximum adsorptive amount of adsorbate (q_m) through the slope and the intercept of (5) by plotting c_e/q_e against c_e.

Figure 2 presents the experimental data with linear relation between c_e/q_e against c_e at different temperatures. According to (5), one can deduce the parameters K_L and

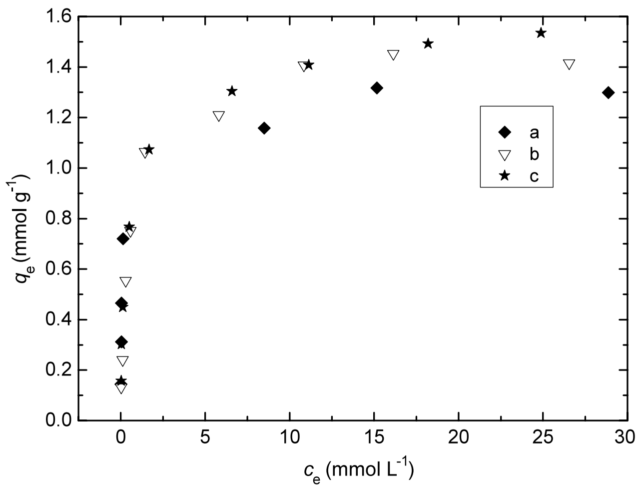

Fig. 1 Equilibrium isothermal adsorption of DBT onto NaY zeolite at different temperatures (*a*. 30 °C; *b*. 45 °C; *c*. 60 °C)

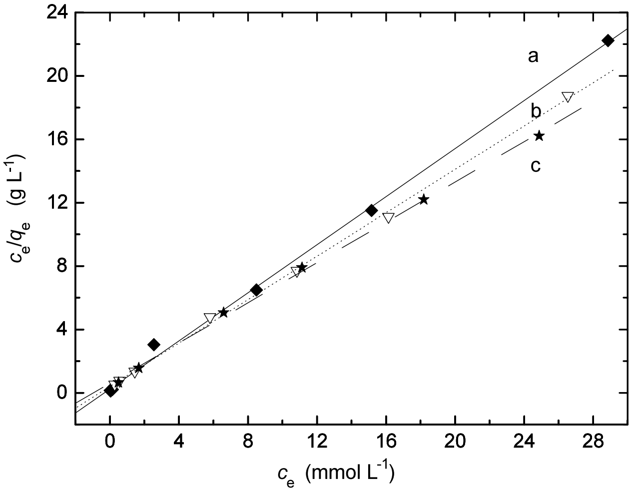

Fig. 2 Langmuir model linear equations obtained by using the linear fitting method for the adsorption of DBT onto NaY zeolite at different temperatures (*a*. 30 °C; *b*. 45 °C; *c*. 60 °C)

Table 1 Langmuir model equilibrium parameters obtained by a linear fitting method at different temperatures

Parameters	30 °C	45 °C	60 °C
q_m (mmol g^{-1})	1.32	1.46	1.57
K_L (L mmol^{-1})	3.16	1.72	1.07
R^2	0.999	0.999	0.999

q_m. The results and the corresponding regression coefficient (R^2) at different temperature are shown in Table 1. From Fig. 2, one can find that with the increase in temperature, the slope decreases slightly which suggests that the adsorptive amount of DBT increases slightly with the increase in temperature as shown in Table 1. The values of q_m obtained from Fig. 2 are in agreement with the results in Fig 1. From Table 1, one can also find that the Langmuir constant decreases with the increase in temperature indicating the adsorptive process is exothermic. It should be noted the effect of temperature on q_m and K_L should be interpreted with caution since there are scatter in the data. More extensive experiments are required to confirm these values.

3.2 Effect of contact time on the adsorption

The rate of sulfur removal from fuels is of great significance for developing adsorbent-based adsorptive desulfurizaiton technology. The necessary contact time to reach the equilibrium depends on the initial concentration of adsorbate, the temperature and other variables. In this experiment, a series of contact time experiments have been carried out with a constant initial DBT concentration of 9.00 (mmol L^{-1}) at 45 °C and a constant shaking speed of 150 rpm. The effect of contact time on the adsorption of DBT (q_t, (mmol g^{-1})) on NaY zeolite is shown in Fig. 3.

