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Adsorption kinetics and isotherm parameters of naphthalene onto natural- and chemically modified bentonite from aqueous solutions

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Abstract Polycyclic aromatic hydrocarbons (PAHs) have widely been studied and a special concern because of their mutagenic and carcinogenic activities. In this study, natural- and chemically modified-bentonite were characterized by means of N_2 adsorption method, XRD, SEM, FT-IR, elemental and thermal analysis and zeta potential techniques and their adsorption behavior were then investigated toward naphthalene, which is the first member of the PAHs. The effects of various experimental parameters such as pH, contact time and temperature on adsorption were tested in the experiments. The optimum pH values for naphthalene adsorption onto natural bentonite (NB) and hexadecyltrimethylammonium bromide modified bentonite (HB) were found to be as 4.00 and 5.97, respectively. The equilibrium contact time was 60 min for both of the adsorbent. A comparison of the linear and nonlinear method of three widely used kinetic models, which are Lagergren-first order, the pseudo-second-order and Elovich kinetics, and the most popular isotherms, which are Langmuir and Freundlich, were examined to the experimental data of the adsorption of naphthalene onto NB and HB. The kinetic results indicated that the pseudo-second-order kinetic model with high correlation coefficients was more suitable than the other kinetic models e.g. Lagergren first-order and Elovich. All results showed that the modified bentonite can be used as an adsorbent to remove PAHs from aqueous solutions by using adsorption method due to its effectiveness, simplicity and low-cost than the other conventional methods.

Keywords Adsorption · Bentonite · Characterization · Naphthalene · Modification

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals that are formed during the incomplete burning of coal, oil, gas, wood, garbage or other organic substances, such as tobacco and charbroiled meat. Owing to atmospheric emissions of PAHs even at low concentrations, they can usually be found everywhere. Highly polluted areas are associated with industrial activities. Many PAH compounds are also toxic, mutagenic, and/or carcinogenic (Laor et al. 1998; Badr et al. 2004; Chang et al. 2004; Kishikawa et al. 2004; Chatterjee et al. 2010) and can have both short- and long-term health effects. Lower molecular mass of PAHs such as naphthalene are characterized by high volatility and can cause short-term toxicity problems via inhalation but they are not carcinogens, whereas high molecular mass of PAHs such as benzo(a)pyrene are known as human carcinogens released into the environment (Menzie et al. 1992; Lin et al. 2010). Due to the resistance of PAHs, it is found that they have accumulated in the air, water bodies, soil and foods. Once inside the human body, PAHs can easily pass through cell membranes and are readily adsorbed into cells and therefore the immune system converts PAHs to diolepoxides and epoxide hydrolase, which react DNA and blocks its synthesis

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(Tran-Duc et al. 2010; Chuang et al. 2010). PAHs can enter natural water sources via atmospheric fallout, urban runoff, municipal wastes, industrial effluents and oil spillage or leakage (Yuan et al. 2010).

Several traditional methods have been used for the removal of PAHs from wastewater such as chlorination, oxidation, ultrasonic irradiation, biodegradation, adsorption, etc. In view of its high removal efficiency, adsorption method is commonly used for the PAHs removal from wastewater. Although the most promising adsorbent for the adsorption method is activated carbon (Luna et al. 2011; Ania et al. 2008), it is still has some limitations in the applications. For instance, it is high price and is ineffective in the removal of the oil, grease, natural organic matter, and other high molecular mass organic compounds (Alther 2002). In this manner, there is a need to find the low-cost and locally available adsorbent. Clay minerals such as bentonite, sepiolite, zeolite, montmorillonite and their modified forms are being considered as the alternative adsorbents instead of activated carbon (Zhang et al. 2011).

Bentonite is 2:1 type of aluminosilicate having crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina fused to two external silicate layers. Isomorphic substitution within the layers generates negative charges that are counterbalanced by alkali or alkaline earth cations that are easy to replace. These cations are defined as exchangeable cations. Forces holding the stacks together are relatively weak and hence intercalation of small molecules between the layers is easy. Most of clay minerals have high surface areas, but they are hydrophilic and thus they do not have large adsorption capacities for hydrophobic organic compounds. However, they may be modified by a surfactant molecule by simple ion-exchange reactions to lead interaction between organic surfactant cations and adsorbate that significantly enhances their capability to remove hydrophobic contaminants from aqueous solution. The modification of clay minerals with a surfactant are called as organoclay to cause to transform organophobic to strongly organophilic and this transformation leads to increase in the adsorption capacity. During the modification, the exchangeable inorganic cations are replaced by organic cations including quaternary ammonium compounds, which have cationic head groups with long chain hydrocarbon molecule forming the surfactant tail (Shen 2001; Özcan et al. 2004; Ramesh et al. 2002; Kukkadapu and Boyd 1995; Bergaya and Lagaly 2001; Park et al. 2011; Gök et al. 2008). The obtained organoclay can be effectively used to remove PAHs, which are the hydrophobic nonionic organic compounds, from aqueous solutions.

