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Dearomatization of Normal Paraffin by Synthesized Nax Zeolite

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Abstract

Aromatic compounds produced in linear alkyl benzene (LAB) production process decrease the yield and quality of the product and enhance the deactivation rate of the catalysts. Therefore, the de-aromatization of different streams in LAB production complex is inevitable. In this research, the recycled paraffin from alkylation to dehydrogenation unit was de-aromatized by synthesized NaX zeolite. The effect of different parameters such as temperature, amount of the adsorbent, contact time and initial aromatic concentration was studied and optimized. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms. It was concluded that the Langmuir model agreed very 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. To examine the re-generation ability of the adsorbent a fixed bed column was designed and the breakthrough curves were prepared for three successive regeneration cycles. The results indicated that the adsorbent capacity remained unchanged after three regeneration cycles.

Keywords: Zeolite; Chemical process; Petroleum; Adsorption; Separations; Dearomatization

Introduction

Linear alkylbenzene produced by C_{10}-C_{13} linear olefins, constitutes the active ingredients of many household detergents [1]. In the Universal Oil Products (UOP) design, the linear alkylbenzene process consists of pre-fraction, hydro-treating, extraction, dehydrogenation and alkylation units [2]. In the dehydrogenation unit, due to some side reactions such as dehydrocyclization, aromatization, cracking and isomerization processes non-linear by-products are formed that undergoes additional alkylation processes to form aromatic by-products such as alkylated benzenes, poly alkylbenzenes, naphthalenes and biphenyls [3,4]. These aromatic by-products are accumulated on the surface of the catalyst increasing its deactivation rate and decreasing dehydrogenation, alkylation selectivity and sulfonability of LAB. On the other hand, the sulfonated alkyl benzene will be colorful due to facile electron transition in the conjugated double bonds of polyaromatic by-products [5]. Among the method used for de-aromatization, adsorption is an effective method [6]. Different activated carbon has been studied for adsorption of phenanthrene as a model aromatic compound [7]. Susu [8] developed a mathematical model to predict the effluent concentration and breakthrough profiles of aromatic compounds in kerosene deodorization by commercial clays. Molecular sieve zeolites as low price and resistant materials are increasingly used in commercial separations. A controlling factor in whether molecules can be adsorbed in the cavities of the adsorbent is the pore-opening of the channels. Additionally, adsorption capacity can be enhanced by electrostatic interactions between the sorbent and the cations held within the pores of the adsorbent [9]. Adsorption of aromatic compounds occurred as a result of interaction between π-electron of the aromatic ring with the cation or hydroxyl group of the zeolites. Adsorptive separation of aromatics from kerosene cut by NaX has been reported [10]. In a recent study, adsorption of liquid aromatic/alkane mixtures on NaY zeolite has been investigated [11]. Many patents relevant to the separation of aromatic by-products in linear alkylbenzene process for either improving the quality of linear alkylbenzene or for economic aspect have been registered [12, 13].

In this paper, we report the application of synthetic zeolite NaX for aromatics adsorption from recycled paraffin. The experimental breakthrough data in a fixed bed adsorption column are given and the regeneration ability of the adsorbent has been reported.

Material and Methods

Synthesis of NaX zeolite

To prepare spherical type NaX zeolite, aluminum and silicon gels were prepared separately. Typically 7.2 g sodium metasilicate pentahydrate (Fluka, purum, ≥ 97%) was dissolved in 48.0 g of de-ionized water. After addition of 8.0 g of triethanolamine (TEA, Merck, 99%) under stirring, the solution was filtered through a 0.2 μm membrane filter (solution A). Solution B was prepared by dissolving 2.9 g sodium aluminate (Riedel–de Hae¨n, technical grade, 54 wt.% Al_2O_3, 41 wt.% Na_2O, rest: water) in 48.0 g of deionized water. After adding 8.0 g of TEA under stirring, the resulting solution was filtered through a 0.2 μm membrane filter. Solution A was mixed with solution B in a polypropylene bottle. The mixture was thoroughly shaken for 5 min. Zeolite crystallization occurred within 8 day at 85°C [14]. The spherical type zeolite adsorbent was prepared by thoroughly mixing of 20 wt.% kaolin clay with the synthesized NaX zeolite powder. The mixture was converted to paste and to spherical shaped by a granulator with size of 1mm × 2 mm. The products were air-dried for 24 h, and then calcined at 600-650°C 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 °C for 6-8 h to convert the kaolin binder into zeolite. The treated products were separated, washed and dried [15]. The adsorbent was characterizes by FT-IR, XRD and XRF techniques. The FT-IR spectrum of the adsorbent was recorded by an Impact-

400D FT-IR instrument (Nicolet Co.) in region of 4000-400 cm^{-1} using KBr wafer technique. The crystalline structure of the adsorbent was examined through X-ray diffraction method (Bruker D8ADVANCE diffractometer using CuK αradiation). The chemical composition of the adsorbent was obtained with PANalytical Magix instrument. The samples for de-aromatization were prepared from the recycled C_{10}-C_{13} normal paraffin stream, with 3.5wt.% aromatic content from Iranian Chemical Industries Investment Company. A Hach Brand DR-5000 spectrophotometer was used for determination of aromatic concentration according to the procedure suggested by the UOP (Test method 495).