As seen from Fig. 3, initially, the adsorption amount of DBT (q_t) increases sharply with time (t). When t reaches beyond 180 minutes, the q_t value slightly increases and finally at some point in time, q_t reaches a constant value. At this point, the adsorption of DBT on NaY zeolite is in a state of dynamic equilibrium with the desorption of DBT from NaY to the solution. The time required to attain such a state of equilibrium of DBT reflects the equilibrium adsorption capacity of the adsorbent under the operating conditions, namely, q_t equal to q_e when t reaches this point in time.

The adsorptive behavior of hydrocarbons in porous materials has been explained using a pore diffusion model (Liapis and Rippin 1977). Several simpler models such as a pseudo-first-order model, pseudo-second-order model and double exponential model have been used successfully to fit the experimental kinetic adsorption data (Bektas et al. 2004; Chiron et al. 2003; Ho and Ofomaja 2006; Nouri et al. 2007). Among these models, the pseudo-second-order model is the one most frequently used and generally accepted (Wu et al. 2009). The pseudo-second-order equation can be expressed as:

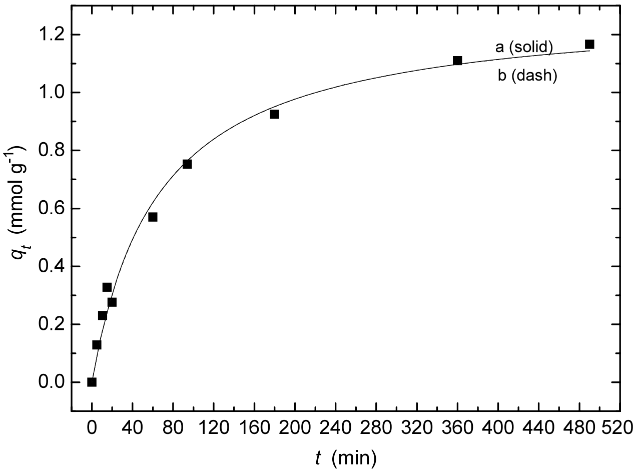

Fig. 3 Effect of contact time on the adsorption of DBT onto NaY zeolite (*a*. Langmuir model, *b*. pseudo-second-order model, $c_{\mathrm{DBT}} = 9.00$ (mmol L^{-1}), $T = 45\,^\circ$C; curves (*a*) and (*b*) are overlapped with each other)

$$\frac{dq_t}{dt} = k_2(q_t - q_e)^2. \tag{6}$$

After integration and applying the boundary conditions of $q_t = 0$ at $t = 0$, then,

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{7}$$

where k_2 is the pseudo-second-order rate constant (g mmol^{-1} min^{-1}) and q_e is the amount of DBT adsorbed at equilibrium (mmol g^{-1}).

Equation (7) has been used to fit the adsorption of DBT on NaY zeolite at 45 °C with an initial concentration of DBT of 9.00 (mmol L^{-1}). Curve (a) in Fig. 3 shows the non-linear fitting results. The corresponding parameters of k_2 and q_e are found to be 11.81×10^{-3} (g mmol^{-1} min^{-1}) and 1.30 (mmol g^{-1}), respectively.

Although the Langmuir model is widely used to describe the adsorption isotherm, it may also be used to describe the adsorption kinetics. By combining (2) and (3), the adsorptive rate at any time can be described by (8):

$$v_t = v_{\mathrm{ads}} - v_d. \tag{8}$$

The adsorptive rate can be also written in the differential form in terms of the adsorptive amount of DBT, namely,

$$v_t = \frac{dq_t}{dt}. \tag{9}$$

Thus, based on (2) and (3), one can obtain:

$$\frac{dq_t}{dt} = k_{\mathrm{ads}} c_t (1 - \theta) - k_d \theta. \tag{10}$$

Using $\theta = \frac{q_t}{q_m}$ and (1), (10) is represented by (11):

$$\frac{dq_t}{dt} = k_{\text{ads}}\left(c_0 - \frac{q_t W}{V}\right)\left(1 - \frac{q_t}{q_m}\right) - k_d \frac{q_t}{q_m}. \tag{11}$$