Naphthalene is a natural constituent of coal tar and commonly used as a wood preservative, moth repellent and raw material to produce methylanthranilate, phthalate esters, chloronaphthalene and synthetic resins, etc. Due to its relatively high volatility, naphthalene is also considered as a hazardous air pollutant (Chang et al. 2004; Bautista et al. 2010). Therefore, the adoption of naphthalene as the target compound in this study cannot only provide useful information for the removal of naphthalene but also it will be viewed as the primary method of inquiry for dealing with complicated PAHs. The objective of this work is the characterization of natural- and surfactant modified-bentonite and then to determine their adsorption behavior toward naphthalene, which is a nonpolar neutral PAH. The experimental data were fitted into Lagergren first-order, pseudo-second-order and Elovich kinetic models to interpret the kinetic data. Furthermore, experimental isotherm data adopted into the Langmuir and Freundlich isotherm equations to determine which isotherm gives the best correlation with the experimental data. The linear and nonlinear correlation analysis methods by using a computer programme were employed for both kinetic and isotherm models to compare the correlation between experimental data and the models.

2 Experimental

2.1 Materials and characterization

Naphthalene was obtained from Merck and was used as a representative compound for the experiments in this study. The solubility of naphthalene is low in water (19.40 mg/L at 10 °C; 21.63 mg/L at 15 °C and 26.54 mg/L at 20 °C) but it is soluble in the selected experimental concentration range (Shaw and Maczynski 2006). Natural bentonite (NB) was provided from Çanakkale, Turkey. It was crushed, ground, sieved through a 63-µm sieve, and dried at 120 °C in an oven for 2 h before to use. NB was characterized with respect to the cation exchange capacity (CEC) by the methylene blue method which was 1.077 mmol g^{-1} (Taylor 1985). The BET surface area of NB and hexadecyltrimethylammonium (HDTMA)-bentonite (HB) were determined from N_2 adsorption isotherm with a surface area analyzer (Quantachrome Instruments, Nova 2200e) and the results were found as 67.49 and 19.28 m^2 g^{-1}, respectively.

The chemical analysis of NB was done by using a wavelength dispersive X-ray fluorescence (XRF) spectrometer (Bruker S8 Tiger Model, Germany). The crystalline phases present in NB were determined via X-ray diffractometry (XRD-Rigaku Rint 2000, Japan) using Cu K_α radiation. NB and HB were analyzed by X-ray powder diffraction equipment, before and after the modification procedure to observe the intercalation of surfactant into bentonite layers. Scanning electron microscopy (SEM) (Zeiss Ultra Plus Model, Germany) images were performed to define the changes in the surface of adsorbent with the modification.

FTIR spectra for NB and HB were taken by using KBr discs on a Perkin Elmer Spectrum 100 Model infrared spectrophotometer to observe the surface functional groups of NB and HB. The elemental analysis (Vario EL III Elemental Analyzer, Hanau, Germany) of NB and HB were performed to determine C/N ratio in HB. Thermal analysis (Setaram, Labsys TG–DTA Model, France) was done to observe the differences in thermal behaviour between NB and HB. The temperature range for the analysis was selected as 25–1,000 °C at a heating rate of 10 °C min^{-1}. Zeta potential analysis for NB and HB were carried out by using Malvern Zetasizer Nano Series (UK) instrument.

2.2 Preparation of HDTMA-bentonite (HB)

A 30 g of NB was dispersed in 0.8 L of deionized water. HB was prepared by adding the respective quantities of HDTMA bromide $[CH_3(CH_2)_{15}N(CH_3)_3Br]$, which was used as a surfactant, equal to 1.5 fold of the cation exchange capacity of bentonite and stirred for 24 h. The prepared HB was then washed with deionized water until it was free of salts and a negative bromide test had been obtained with 0.1 M $AgNO_3$ (Li and Bowman 2001). It was then dried, and sieved through a 63 μm size sieve and samples collected from under the sieve and dried in an oven at 65 °C for 24 h before to use for the naphthalene adsorption studies.

2.3 Adsorption kinetic and isotherm studies

The pH experiments were undertaken by 50 mL of a 10 mg dm^{-3} aqueous naphthalene solution with 0.05 g of NB or HB at 20 °C for 1 h. At the beginning of the pH experiments, the pH of solution was carefully adjusted between 1 and 8 by adding small amounts of HCl or NaOH solution and it was measured using a pH meter (Fisher Accumet AB15), while naphthalene solutions contained in 100 mL Erlenmeyer flasks closed with glass stoppers to avoid evaporation were stirred using a mechanical magnetic stirrer. The blank experiments were also carried out to observe the effect of vaporization of naphthalene. The amount of vaporization during the experiments was subtracted from the experimental data. The optimum pH was then determined as 4.00 and 5.97 for NB and HB, respectively. Then it was used throughout all of the adsorption experiments, which were conducted at various time intervals and temperatures (10, 15 and 20 °C) to determine when the adsorption equilibrium was reached and the maximum removal of naphthalene was attained. After the equilibrium contact time, the samples were filtered and the equilibrium concentrations ascertained by spectrophotometer (Shimadzu UV-2101PC, Japan) at the respective λ_{max} value, which is 219 nm for naphthalene.

In order to deduce the adsorption isotherm, 0.05 g of NB or HB was kept in contact with 50 mL of naphthalene solution at various concentrations (7.5–20 mg dm^{-3}) for 2 h to allow the attainment of equilibrium at constant temperatures (10, 15 and 20 °C).

3 Results and discussion

3.1 Chemical composition of natural bentonite

The chemical analysis of NB (65.13 % SiO_2, 14.41 % Al_2O_3, 0.56 % K_2O, 1.91 % CaO, 3.31 % MgO, 0.74 % Fe_2O_3 and 0.56 % Na_2O) obtained from XRF analysis indicates that the presence of silica and alumina as the major constituents along with traces of potassium, calcium, magnesium, iron and sodium oxides in the form of impurities and the loss of ignition for NB was found to be as 11.21 %.

