Dearomatization of normal paraffin by adsorption process using synthesized NaX zeolite

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Abstract: Linear alkyl benzenes (LABs) are the main materials for detergent production. The presence of aromatic compounds in this material can decrease the quality of the final product and enhance the deactivation rate of catalysts. In this research we used zeolite NaX for de-aromatization of the recycled paraffin from the alkylation unit of an LAB production complex. The effect of different parameters on the removal efficiency of adsorbent was studied and optimized. To study the re-usability of the adsorbent, the breakthrough curves were obtained by using a fixed bed column filled with the adsorbent. The results indicated that the adsorbent capacity remained unchanged after three regeneration cycles. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms. It was concluded that the Langmuir model agreed well with the experimental data. The calculated thermodynamic parameters of the adsorption showed that the adsorption process was spontaneous and exothermic. The reaction rate was estimated by the pseudo-second order kinetic model.

Key words: Dearomatization, LAB, zeolite, adsorption, separation

1 Introduction

Linear alkylbenzene made from C_{10}-C_{13} linear olefins are widely used as the active ingredients of many household detergents (Almeida et al, 1994). According to Universal Oil Products (UOP) design, a linear alkylbenzene plant consists of pre-fraction, hydro-treating, extraction, dehydrogenation and alkylation units (Kocal et al, 2001). In the dehydrogenation unit, side reactions such as dehydrocyclization, aromatization, cracking and isomerization take place and lead to formation of some non-linear by-products. By additional alkylation reactions, these by-products can be further converted to new aromatic compounds like alkylated benzenes, poly alkylbenzenes, naphthalenes and biphenyls (Kocal, 1994; Kocal and Korous, 1994). Accumulation of these aromatic by-products on the surface of a catalyst will result in several problems such as enhancement in the deactivation rate of the catalyst, and reduction in dehydrogenation, alkylation selectivity and sulfonatability of the synthesized LAB. Under these circumstances, facile electron transition in the conjugated double bonds of polyaromatics by-products colors the produced sulfonated alkyl benzene (Goncalvez et al, 2009). Adsorption separation as an effective method for removal of pollutants can be considered as a candidate for purification of LAB from aromatic compounds (Yang, 1973). Different activated carbons have been studied for adsorption of phenanthrene as a model aromatic compound

(Murillo et al, 2004). Susu (2000) developed a mathematical model to predict the effluent concentration and breakthrough profiles of aromatic compounds in kerosene deodorization by using commercial clays. Zeolite-based molecular sieves are commonly used as adsorbent in commercial separation processes. Zeolite pore size as a governing parameter determines the extent of aromatic compound entrapment. In fact, interaction between π-electrons of aromatic rings and cations held within pores of the absorbent can be considered as a driving force behind this separation process. Therefore, formation of more intense electrostatic interaction between cations of zeolite and adsorbate can significantly enhance the efficiency of the separation process. In addition, adsorption capacity can be enhanced by electrostatic interactions between the sorbent and the cations held within the pores of the adsorbent (Breck, 1974). Adsorptive separation of aromatics from kerosene cut by using NaX has been reported (Dorogochinskii et al, 2004). In a recent study, adsorption of liquid aromatic/alkane mixture on NaY zeolite has been investigated (Fathizadeh and Nikazar, 2009). Many patents relevant to the separation of aromatic by-products in the linear alkylbenzene process for either improving the quality of linear alkylbenzene or for economic benefit have been registered (Plee, 1998, Al-Zaid et al, 1989).

2 Material and methods

2.1 Synthesis and characterization of NaX zeolite

To prepare spherical type NaX zeolite, aluminum and

silicon gels were prepared separately. Typically 7.2 g (0.034 mole) of sodium metasilicate pentahydrate (Fluka, purum, ≥97%) was dissolved in 48.0 g (3.0 mole) of de-ionized water. Then 8.0 g (0.054 mole) of triethanolamine (TEA, Merck, 99%) was added and the solution was stirred for 30 minutes, and then the solid was separated by a 0.2 μm membrane filter (to obtain solution A). Solution B was prepared by dissolving 2.9 g (0.035 mole) of sodium aluminate (Riedel–de Haen, technical grade, 54wt% Al_2O_3, 41wt% Na_2O, rest: water) and 8.0 g (0.054 mole) of TEA in 48.0 g (3 mole) of deionized water under stirring condition. The resulting solution was filtered through a 0.2 μm membrane filter (to obtain solution B). The two solutions were mixed in a polypropylene bottle and the mixture was thoroughly shaken for 5 min. The mixture was kept at 85 ºC for 8 days until the crystallization of zeolite was completed (Berger et al, 2005). To prepare cylindrical shaped adsorbent, a paste was prepared by mixing zeolite and kaolin (80/20 wt%) and then it was passed through a granulator (1mm×2mm). The products were air-dried for 24 h, and then calcined at 600-650 ºC for 2 h to convert kaolin into metakaolin. The thus-obtained solid product was treated with sodium hydroxide solution (1.0-1.2 M) at 90 for 6-8 h to convert the kaolin binder into zeolite. The treated products were separated, washed and dried and the adsorbent NaX zeolite was obtained (Zhao et al, 2007).