After rearrangement and integration from (11), q_t can be expressed by (12) (Chiron et al. 2003):

$$q_t = q_e \frac{q_L(1 - e^{\alpha t})}{q_e - q_L e^{\alpha t}} \tag{12}$$

where $\alpha = \frac{k_d K_L W(q_L - q_e)}{V q_m}$; q_e and q_L are the two solutions of the second-order polynomial expression $P(q_t) = K_L W q_t^2 - (K_L q_m W + K_L c_0 V + V)q_t + K_L c_o V q_m$ during the rearrangement and $q_L > q_e$.

In this experiment, (12) is also used to fit the results, as shown by curve (b) in Fig. 3 which overlapped with curve (a) fitted according to (7). The parameter q_e was found to be 1.28 (mmol g^{-1}), which is very close to what was obtained by the pseudo-second-order model. Therefore apparently both the pseudo-second-order model and Langmuir model can be successfully used to fit the experimental kinetic data.

Linear regression is frequently used to determine the best-fitting kinetic parameters. With the arrangement of (7), the pseudo-second-order equation can be written into a linear form,

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}. \tag{13}$$

From the linear fitting results according to (13), based on the slope and intercept, one can deduce the corresponding parameters q_e and k_2. Figure 4 shows the results. The slope and intercept values are 0.77 (g mmol^{-1}) and 46.33 (g min mmol^{-1}), thus, one can deduce the q_e and k_2 to be 1.29 (mmol g^{-1}) and 12.89×10^{-3} (g mmol^{-1} min^{-1}). The results are similar to what are obtained through the non-linear fitting results.

3.3 Effect of the initial concentration on the kinetics of adsorption

The initial concentration provides an important driving force to overcome mass transfer resistances of solutes between the liquid and solid phase. The effect of the initial DBT concentration on the rate of adsorption at 45 °C is shown in Fig. 5. From Fig. 5, it is observed that the rate of adsorptive removal of DBT varied with its initial concentration. The DBT adsorption occurs rapidly initially and then increases gradually with increasing contact time and eventually reaches a plateau. An increase in the initial concentration of DBT leads to an increase in the adsorption capacity of DBT and it can be found that the initial rate of adsorption is greater for a higher initial concentration of DBT.

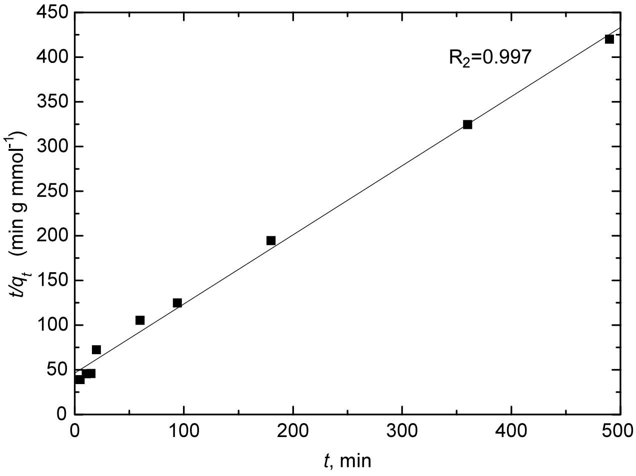

Fig. 4 Linear fitting according to pseudo-second-order model ($c_{\text{DBT}} = 9.00$ (mmol L^{-1}), $T = 45$ °C)

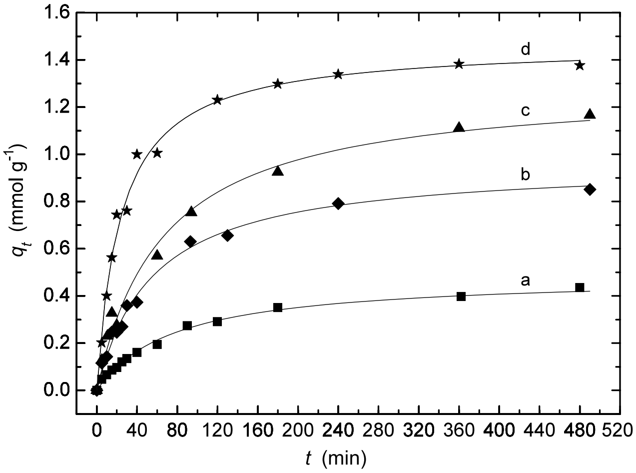

Fig. 5 Effect of initial concentration of DBT on the adsorption with NaY zeolite as the adsorbent (*a*. 2.88, *b*. 8.58, *c*. 9.00, *d*. 27.23 (mmol L^{-1}), $T = 45$ °C)