The XRD patterns of NB and HB were recorded (Fig. 1) and their basal spaces were observed at 14.87 and 19.03 Å, respectively. The expansion in the basal spacing of NB due to its modification with HDTMA-Br was calculated as 4.16 Å. This result suggests that an expansion in the basal spacing of NB with modification was observed and it confirms that $HDTMA^+$ intercalated into bentonite layers.

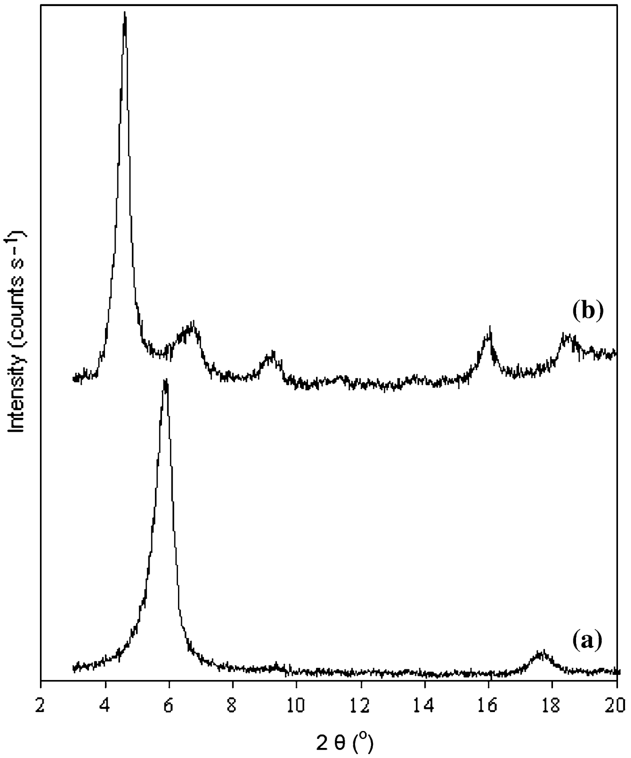

Fig. 1 XRD patterns of **a** NB and **b** HB

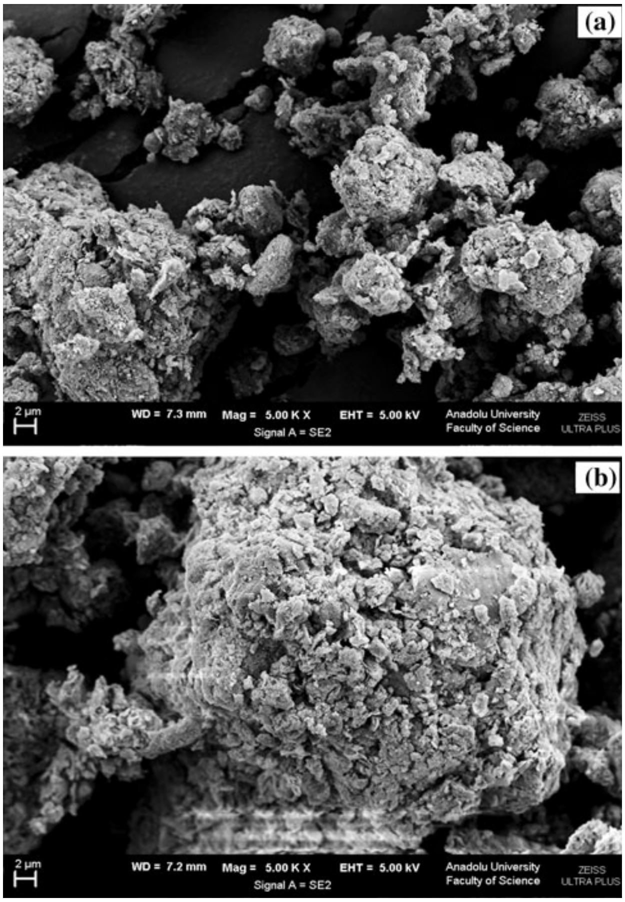

Fig. 2 SEM images of **a** NB and **b** HB

The SEM photographs obtained for NB and HB are illustrated in Fig. 2. Apparently the surface of NB was more rough appearance. After the modification of NB with a cationic surfactant, the surface of HB loses its foliated structure and transforms more smooth and spongy surface.

3.2 FTIR analysis

The FTIR spectra of NB and HB (Fig. 3) were performed in the range of 400–4,000 cm^{-1} and compared with each other to obtain information on the modification of bentonite with HDTMA^{+} functional groups.

A group of absorption peaks was observed between 3,430 and 3,387 cm^{-1}, which is due to H–O–H stretching vibration bands of water molecules weakly hydrogen bonded to the Si–O surface in NB (Fig. 3a) and HB (Fig. 3b) and their bending vibrations at 917 and 912 cm^{-1}. The band intensities of HB in this area of the spectra were rather lower than that of NB.

A pair of strong bands at 2,851 and 2,920 cm^{-1} was observed only in HB and they can be assigned to the symmetric and asymmetric stretching vibrations of the methylene group ($\nu_{\mathrm{CH_2}}$) and their bending vibrations between 1,372 and 1,469 cm^{-1}, supporting the modification of NB with the surfactant cation (Madejová 2003), but these stretching bands are not observed in NB. The bands between 1,640 and 1,635 cm^{-1} also correspond to the –OH deformation of water to observe NB and HB.