Adsorption studies

Batch experiments were designed and conducted at room temperature in order to determine the adsorption capacity, isotherm data and the effect of operating parameters. Before each experiment the synthetic zeolite was activated at 350°C for 2 hour and then cooled to room temperature in desiccators. Known amount of the activated sample was transferred to a beaker containing 50 ml of the recycled normal paraffin. The mixture was shaken for equilibration time and then filtered. The aromatics concentration was measured in the liquid phase and the removal percentage was calculated according to the equation 1.

Removal (%) = $((C_0-C_e)\times100)/C_0$ (1)

where C_0 and C_e are respectively the initial and equilibrium concentrations of aromatic compounds (mg/L).

Effete of adsorbent dose: To evaluate the effect of adsorbent dose, 50 ml of the sample was mixed with varying amounts of adsorbents in a 250 ml Teflon beaker. The mixture was shaken for 24 hour at 25°C. The solid phase was separated by filtration and the aromatic content of the filtrate were measured.

Kinetic Study: In order to evaluate the requisite time for maximal removal of aromatics, 10 g of the activated NaX zeolite was exposed to 50 ml of the recycled normal paraffin. The mixture was shaken at 25°C and the samples were taken at different interval time until equilibrium was attained. The solid phase was separated by filtration and the aromatic content of the samples was measured.

Effect of initial concentration: 50 ml of normal paraffin mixture with different aromatic content (0.01-5 wt.%) was mixed with 10 g of zeolite NaX and shaken for equilibrium time at 25°C. The solids were separated by filtration and the aromatic content of the filtrate was measured.

Effect of temperature: To study of the effect of the temperature, a rotary evaporator was used in which 50 ml of the recycled normal paraffin was mixed with 10 g of the activated NaX zeolite at different temperature from 25°C to 145°C. After equilibration, each sample was filtered and the aromatic content was measured in the filtrate.

Regeneration studies

To study the regeneration ability of the adsorbent, a pilot scale fixed bed column was designed and constructed (80 cm length and 2.54 cm inner diameter). All required auxiliary systems including, electrical furnace, injection pump, feed pre-heater, and collecting vessels were predicted. The column was packed with 265 g of the adsorbent and placed inside the electrical furnace (Excition model). Electrical heating was supplied to the column to control the bed temperature (Figure 1). Before each experiment, the adsorbent was activated in situ by
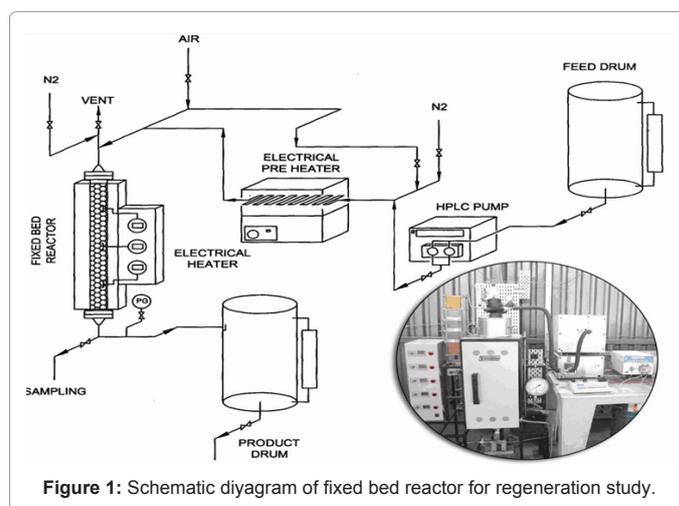

Figure 1: Schematic diyagram of fixed bed reactor for regeneration study.

electrically heating furnace at 350°C for two hours and then allowed to cool to room temperature at dry nitrogen atmosphere (5 ml/min). Once the adsorption process was started, samples were collected from the bottom of the bed at known time intervals. The concentration of aromatic in inlet and the outlet were determined in order to construct breakthrough curves and to calculate the adsorbent capacity. When the adsorbent was saturated, the regeneration cycle was carried out under dry nitrogen flow at 500°C for 15h. The adsorption-regeneration cycles were repeated three times, and adsorption capacity of the regenerated adsorbent was calculated for each cycle.