According to (6), the initial adsorptive rate of DBT on NaY zeolite can be written as:

$$v_0 = k_2 q_e^2. \tag{14}$$

Table 2 shows the pseudo-second-order kinetic parameters for different initial concentrations of DBT utilizing the non-linear curve fitting analysis method. The adsorption of DBT on NaY zeolite for different initial concentrations was found to be adequately represented by the pseudo-second-order model. With the increase of the initial concentration of DBT, both the initial adsorption rate and theoretical amount of adsorption of DBT at equilibrium increased.

From (10), one can also find that the initial rate of adsorption of DBT on NaY zeolite can be expressed through the Langmuir model. Since $t = 0$, the coverage rate of surface θ

Table 2 Pseudo-second-order kinetic parameters obtained by using the non-linear fitting method for different initial concentration of DBT ($T = 45\,^\circ\mathrm{C}$)

c_0 (mmol L^{-1})	2.88	8.58	9.00	27.23
k_2 (g mmol^{-1} min^{-1})	24.94×10^{-3}	19.49×10^{-3}	11.81×10^{-3}	28.61×10^{-3}
q_e (mmol g^{-1})	0.50	0.95	1.30	1.46
v_0 (mmol g^{-1} min^{-1})	6.23×10^{-3}	17.59×10^{-3}	19.96×10^{-3}	60.98×10^{-3}
R^2	0.995	0.992	0.990	0.992

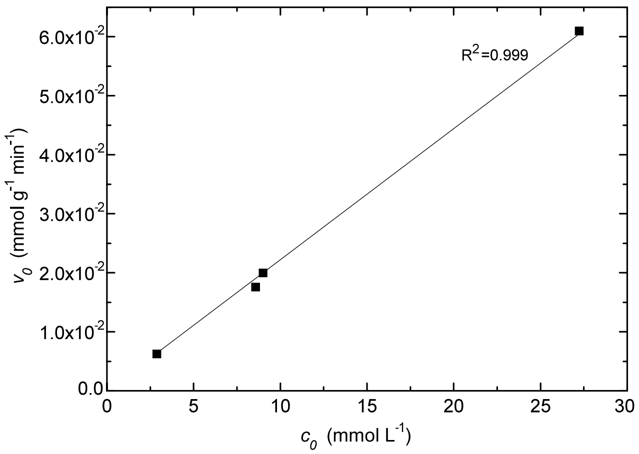

Fig. 6 Plot of v_0 against c_0 at 45 °C

is supposed to be zero, thus, the initial rate of adsorption at $t = 0$ can be given as:

$$v_0 = k_{\mathrm{ads}} c_0 \tag{15}$$

where k_{ads} is a constant dependent on temperature. Based on the values of c_0 and v_0 shown in Table 2, after a linear fitting, the value of k_{ads} has been obtained as plotted in Fig. 6. From Fig. 6, one can find that the value of k_{ads} is to be 2.22×10^{-3} (L g^{-1} min^{-1}). Based on the Langmuir constant for adsorption $K_L = \frac{k_{\mathrm{ads}}}{k_d}$ and its value of 1.72 (L mmol^{-1}) at 45 °C as shown in Table 1, one can deduce the related desorptive constant, k_d, to be 1.29×10^{-3} (mmol g^{-1} min^{-1}).