The adsorbent was characterized by FT-IR, XRD, XRF, SEM and BET techniques. The FT-IR spectrum of the adsorbent was recorded on an Impact-400D FT-IR instrument (Nicolet Co.) in the region of 4000-400 cm^{-1} using KBr wafer technique. The crystalline structure of the adsorbent was examined by X-ray diffraction (Bruker D8ADVANCE diffractometer using CuKα radiation). The chemical composition of the adsorbent was obtained by the XRF technique (PANaltical Magix instrument). The samples for de-aromatization were taken from the recycled C_{10}-C_{13} normal paraffin stream, with 3.5 wt% aromatic content from Iranian Chemical Industries Investment Company. A Hach DR-5000 spectrophotometer was used for determination of aromatic concentration according to the procedure suggested by the UOP (Test method 495). The surface area of the adsorbent NaX zeolite sample was calculated from the Brunauer–Emmett–Teller (BET) equation. Pore volume and pore size distribution of the adsorbent were determined by N_2 sorption using a BELsorp max system 113 (BEL Japan, Inc.). The size distribution, shape and morphology of the sample were obtained by scanning electron microscopy (SEM), and the SEM images were taken using an AIS2100 scanning electron microscope (Seron Technology, Korea).

2.2 Adsorption experiment

Batch experiments were designed and conducted at room temperature in order to determine the adsorption capacity and the isotherm data of adsorbent NaX zeolite and the effect of the experimental parameters, such as initial aromatics concentration and temperature on the adsorption efficiency. Before each experiment the synthesized NaX zeolite was activated at 350 °C for 2 h and then cooled to room temperature in a desiccator. Then 10 g of the activated

sample was transferred to a beaker containing 50 mL of the recycled normal paraffin. The mixture was shaken until it reached equilibrium, and then the solid phase was separated by filtration. The aromatics concentration in the liquid phase was measured and the removal efficiency of aromatics was calculated according to Eq. (1).

$$\text{Re}\,\text{moval}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

where C_0 and C_e are respectively the initial and equilibrium concentrations of aromatic compounds (mg/L). To evaluate the effect of adsorbent dose on adsorption of adsorbent NaX zeolite, 50 mL of the sample was mixed with different amounts of adsorbents in a 250 mL Teflon beaker. The mixture was shaken for 24 hours at 25 °C and the solid phase was separated by filtration and the aromatic content of the filtrate was measured. To determine the time for maximal adsorption capacity of adsorbent NaX zeolite, samples containing 10 g of the activated zeolite and 50 mL of the recycled normal paraffin were shaken for different interval times at 25 °C. The solid phase was then separated by filtration and the aromatic content of the filtrate was measured.

2.2.1 Effect of initial aromatics concentration on adsorption of the adsorbent

A mixture (50 mL) of normal paraffin with different aromatic contents (0.01-5 wt%) was mixed with 10 g of zeolite and shaken until it reached equilibrium at 25 °C. The solids were separated by filtration and the aromatic content of the filtrate was measured.

2.2.2 Effect of temperature on adsorption of the adsorbent

To study of the effect of the temperature, the mixture of the recycled normal paraffin (50 mL) and the activated NaX zeolite (10 g) was put in a rotary evaporator at different temperature from 25 °C to 145 °C. After equilibration, each sample was filtered and the aromatic content in the filtrate was measured.