Results and Discussion

Adsorbent characterization

In the FT-IR spectrum of the adsorbent (Figure 2), the band at 3400-3600 and 1630-1660 cm^{-1} were attributed respectively to OH stretching mode and bending mode of OH group of the water molecules. The two most intense bands of zeolites appeared at 980-1230 cm^{-1} and 420-500 cm^{-1} were clearly observed in the spectra. The first bands at 1630-1660 cm^{-1} was assigned to the asymmetric stretching mode of the T-O and the second one was related to bending mode of the T-O. 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. These vibrations related to the external linkage of the TO_4 units in the structures that are sensitive to structural vibrations. All these observations confirmed that the adsorbent has an alumina silicate structure [16]. In the XRD pattern of the synthesized zeolite the line positions and the relative intensities were similar to those of the references, confirming that the synthesized adsorbent was pure NaX zeolite (Figure 3). The chemical composition of the sample obtained by XRF method agreed well with the results of the other workers (Table 1) [17].

Adsorption Studies

Effete of adsorbent dose: The removal efficiency of the aromatics was increased with increasing the adsorbent dosage, and remained constant at adsorbent dosage of 16 g (Figure 4). To economize the procedure, 10 g of adsorbent was considered as optimal adsorbent dosage.

Effect of contact time: By increasing the contact time from 0 to 195 min, the removal efficiency was first increased and then followed
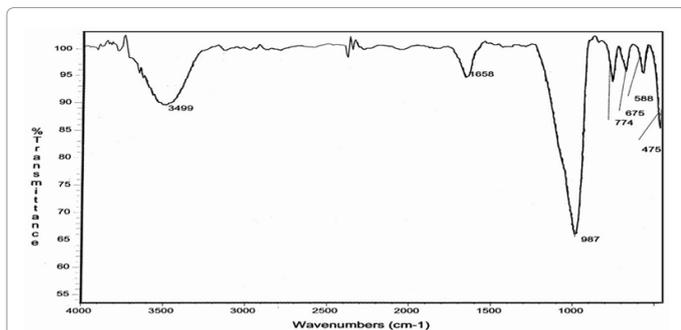
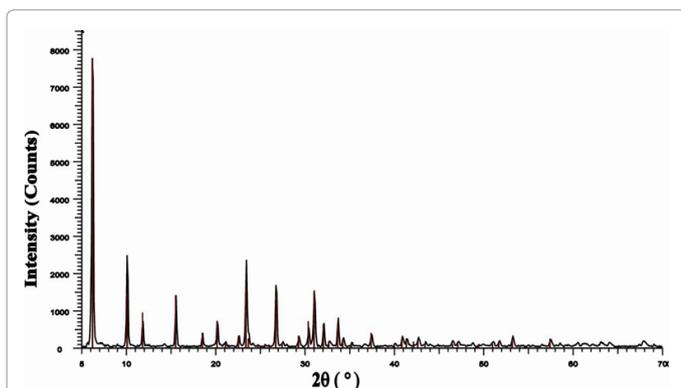**Figure 2:** FT-IR spectrum of the synthetic zeolite NaX.

Figure 3: XRD pattern of synthetic zeolite NaX.

Constituent	Value (wt.%)
SiO_2	37.17
Al_2O_3	25.98
Na_2O	14.73
MgO	1.57
CaO	1.48
K_2O	0.27
Fe_2O_3	0.71
P_2O_5	0.11
LOI	17.8

Table 1: XRF analysis of synthetic zeolite NaX.
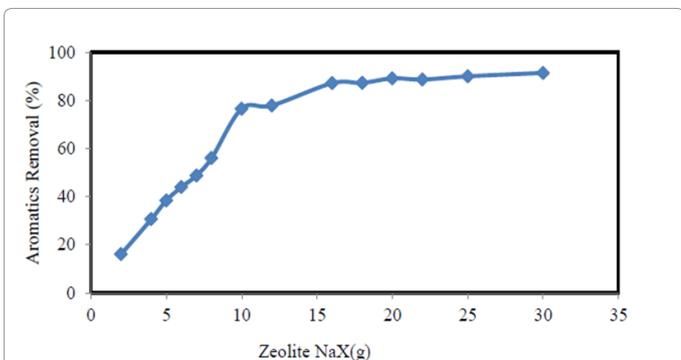

Figure 4: Effect of adsorbent dosage on the removal of aromatics (Init.Conc= 3.5%w, T= 25°C).

by constant adsorption (Figure 5). The results also revealed that the uptake of aromatics at initial stages was fast, with reduction in uptake rate being closer to equilibrium time. The rapid initial uptake is attributed to the adsorption of the aromatics on the surface sites. 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 an increase in the diffusion resistance as the molecules have to travel further into the interior pores. The interior surfaces were active and showed affinity towards aromatics molecules, but the adsorption on the interior sites needed more contact time and the aromatics uptake after 3 hours was controlled by micro pore diffusion.