3.4 Effect of the temperature on the adsorption kinetics

Normally, the temperature has two major effects on the adsorption process (Nouri et al. 2007). Increasing the temperature of the system is known to greatly increase the rate of diffusion of the adsorbate, owing to the decrease in the viscosity of the solution. Meanwhile, changing the temperature of the system will lead to another equilibrium capacity of the adsorbent as shown in Table 1. Figure 7 presents the effect of contact time on the adsorption dynamics at different temperatures, namely, 30, 45 and 60 °C with the initial concentration of DBT being 9.00 (mmol L^{-1}). The measurement of the kinetics of the process at different temperatures exhibits an apparent increase in the sulfur removal, i.e., the q_e value apparently increases with the increase in temperature. More data should be obtained at longer reaction times to ascertain indeed the q_e value is temperature dependent.

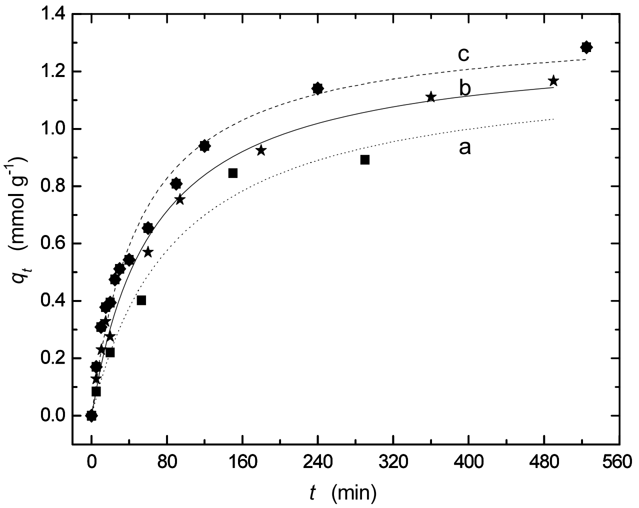

Fig. 7 Effect of temperature on the kinetics of adsorption (*a*. 30, *b*. 45, *c*. 60 °C; $c_0 = 9.00$ (mmol L^{-1}))

Table 3 Pseudo-second-order kinetic parameters obtained by using the non-linear method for different temperature ($c_0 = 9.00$ (mmol L^{-1}))

T, °C	30	45	60
k_2 (g mmol^{-1} min^{-1})	9.10×10^{-3}	11.81×10^{-3}	14.13×10^{-3}
q_e (mmol g^{-1})	1.22	1.30	1.36
v_0 (mmol g^{-1} min^{-1})	13.54×10^{-3}	19.96×10^{-3}	26.13×10^{-3}
R^2	0.984	0.990	0.981

The kinetic data have been analyzed by the pseudo-second-order rate equation using a non-linear curve fitting analysis method. The model parameters are listed in Table 3. As seen from Table 3, the theoretical adsorptive amount of DBT on NaY zeolite, the pseudo-second-order rate constant and the initial adsorptive rate all increase with an increase in temperature. This result indicates the process of adsorption of DBT in hexadecane on NaY is more effective at higher temperatures since both the amount of adsorption and the rate of adsorption increases with an increase in temperature.

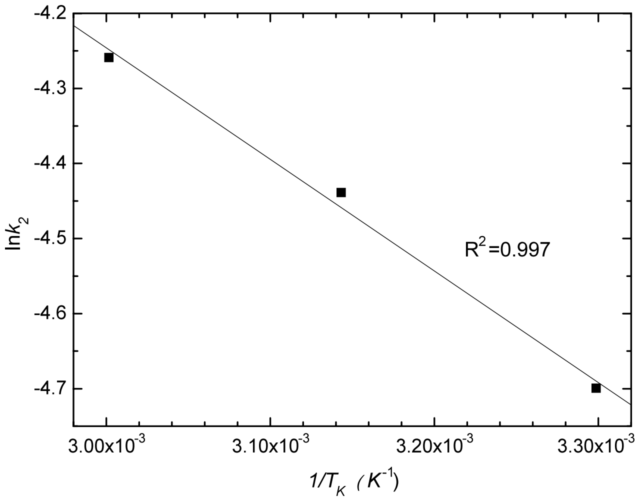

Fig. 8 Plot of $\ln k_2$ versus $1/T_K$ ($c_0 = 9.00$ (mmol L^{-1}))