2.3 Regeneration of adsorbent

To study the regeneration ability of the adsorbent, a pilot scale fixed-bed column (80 cm length and 2.54 cm inner diameter) was designed and constructed. The required auxiliary system including electrical furnace, injection pump, feed pre-heater, and collecting vessels were prepared. The column packed with 265 g of the adsorbent was placed inside the electrical furnace (Excition model). Electrical heating was supplied to the column to control the bed temperature (Fig. 1). Before each experiment, the adsorbent was activated in situ by electrically heating furnace at 350 °C for two hours and then allowed to cool to room temperature under a dry nitrogen atmosphere (5 mL/min). Once the adsorption process was started, the samples were collected from the bottom of the bed at predetermined time intervals. When the adsorbent was saturated, the regeneration cycle was carried out under dry nitrogen flow at 500 °C for 15 h. In order to construct the breakthrough curves and to calculate the adsorbent capacity, the concentration of aromatics in inlet and the outlet were
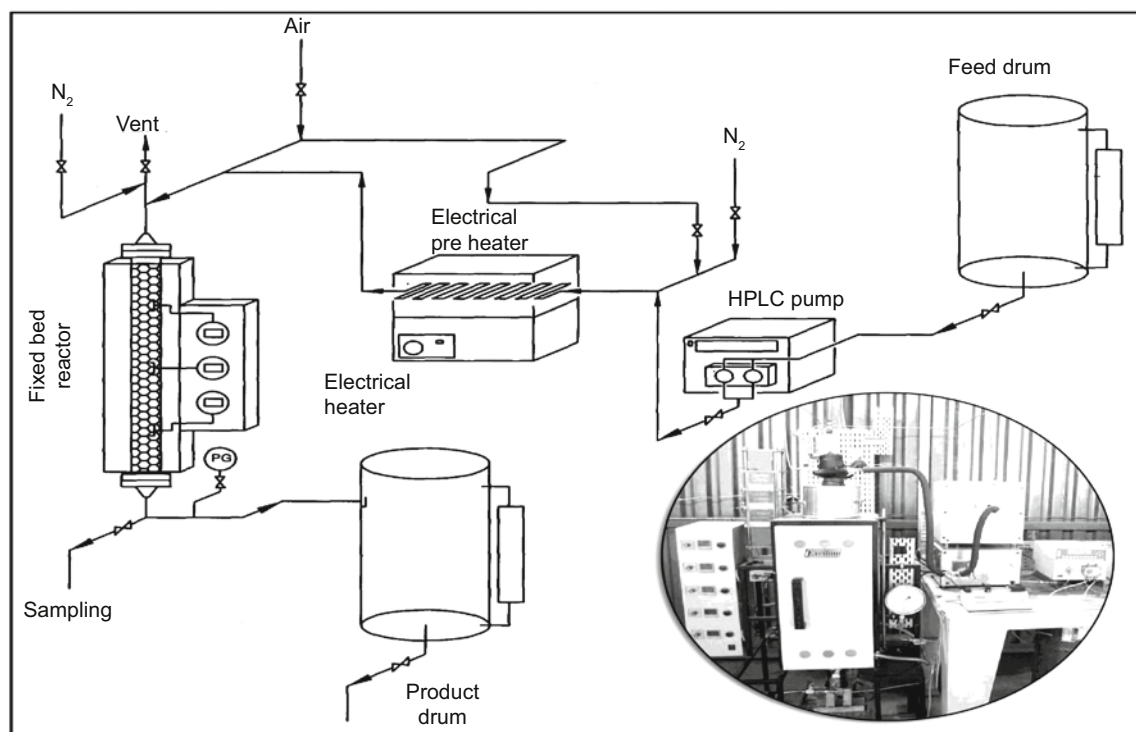
Fig. 1 The schematic illustration of the aromatics removing plant

measured. The adsorption-regeneration cycle was repeated three times, and the adsorption capacity of the regenerated adsorbent was calculated for each cycle.

3 Results and discussion

3.1 Characterization of adsorbent

In the FT-IR spectrum of the adsorbent (Fig. 2), the band at 3400-3600 cm^{-1} and 1630-1660 cm^{-1} were attributed respectively to the OH stretching and bending modes of water molecules. The two most intense bands of zeolites appeared at 980-1230 cm^{-1} and 420-500 cm^{-1}. The absorbance band at 700-800 cm^{-1} was assigned to symmetric stretching mode of the T-O. The mid-infrared region of the spectrum contained the fundamental framework vibration of $Si(Al)O_4$ groupings. All these observations confirmed that the adsorbent has an aluminasilicate structure (Keka et al, 2004).
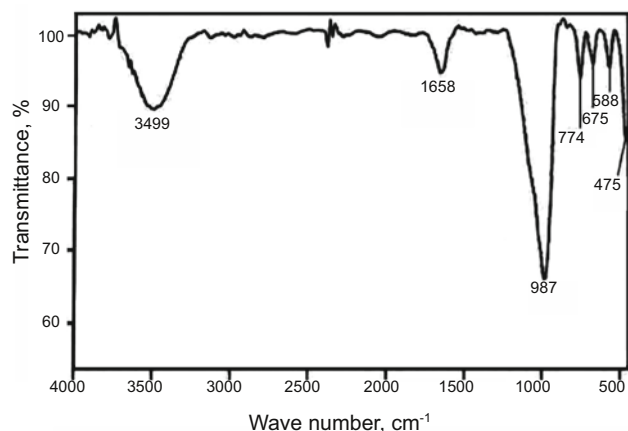
In the XRD pattern of the synthesized zeolite the line positions and the relative intensity were similar to those reported by Hong et al (2008), confirming that the synthesized adsorbent was pure NaX zeolite (Fig. 3). The chemical composition (see Table 1) of the synthesized adsorbent sample obtained by XRF method also agreed well with the results reported by Hong et al (2008).
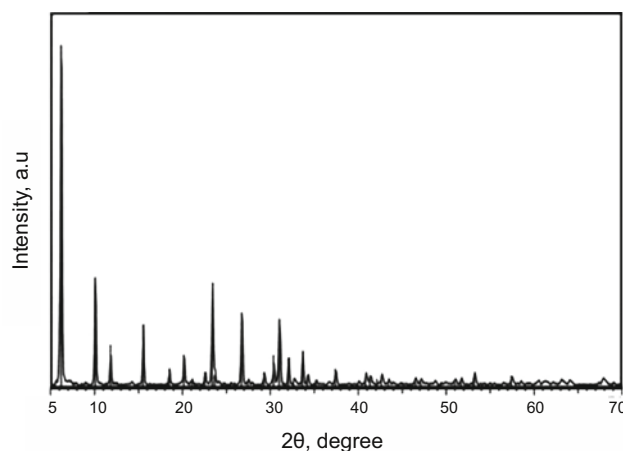