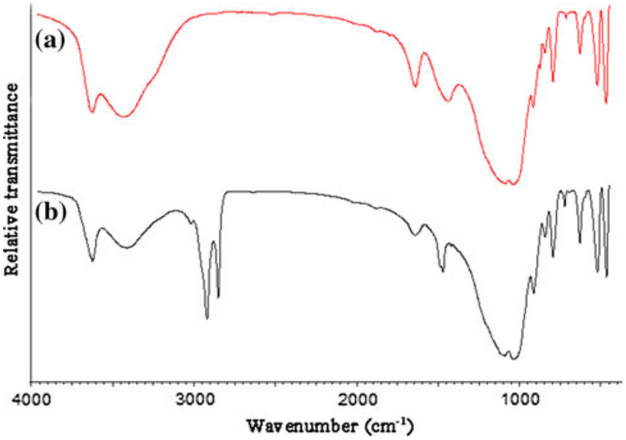

Fig. 3 FTIR spectra of **a** NB and **b** HB

The Si–O coordination bands at 1,091 and 1,039 cm^{-1} are observed as a result of the Si–O vibrations. The deep band at around 1,039 cm^{-1} represents the stretching of Si–O in the Si–O–Si groups of the tetrahedral sheet. The bands at 522 and 467 cm^{-1} are due to Si–O–Al (octahedral) and Si–O–Si bending vibrations respectively, for NB and HB.

3.3 Elemental and thermal analysis

The ratio of C/N for HB from elemental analysis results was obtained as 15.32 and the theoretical value of C/N ratio for HDTMA^{+} was calculated as 16.29. These results confirm that the modification of NB with HDTMA^{+} occurs and they are also consistent with above XRD and FTIR spectroscopic analysis results.

Thermal analysis curves of NB and HB were illustrated in Fig. 4a, b. The thermogravimetric (TG) analysis curve related to NB (Fig. 4a) exhibited mass losses by 6.23 and 5.80 % in temperature ranges 25–200 and 600–800 °C, respectively. The two endothermic peaks in the differential thermogravimetric (dTG) analysis curve of NB in the range of 25–200 °C denote the release of different water species coordinated to the interlayer cations and surface humidity. The third endothermic peak in the temperature region of 600–800 °C was connected with the dehydroxylation of the layer silicate minerals and the elimination of structural –OH groups. The TG curve related to the surfactant modified bentonite (Fig. 4b) exhibited mass loss 0.70 % at 25–200 °C and 34.04 % at 200–400 °C and 2.94 % at 600–800 °C, which due to the thermal evolution of moisture and interlayer water, and the thermal oxidation of the surfactant cation and structural –OH groups, respectively.