The influence of temperature on the adsorptive rate is calculated using the Arrhenius equation (16):

$$k_2 = k_0 \exp\left(-\frac{E_a}{R_g T_k}\right) \tag{16}$$

where k_0 is the temperature independent factor (g mmol^{-1} min^{-1}), E_a is the activation energy of adsorption (kJ mol^{-1}), R_g and T_k is the universal gas constant (8.314 (J mol^{-1} K^{-1})) and the temperature in Kelvin (K), respectively. Typically, the slope of the plot of $\ln k_2$ versus $1/T_k$ is used to evaluate the activation energy, which is shown in Fig. 8. The low activation energy (12.4 (kJ mol^{-1})) determined for the adsorption of DBT on NaY zeolite in hexadecane suggests the adsorption is mass transfer controlled (Nollet et al. 2003; Nouri et al. 2007).

3.5 Effect of naphthalene and quinoline on the adsorption kinetics

Normally, in gasoline or diesel, there are plenty of aromatic, aza and thia compounds. Aza and thia compounds should be further removed to obtain high quality fuels. In an adsorptive sulfur removal process, the aromatic, aza compounds will compete to reach and occupy the adsorption sites of the zeolite (Ng et al. 2005; Thomas et al. 2010) Therefore naphthalene and quinoline are selected to consider the influence of aromatic and aza compounds on the adsorption of DBT onto NaY zeolite. To better understand the competition between DBT and naphthalene and quinoline, a mixture with the same initial concentration of the three components is prepared and used to carry out the kinetic experiment at 45 °C.

Figure 9 indicates the competitive adsorption between equimolar concentrations of DBT, naphthalene and quinoline. As seen from Fig. 9, both the adsorptive amount and the initial adsorptive rate of the three components follows the order, quinoline > naphthalene > DBT. This indicates that quinoline in the solution is preferentially adsorbed. In Fig. 9, the initial concentration of DBT is 5.65 mmol L^{-1} and the maximum amount of DBT adsorbed is around 0.22 mmol g^{-1} which is much lower than the value of 0.40 mmol g^{-1} adsorbed at an initial DBT concentration of 2.88 mmol L^{-1} (see Fig. 5). According to the chemical structure and the electronegativity of the three compounds, quinoline has a more nucleophilic N atom and DBT has one more aromatic ring than the others. Thus, quinoline has the tendency to have the strongest interaction with zeolite since zeolite is rich in electrophilic centers based on Na$^+$ and Al^{3+} in the framework of zeolite. DBT has a larger molecular size than naphthalene and quinoline and the steric hindrance factor might play a more important role compared to its weak nucleophilic group. Therefore, the rate and amount of adsorption of DBT is the least. The results above indicate that NaY zeolite is an efficient adsorbate to remove DBT, but it removes aromatic and aza compounds simultaneously. Thus, the utilization of NaY on the removal of sulfur compounds from fuels needs further investigation.

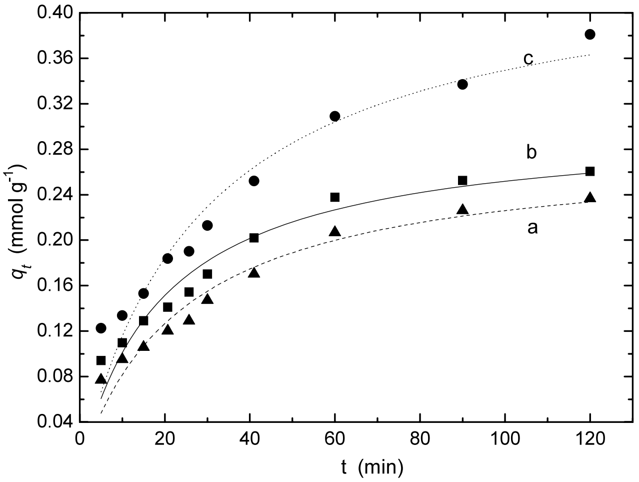

Fig. 9 Competitive adsorption of DBT, naphthalene and quinoline on NaY (*a*. DBT, *b*. naphthalene, *c*. quinoline; $c_0 = 5.65$ (mmol L^{-1}); $T = 45\,^\circ$C)