Fig. 3 XRD spectrum of the synthesized NaX zeolite

Table 1 XRF analysis of synthesized NaX zeolite

Composition	SiO_2	Al_2O_3	Na_2O	MgO	CaO	K_2O	Fe_2O_3	P_2O_5	LOI
Weight, wt%	37.17	25.98	14.73	1.57	1.48	0.27	0.71	0.11	17.8

SiO_2/Al_2O_3 molar ratio=2.43

An SEM image of the synthesized NaX zeolite is shown in Fig. 4. The formation of roughly spherical particles is evident in the SEM image.
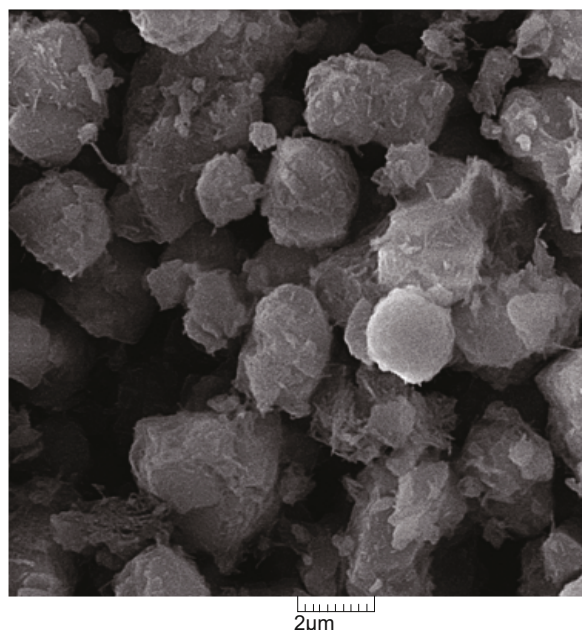

Fig. 2 FTIR spectrum of the synthesized NaX zeolite

Fig. 4 SEM image of NaX zeolite

The surface area of the zeolite calculated by N_2 adsorption (Fig. 5) by the Brunauer, Emmett and Teller (BET) method was 294 m^2/g. The total pore volume and mean pore diameter were respectively 0.224 cm^3/g and 3.05 nm.
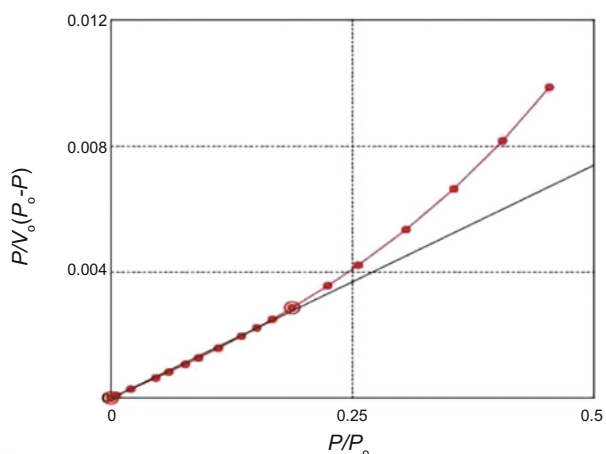

Fig. 5 BET plot of NaX zeolite

3.2 Adsorption studies

The removal efficiency of the aromatics increased with increasing adsorbent dosage but changed very little when the adsorbent dosage greater than or equal to 16 g (Fig. 6).