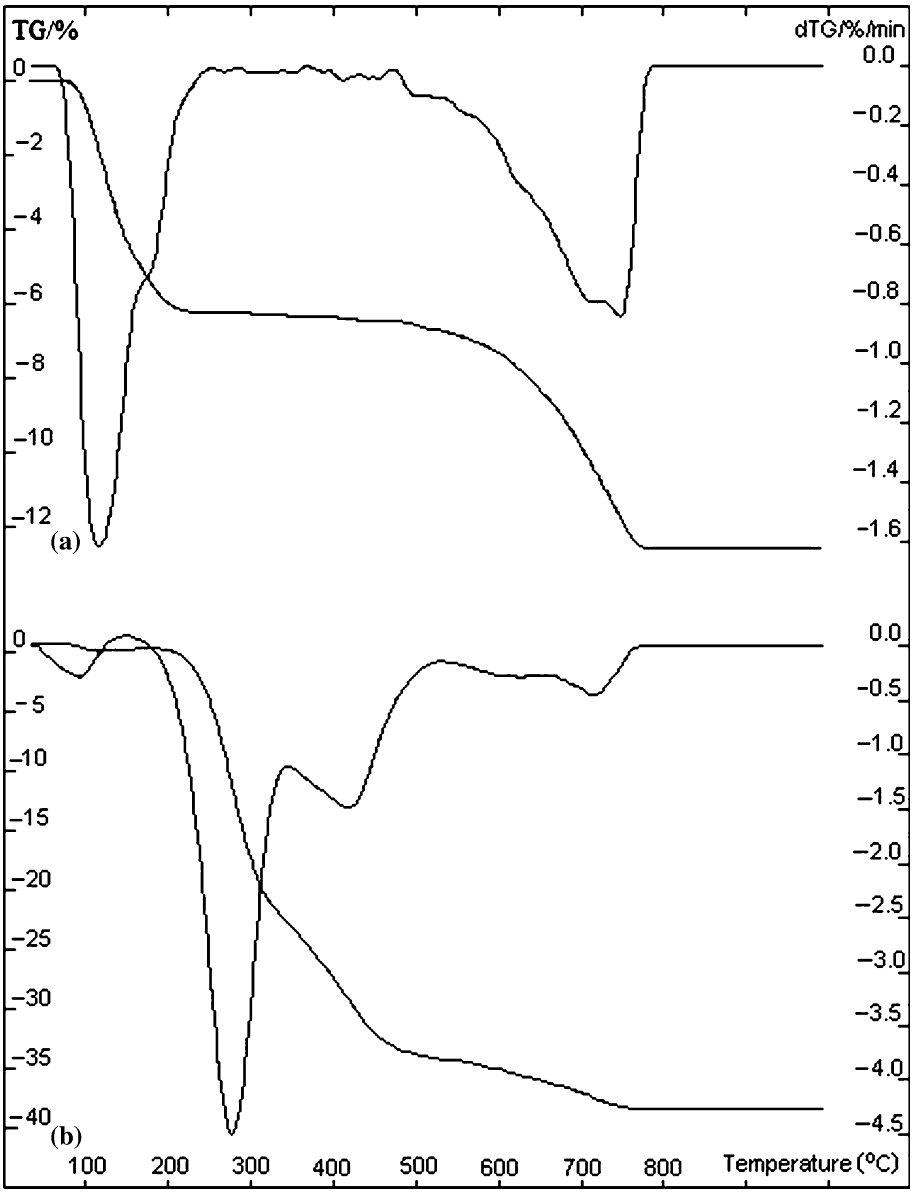

Fig. 4 TG and dTG curves of **a** NB and **b** HB

The intensity of the dTG peaks for HB in the temperature regions of 25–100 and 600–800 °C was lower than that in the dTG curve of unmodified NB due to the hydrophobicities of HB as it can be seen from Fig. 4a, b. The dTG peaks between 250 and 420 °C were observed in HB (Fig. 4b) and they confirm the modification of bentonite with the surfactant cation, but these peaks are not observed in NB (Fig. 4a). Thermal analysis results are also consistent with above characterization results.

3.4 Zeta potential measurements

The zeta potential graphs for NB and HB in the presence of naphthalene were depicted in Fig. 5, as a function of suspension pH. As shown in Fig. 5a NB has no the isoelectronic point (pH_{iep}) and exhibits negative zeta potential values at all studied pH's values. This result agrees with those obtained from the electrokinetic measurements of clay minerals (Delgado et al. 1986; Horikawa et al. 1988; Williams and Williams 1978; Chakir et al. 2002; Hunter 1988).

The zeta potential is important in the case of HB in naphthalene solution but it is not fully dependent on pH in this study (Fig. 5b). The isoelectronic point was measured as 5.97 for HB in the presence of naphthalene.

3.5 Effect of pH

Figure 6 indicates the effect of pH on the adsorption of naphthalene onto NB and HB from aqueous solution. As can be seen from Fig. 6, the maximum naphthalene removal was

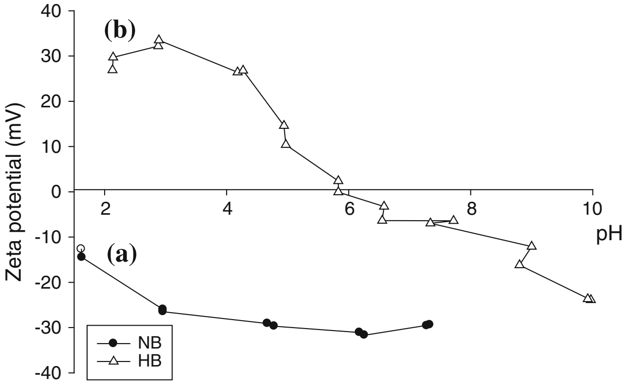

Fig. 5 The zeta potentials of **a** NB and **b** HB in the presence of naphthalene

found to be at pH value of 4.0 for NB. Naphthalene adsorption increases from low pH values at around 1.5–4.0, and then it slightly decreases up to pH = 7 due to more negative surface charge according to the zeta potential measurements. On the other hand, the amount of adsorption onto HB was not gradually changed at the pH values between 1.5 and 7.0. It can be concluded that naphthalene adsorption onto NB was more effected by changing in pH than HB, because the surface of clay became more homogenous after modification according to the SEM results and also naphthalene is a non-ionizable compound (Pei et al. 2013).

3.6 Adsorption kinetic considerations

The effect of contact time on the amount of naphthalene adsorbed onto NB (Fig. 7) at the various temperatures was examined at 10 mg dm^{-3} concentration of naphthalene. It is seen that the amount of adsorption increased with an increase in the contact time. The maximum adsorption was observed at 60 min, beyond which there was almost no further increase in the amount of adsorption, and this was therefore fixed as the equilibrium contact time. The equilibrium adsorption of naphthalene onto NB and HB was found to increase with a rise in the temperature from 10 to 20 °C (Fig. 7), indicating that naphthalene adsorption on the adsorbent was favored at higher temperatures. This effect suggests that an explanation of the adsorption mechanism associated with the removal of naphthalene onto NB and HB involves a temperature dependent process.

Three kinetic model equations, i.e. the Lagergren first-order, pseudo-second-order and Elovich equations, were considered to interpret to the experimental data with linear and nonlinear forms (Ho and McKay 2002; Plazinski et al. 2009). In the case of the nonlinear method, which is applicable to computer operation, were determined between the experimental data and kinetics in a simple statistical programme. It is also a better way to obtain the kinetic parameters. The related best-fit nonlinear graphs were illustrated in Fig. 7.