3.6 Discussions on the thermodynamic parameters

The Gibbs free energy change (ΔG^0) can be expressed by the Langmuir constant K_L in the form of (Bektas et al. 2004; Nouri et al. 2007):

$$\Delta G^0 = -R_g T_k \ln K_L. \tag{17}$$

Since $\Delta G^0 = \Delta H^0 - T_k \Delta S^0$, (17) can be rearranged in the form of:

$$\ln K_L = -\frac{\Delta H^0}{R_g T_k} + \frac{\Delta S^0}{R_g} \tag{18}$$

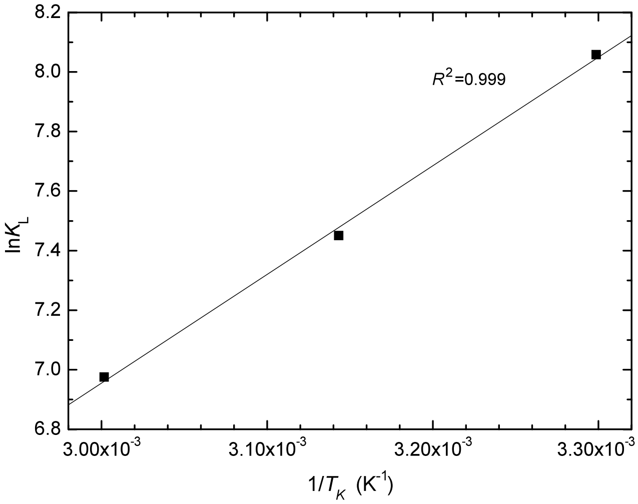

Fig. 10 Relationship between $\ln K_L$ and $1/T_K$

where ΔH^0 is the standard enthalpy of adsorption (kJ mol^{-1}).

According to the data shown in Table 1, the relationship between $\ln K_L$ against $1/T$ has been plotted in Fig. 10, of which the slope and the intercept is 3650 K and -3.994, respectively. Therefore, one can deduce the values of ΔH^0 and ΔS^0 to be -30.3 (kJ mol^{-1}) and -33.2 (J mol^{-1} K^{-1}), respectively. It is important to point out the ΔH^0value is very close to the value of -28.6 kJ measured for the heat of adsorption of DBT in hexadecane on NaY (Thomas et al. 2010) using flow calorimetry. Furthermore, according to either (6) or $\Delta G^0 = \Delta H^0 - T\Delta S^0$ based on the values of ΔH^0 and ΔS^0 above, one can find the corresponding ΔG^0 value at 30, 45 and 60 °C to be around -20.3, -19.7 and -19.3 (kJ mol^{-1}), respectively. These results indicate that the adsorption of DBT on NaY zeolite is a spontaneous process and exothermic. The negative entropy change ΔS^0 value corresponds to a decrease in the degree of freedom of the adsorbed species.

4 Conclusions

Equilibrium and kinetic studies on the adsorption of DBT from hexadecane solution by NaY zeolite have been investigated. The parameters which influence the removal of sulfur-containing compounds are discussed.

Equilibrium isotherm shows that the adsorption can be represented by the Langmuir model and the adsorptive capacity increases slightly with an increase of temperature while the Langmuir adsorption constant decreases with an increase of temperature. The analysis of the thermodymanic parameters according to the van't Hoff equation indicates that the adsorption is exothermic and the value of ΔH^0 and ΔS^0 are determined to be -30.3 (kJ mol^{-1}) and -33.2 (J mol^{-1} K^{-1}), respectively.

Kinetic studies indicate that the uptake rate of DBT is rapid at the initial stages and then decreases gradually until an equilibrium is reached. The adsorption process can be modeled by either the Langmuir model or the pseudo-second-order model. The maximum adsorption capacities at different temperatures increase within the studied temperature range. Thermodynamic parameters of the desorption process are also determined. The results indicate that the pseudo-second-order kinetic constant increases with an increase in the temperature and the activation energy is determined to be 12.4 (kJ mol^{-1}). The competitive adsorption of DBT, naphthalene and quinoline in hexadecane indicates that the rate and the adsorption amount is in the following order: quinoline > naphthalene > DBT which could be rationalized by both the electronic and steric effects of the adsorbates.

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