Considering the economic cost, 10 g of adsorbent was considered as optimal adsorbent dosage. Fig. 7 shows that the aromatics were removed fast at the initial stages, with reduction in uptake rate closer to the equilibration time. The rapid initial uptake was attributed to the adsorption of the aromatics on the surface sites of the adsorbent (Fig. 7).

When the aromatics adsorption at the exterior sites reached the saturation level, the aromatics begins to enter the pores of the adsorbents and the adsorption rate decreased due to the increase in the diffusion resistance as the molecules
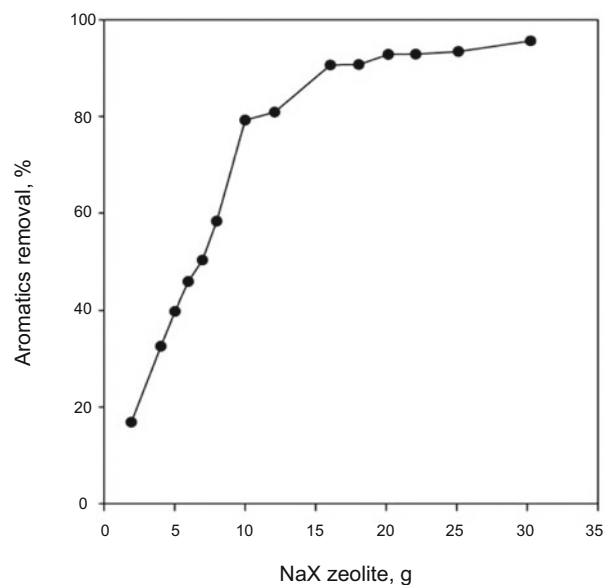

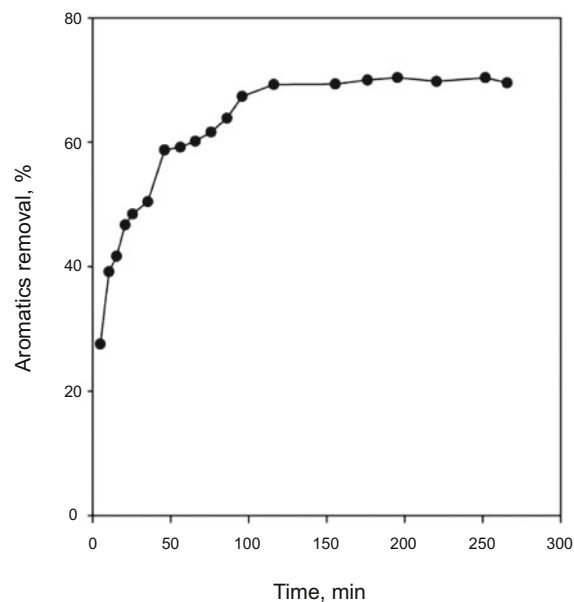**Fig. 6** Effect of NaX zeolite dosage on aromatic removal efficiency

Fig. 7 Effect of zeolite/feed contact time on efficiency of aromatic removal at the optimal zeolite amount of 10 g

have to travel further into the interior pores. The influence of initial aromatics concentration on its removal efficiency is illustrated in Fig. 8.

At a low initial aromatics concentration, sufficient adsorption sites were available on the adsorbent for adsorption. As the concentration increased, the amount of aromatic compounds overwhelmed the adsorption sites. However the fractional adsorption was independent of the initial aromatics concentration. The removal of aromatics decreased with increasing temperature (Fig. 9). The reason was that higher temperature was unfavorable to exothermic reaction once equilibrium was reached. The optimal temperature was found to be around room temperature.

3.3 Equilibrium modeling

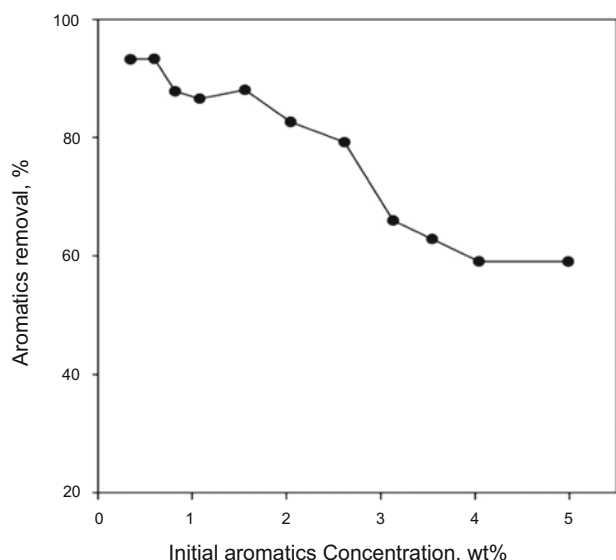The Langmuir and Freundlich models as the most