The Lagergren first-order rate expression (Lagergren 1898) is given as:

$$\frac{dq_\mathrm{t}}{dt} = k_1(q_1 - q_\mathrm{t}) \tag{1}$$

When solving Eq. (1) with the boundary condition $q(t = 0) = 0$, and then it can be obtained:

$$\ln(q_1 - q_\mathrm{t}) = \ln q_1 - k_1 t \tag{2}$$

The pseudo-second-order kinetic equation (Ho and McKay 1998; Azizian 2004, Marczewski 2010) is expressed in its differential form as:

$$\frac{dq_\mathrm{t}}{dt} = k_1(q_1 - q_\mathrm{t})^2 \tag{3}$$

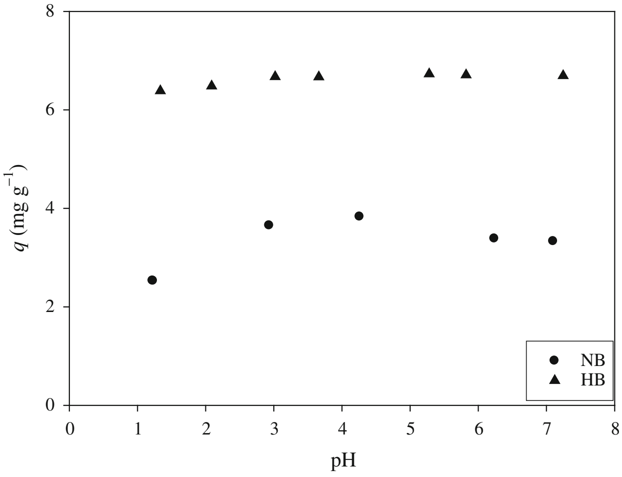

Fig. 6 Effect of pH for the adsorption of naphthalene onto NB and HB at 20 °C

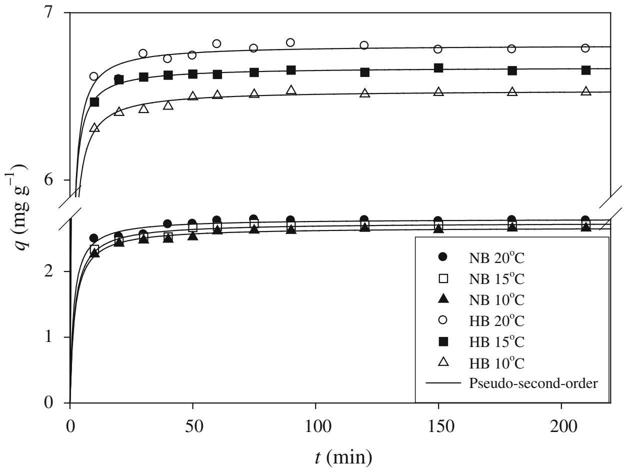

Fig. 7 Experimental kinetic data and fitted curves obtained by using the non-linear method for the adsorption of naphthalene onto **a** NB and **b** HB at various temperatures

After integrating the above expression with the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ and then rearrangement:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \tag{4}$$

The Elovich equation is generally expressed as follow (Elovich 1957; Low 1960):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{5}$$

To simplify the Elovich equation, Chien and Clayton (1980) assumed $\alpha\beta t \gg 1$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq. (5) becomes (Sparks 1999):

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{6}$$

where q_1 and q_t are the amounts of naphthalene adsorbed on the adsorbent at equilibrium and at various times t, (mg g^{-1}), k_1 is the rate constant of the Lagergren first-order equation for the adsorption process (min^{-1}), q_2 is the equilibrium adsorption capacity (mg g^{-1}) and k_2 is the rate constant (g mg^{-1} min^{-1}) for the pseudo-second-order equation, α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g mg^{-1}) for Elovich equation during any one experiment. The straight-line plots of $\ln(q_1 - q_t)$ versus t for the Lagergren first-order kinetic equation, t/q_t against t for the pseudo-second-order kinetic and the plots of q_t versus $\ln(t)$ for the Elovich kinetic equation for the adsorption of naphthalene onto NB and HB have been drawn to obtain the rate parameters.

The kinetic parameters of naphthalene under different conditions were calculated from these plots and are given in Tables 1 and 2 for linear and nonlinear forms of the equations, respectively. It can be seen from Tables 1 and 2, the correlation coefficients (r_1^2) for the Lagergren first-order kinetic model are between 0.541 and 0.848 for the linear form and between 0.369 and 0.878 for the nonlinear form. The correlation coefficients (r_2^2) for the pseudo-second-order kinetic model are 0.999 for the linear form and between 0.734 and 0.956 for the nonlinear form. The correlation coefficients (r_E^2) for the Elovich kinetic model are between 0.657 and 0.904 for the linear form and between 0.744 and 0.904 for the nonlinear form. They are probable that these adsorption systems are not followed by the Lagergren first-order or Elovich kinetic models, they are fitted the pseudo-second-order kinetic model with high correlation coefficients.

The pseudo-second-order rate constants increase from 0.157 to 0.262 g mg^{-1} min^{-1} (for the linear form) and from 0.191 to 0.239 g mg^{-1} min^{-1} (for the nonlinear form) for NB and from 0.382 to 0.664 g mg^{-1} min^{-1} (for the linear form) and from 0.394 to 0.429 g mg^{-1} min^{-1} (for the nonlinear form) for HB with an increase in the solution temperatures from 10 to 20 °C (Table 1), indicating that the adsorption of naphthalene onto NB and HB is temperature dependent.

3.7 Adsorption isotherms

The adsorption equilibrium data were analyzed to see whether the isotherm obeyed the Langmuir (1918) or Freundlich (1906) isotherms. The Langmuir isotherm theory is based on the assumption that adsorption on a homogeneous surface possessing identical sites equally available for adsorption and with equal energies of adsorption involves with the adsorbent being saturated after one layer of adsorbate molecules has formed on the surface. The Langmuir isotherm equation is represented by the following equation:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{7}$$

where q_e is the equilibrium naphthalene concentration on the adsorbent (mg g^{-1}), C_e is the equilibrium naphthalene concentration in the solution (mg dm^{-3}), $q_{\max}$ is the monolayer capacity of the adsorbent (mg g^{-1}), and K_L is the Langmuir constant (dm^3 mg^{-1}) and related to the free energy of adsorption.

The adsorption equilibrium data were also analyzed by Freundlich isotherm. The Freundlich isotherm describes adsorption when the adsorbate has a heterogeneous surface with adsorption sites that have different energies of adsorption. One limitation of the Freundlich isotherm is that the amount of adsorbed solute increases indefinitely with the concentration of solute in the solution. The energy of adsorption varies as a function of the surface coverage (q_e) and is represented by the Freundlich constant K_F (dm^3 g^{-1}) in Eq. (8):

$$q_e = K_F C_e^{1/n} \tag{8}$$

Linear form of Eq. (8) as shown as below:

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{9}$$

where n (dimensionless) is the heterogeneity factor which has a lower value for more heterogeneous surfaces. The linear fit of the experimental data to the Freundlich isotherm was explored by plotting $\ln C_e$ versus $\ln q_e$ to generate the intercept value of K_F and the slope value n.

The Freundlich equation generally agrees well with the Langmuir over moderate concentration ranges but, unlike the Langmuir equation, it does not reduce to the linear isotherm at low surface coverage. Equilibrium data over a wide concentration range cannot be fitted with a single set of constants (Allen et al. 2003). However, adsorption can be successfully described by simple Freundlich isotherm

Table 1 Kinetic parameters obtained from linear form of equations for the adsorption of naphthalene onto NB and HB at various temperatures

	t (°C)	Lagergren-first-order			Pseudo-second-order			Elovich		
		k_1 (min^{-1})	q_e (mg g^{-1})	r_1^2	k_2 (g mg^{-1} min^{-1})	q_2 (mg g^{-1})	r_2^2	α (mg g^{-1} min^{-1})	β (g mg^{-1})	r_E^2
NB	10	2.53×10^{-2}	0.360	0.779	0.157	2.690	0.999	1.47×10^{6}	7.990	0.904
	15	1.39×10^{-2}	0.226	0.734	0.207	2.736	0.999	3.33×10^{6}	8.103	0.821
	20	1.56×10^{-2}	0.162	0.628	0.262	2.797	0.999	3.31×10^{8}	9.622	0.777
HB	10	1.54×10^{-2}	0.135	0.848	0.382	6.539	0.999	1.23×10^{38}	14.60	0.850
	15	9.73×10^{-3}	7.71×10^{-2}	0.631	0.614	6.666	0.999	7.42×10^{55}	20.50	0.709
	20	8.46×10^{-3}	0.126	0.541	0.664	6.795	0.999	7.14×10^{43}	15.98	0.657

Table 2 Kinetic parameters obtained from nonlinear forms of equations for the adsorption of naphthalene onto NB and HB at various temperatures

	t (°C)	Lagergren-first-order			Pseudo-second-order			Elovich		
		k_1 (min^{-1})	q_e (mg g^{-1})	r_1^2	k_2 (g mg^{-1} min^{-1})	q_2 (mg g^{-1})	r_2^2	α (mg g^{-1} min^{-1})	β (g mg^{-1})	r_E^2
NB	10	0.197	2.589	0.643	0.191	2.671	0.939	1.47×10^{6}	7.994	0.904
	15	0.198	2.657	0.597	0.190	2.739	0.896	3.00×10^{6}	8.058	0.821
	20	0.231	2.728	0.429	0.239	2.799	0.807	4.81×10^{6}	7.987	0.744
HB	10	0.354	6.491	0.607	0.394	6.536	0.934	7.18×10^{6}	3.293	–
	15	0.364	6.640	0.878	0.505	6.672	0.956	2.46×10^{7}	3.381	–
	20	0.378	6.762	0.369	0.429	6.804	0.734	2.54×10^{7}	3.320	–

for low concentration range (Szymula and Marczewski 2002) as it was observed in this study. Freundlich adsorption is used when more than monolayer coverage of the surface is assumed and the site is heterogeneous with different binding energy. An unlimited source of unoccupied sites is expected to be available. If $n = 1$, then the partition between the two phases are independent of the concentration. If value of $1/n$ is below unity it indicates that sites with the highest binding energies are utilized first and then followed by weaker sites (El Qada et al. 2008). On the other hand, $1/n$ being above unity indicates cooperative adsorption and in this case these data cannot be described by the Langmuir equation as it was seemed in this study (Marczewski 2013).

The linear and nonlinear regressions of Freundlich isotherm were used to calculate the isotherm parameters. The ability of the Freundlich isotherm, to this the equilibrium adsorption data was examined and Fig. 8 indicates the correlation between experimental data and the best nonlinear fitting. The isotherm parameters obtained using the linear and nonlinear methods were given in Table 3. It can be seen that the high correlation coefficient constants were obtained by Freundlich isotherm and the Freundlich constants K_F and n were both closer to those obtained by using the linear and nonlinear methods (Ho 2006).

One of the Freundlich constants K_F is related to the adsorption capacity of the adsorbent. The other Freundlich constants n is a measure of the deviation from linearity of the adsorption. The numerical values of n at equilibrium lie between 0.488 and 0.599 (Table 3) for HB and are smaller than unity.