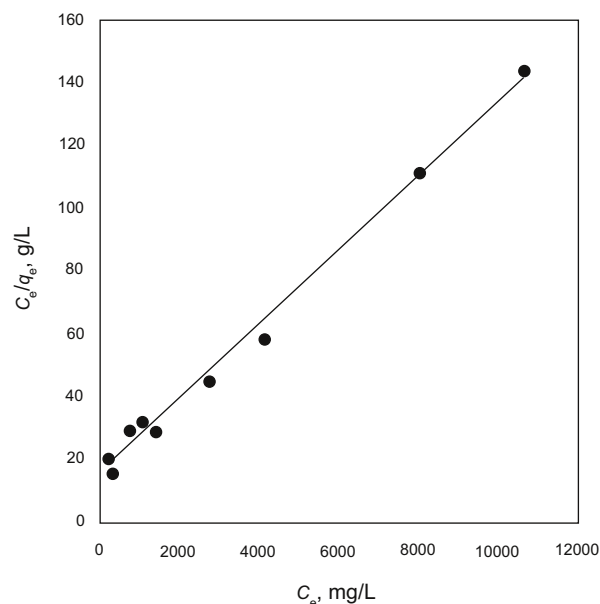**Fig. 8** Effect of initial aromatics concentration on its removal efficiency
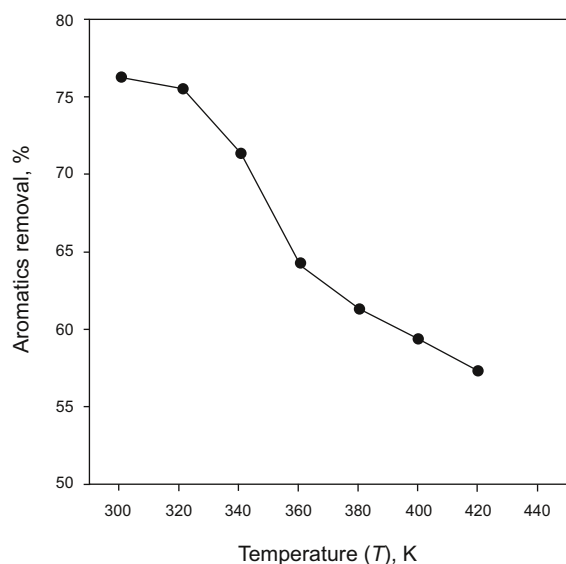

Fig. 9 Effect of temperature on removal efficiency
of aromatics using NaX zeolite

frequently employed models for adsorption processes were used to evaluate the experimental data. The Langmuir model assumes uniform energies of adsorption onto the surface with no transmigration of the adsorbate in the plane of the surface. The linear form of the Langmuir isotherm is given by the following equation (Daneshvar et al, 2007):

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \tag{2}$$

where q_e is the amount of adsorbed species at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), and q_{max} and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. When C_e/q_e was plotted against C_e, a straight line with slope $1/q_{max}$ indicated that the adsorption followed Langmuir isotherm (Fig. 10).

Fig. 10 Langmuir equation plot

The Langmuir constants q_m and b were determined from the slope and intercept of the plot, and are shown in Table 2. The adsorption data was also analyzed by the Freundlich model (Daneshvar et al, 2007). The logarithmic form of the Freundlich model is given by the Eq. (3):

$$\log q_e = \log K_f + (1/n)\log C_e \tag{3}$$

where K_f and n are Freundlich constants related to adsorption capacity and intensity, respectively. When $\log q_e$ was plotted against $\log C_e$, a straight line with slope $1/n$ was obtained, indicating that the adsorption approximately followed the Freundlich isotherm (Fig. 11). The Freundlich constants K_f and n were determined from the slope and intercept of the plot, and are presented in Table 2. The results showed that the Langmuir isotherm fitted the experimental data, better than the Freundlich isotherm indicating the homogeneous distribution of active sites of the adsorbent.
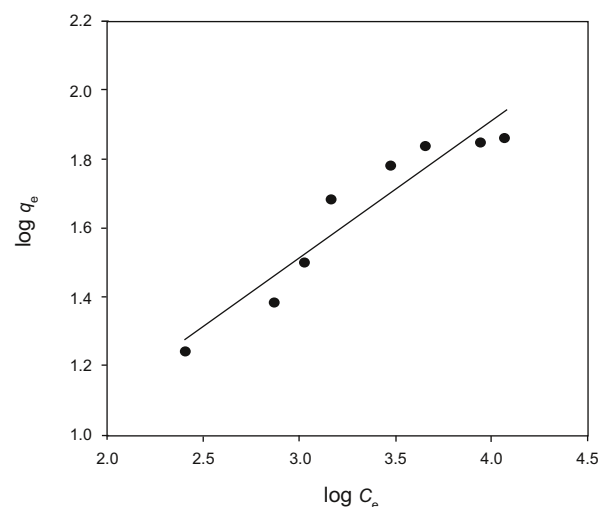

Fig. 11 Freundlich equation plot

**Table 2** Isotherm parameters for removal of aromatics by-products

Freundlich isotherm			Langmuir isotherm		
R^2	n	K_f $(mg/g)(1/mg)^{1/n}$	R^2	b $L \cdot mg^{-1}$	q_{max} $mg \cdot g^{-1}$
0.902	1.98	0.93	0.991	7.3×10^{-4}	90.9

3.4 Thermodynamic parameters

The equilibrium data was used to calculate the thermodynamic parameters, ΔH°, ΔS° and ΔG°. The equilibrium constant was defined by the following equation (Guo et al, 2009):

$$K_d = \frac{C_i - C_e}{C_e} \times \frac{V}{m} \qquad (4)$$

where, C_i and C_e are respectively the initial and equilibrium concentration of aromatics (mg/L), V is the volume of the solution (mL), and m is the adsorbent weight (g). ΔH°, ΔS° were calculated from the slope and intercept of the linear plot of $1/T$ versus $\ln K_d$, according to Eq. (5), where T is the solution temperature (K) and R is the gas constant and is equal to 8.314 J/(mol·K) (Fig. 12).
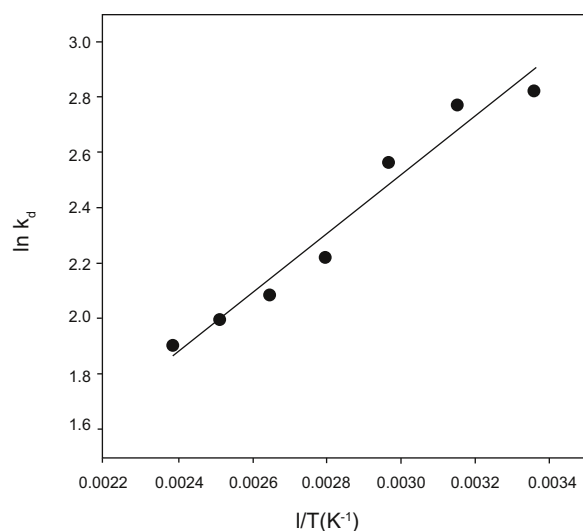
Fig. 12 Estimation of ΔH° and ΔS° using curve fitting technique

$$\ln K_d = -\left(\frac{\Delta H^\circ}{RT}\right) + \left(\frac{\Delta S^\circ}{R}\right) \qquad (5)$$

The value of the Gibbs free energy change for the adsorption process was obtained from Eq. (6):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (6)$$

The values of thermodynamic parameters, ΔH°, ΔS° and ΔG° are summarized in Table 3. The calculated adsorption enthalpy (ΔH°) being negative, the indication of an exothermic process, and their magnitude (<10 kJ/mol from Table 3) showed a physical adsorption process. The negative value of ΔG° indicated the spontaneous nature of the adsorption process. Finally, the negative value of the adsorption entropy (ΔS°) was attributed to the restricted mobility of the adsorbed

molecules of aromatic compounds as compared with those molecules in the bulk.

**Table 3** Thermodynamic parameters of the adsorption process

ΔH° kJ/mol	ΔS° J/Kmol	ΔG°, kJ/mol						
		418°K	398°K	378°K	358°K	338°K	318°K	298°K
-8.54	-4.94	-7.07	-6.97	-6.87	-6.77	-6.67	-6.57	-6.47

3.5 Kinetics of adsorption

In order to investigate the mechanism of the sorption process, various kinetic models were examined. The rate constant for the apparent adsorption of aromatics was obtained from the pseudo second-order equation (Bhattacharyya and Gupta, 2006):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \qquad (7)$$