In this study, the maximum adsorption capacity of HB for naphthalene was calculated from the Freundlich isotherm equation as 22.45 mg g^{-1}. It was comparable to data in the literature with Triton X-100 impregnated chitosan hydrogel beads (TCB) (32.39 mg g^{-1}) (Chatterjee et al. 2010), CTAB impregnated chitosan hydrogel beads (CCB) (31.77 mg g^{-1}) (Chatterjee et al. 2010), SDS impregnated chitosan hydrogel beads (SCB) (28.66 mg g^{-1}) (Chatterjee et al. 2010), petroleum coke-derived porous activated carbon (0.0463 mg g^{-1}) (Yuan et al. 2010), HDTMA-montmorillonite (0.342 mg g^{-1}) (Nzengung et al. 1996), BDTDA-montmorillonite (3.888 mg g^{-1}) (Nzengung et al. 1996), TPMA-montmorillonite (5.141 mg g^{-1}) (Nzengung et al. 1996), HDTMA-kaolinite (21.02 mg g^{-1}) (Lee and Kim 2002), HDTMA-halloysite (28.45 mg g^{-1}) (Lee and Kim 2002) and particulate organic matter (POM) (0.0272 mg g^{-1}) (Guo et al. 2010). As it can be seen from above results, the maximum adsorption capacity of HB was found to be higher than that of many corresponding adsorbents reported in the literature. Meanwhile the price of bentonite is considered very cheap at around US\$0.04–0.12/kg, depending on the quality of bentonite. The cost of industrial grade HDT MA bromide (cetyltrimethylammonium bromide = CTAB),

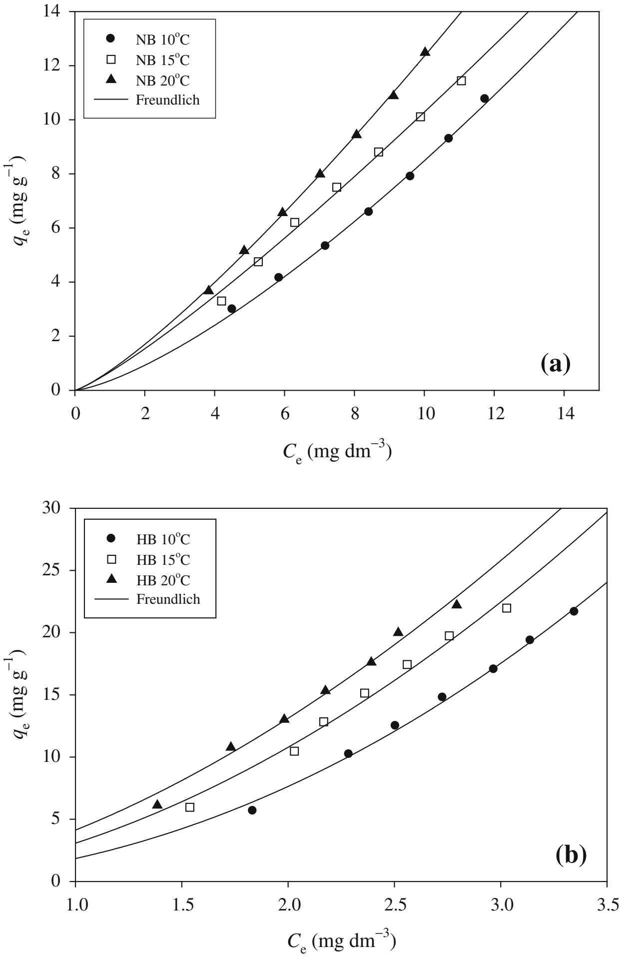

Fig. 8 Experimental isotherm data and fitted curves obtained by using the non-linear method for the adsorption of naphthalene onto **a** NB and **b** HB at various temperatures

Table 3 Isotherm constants obtained from linear and nonlinear forms of isotherm equations for the adsorption of naphthalene onto NB and HB at various temperatures

	t (°C)	Linear form			Nonlinear form		
		n	K_F (dm^3 g^{-1})	r_F^2	n	K_F (dm^3 g^{-1})	r_F^2
NB	10	0.753	0.397	0.998	0.726	0.356	0.998
	15	0.796	0.580	0.991	0.846	0.676	0.994
	20	0.804	0.706	0.999	0.810	0.721	0.999
HB	10	0.455	1.581	0.992	0.488	1.845	0.995
	15	0.505	2.639	0.989	0.553	3.077	0.985
	20	0.550	3.657	0.984	0.599	4.126	0.988

which was used in this study, is around US$5.0–8.0/kg. Therefore the cost of the modified bentonite is estimated at US$2.81/kg. This value can be compared with the market price of activated carbon for industrial grade (about US$20–22.00/kg), depending on the quality of activated carbon (http://minerals.usgs.gov/minerals/pubs/commodity/clays/). It is considered as seven times cheaper than the commercial grade activated carbon.

4 Conclusions

In this study, NB was firstly modified by using a surfactant, HDTMA bromide to obtain HB. The N_2 adsorption, XRD, SEM, FTIR, zeta potential, elemental and thermal analysis methods were used for the characterization of adsorbent. The NB did not indicate an isoelectric point since all of zeta potential values were negative, whereas the isoelectronic point (pH_{iep}) for HB in the presence of naphthalene was determined as 5.97. The adsorption kinetics of naphthalene onto NB and HB was then investigated. The results indicated that adsorption kinetics were the best described by the pseudo-second-order kinetic model. The experimental data have also been applied to calculate the rate constants and the adsorption capacities. The experimental data fitted well to the Freundlich isotherm. The results were also checked by the linear and nonlinear methods.

The research managed to in this study clearly suggests that HDTMA modified bentonite acts as a respective adsorbent for the removal of naphthalene from aqueous solutions.

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