where q_t and q_e are the amount of adsorbate at time t(s) and equilibrium time (mg/g), and k_2 the second order rate constant (g/(mg·min)). If the equilibrium sorption capacity and the rate constant are known, then the adsorption capacity at any time can be calculated. When t/q_t was plotted against t, a straight line was fitted to the data (Fig. 13). The calculated correlation factor ($R^2 = 0.9965$) suggested that aromatic adsorption by NaX zeolite followed pseudo second order kinetics.
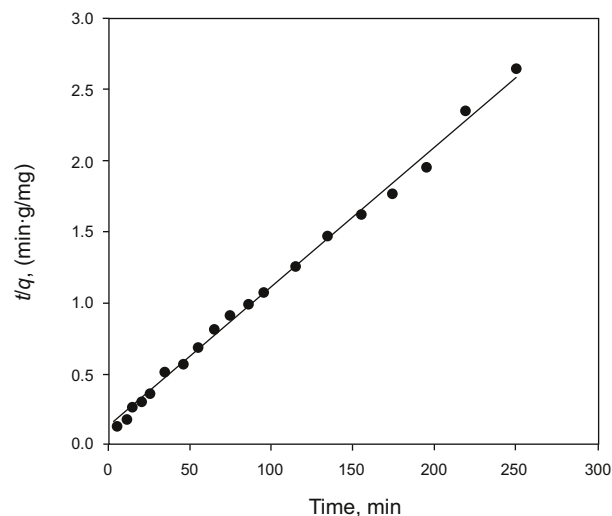
Fig. 13 Evaluating mechanism of adsorption by plotting Eq. (7)

3.6 Adsorbent regeneration

One of the challenging problems of the adsorption process is the regeneration of the adsorbents. Generally, there are two techniques for regeneration of the adsorbents, namely thermal treatment and solvent elution. Zeolite based adsorbents are usually regenerated by solvent elution at ambient temperature, but effective removal of the solvent is difficult. Therefore solvent elution is suitable for certain applications involving heat sensitive materials (i.e. active carbon). In this study, thermal treatment was adopted and the adsorbent was regenerated by heating at 500 °C for 15 h in
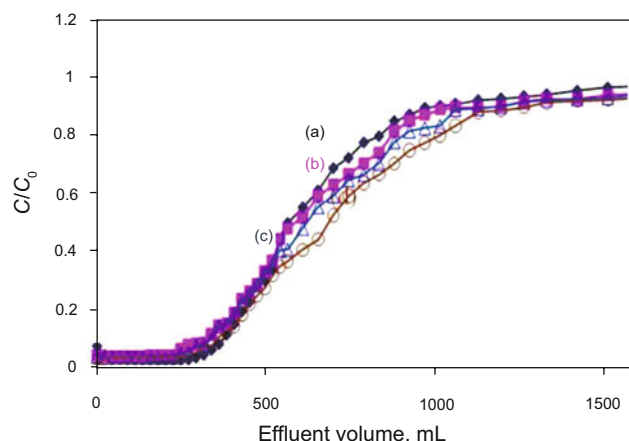
Fig. 14 Adsorption of aromatics by the regenerated adsorbent
(a) 1st regeneration, (b) 2nd regeneration, and (c) 3rd regeneration
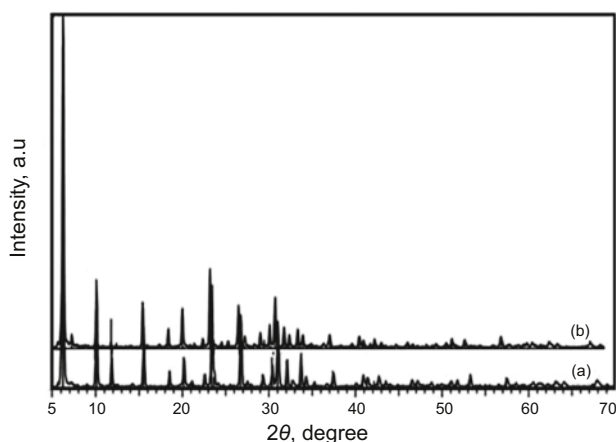

Fig.15 The XRD spectra of synthesized NaX zeolite (a) and
NaX zeolite regenerated by thermal treatment (b)

flowing nitrogen. The breakthrough curve of the regeneration step was constructed (Fig. 14), where C/C_o is the equilibrium to initial concentration.

It was concluded that after three regeneration cycles, the adsorption capacity of adsorbent remained unchanged. The XRD pattern of the regenerated adsorbent showed that the structure of zeolite was not affected by thermal treatment (Fig. 15).

4 Conclusions

Characterization of the synthesized NaX zeolite confirmed that a pure zeolite phase had been prepared. Experimental data fitted well with the Langmuir model. It was also concluded that the aromatics adsorption was a spontaneous and exothermic process. The negative value of the standard entropy change (ΔS°) indicated that randomness decreased with the uptake of the aromatics. The high correlation coefficient value (R^2=0.9965) indicated that the adsorption followed a pseudo second-order model. The adsorbent was thoroughly regenerated with flowing nitrogen at 500 ˚C and the initial adsorption capacity was retained after three successive regenerations. Since the dearomatization increases the dehydrogenation selectivity, alkylation selectivity, and

sulfonability of LAB, the suggested method of this research can be used for dearomatization of different streams in petrochemical industries.

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