Effect of initial concentration: The influence of initial concentration on the removal efficiency is illustrated in Figure 6. The percentage removal decreased as the initial concentration of aromatics increased. At lower initial concentrations, sufficient adsorption sites are available for adsorption. As the concentration increased, the numbers of aromatic compounds is higher than adsorption sites; however the fractional adsorption was independent of initial concentration.

Effect of temperature: The removal of aromatics decreased with the increase of temperature (Figure 7). This is related to this fact that higher temperature is unfavourable to exothermic reaction once equilibrium is attained. The optimal temperature was found to be 25°C.

Equilibrium modeling

The Langmiur and Freundlich models as the most frequently employed models for adsorption processes were used to evaluate the experimental data. 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 Langmuir isotherm is given by the following equation [18]:
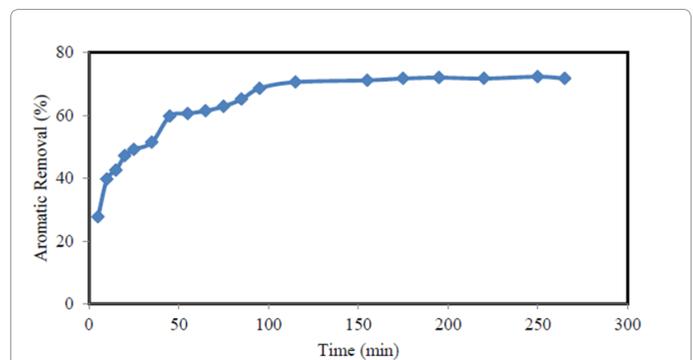

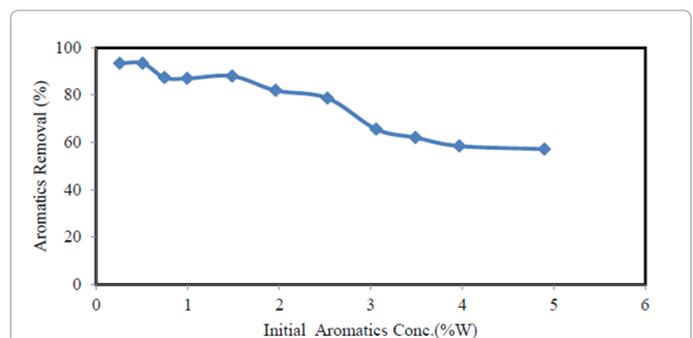**Figure 5:** Effect of contact time on the removal of aromatics (Init.Conc= 3.5%w, T= 25°C).

Figure 6: Effect of contact time on the removal of aromatics (Init.Conc= 3.5%w, T= 25°C).

$$1/q_e = 1/q_m + 1/q_m C_e \qquad (2)$$

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_m and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. When $1/q_e$ was plotted against $1/C_e$, a straight line with slope $1/bq_m$ indicated that the adsorption followed Langmuir isotherm (Figure 8). The Langmuir constants q_m and b were determined from the slope and the intercept of the plot and are shown in Table 2. The adsorption data was also analyzed by the Freundlich model [18]. The logarithmic form of the Freundlich model is given by the equation 3.

$$Log\, q_e = \log K_f + 1/n \log C_e \qquad (3)$$

where K_f and n are Freundlich constants related to adsorption capacity and intensity respectively. When log q_e was plotted against logC_e, a straight line with slope $1/n$ was obtained indicating that the adsorption followed Freundlich isotherm (Figure 9). The Freundlich constants K_f and n were determined from the slope and intercept of the plot and were presented in Table 2. The results showed that Langmuir isotherm fitted well with the experimental data, indicating the homogeneous distribution of active sites of the adsorbent.

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 [19]:

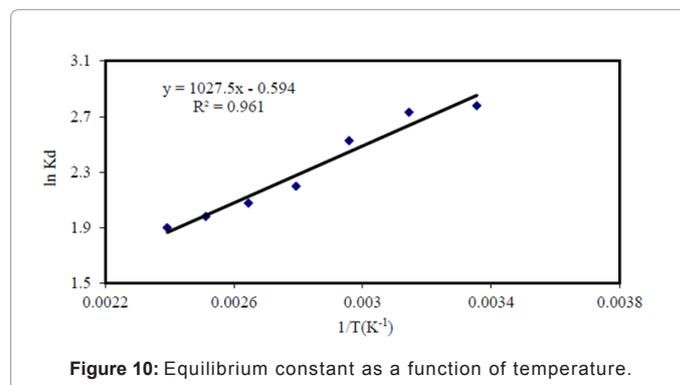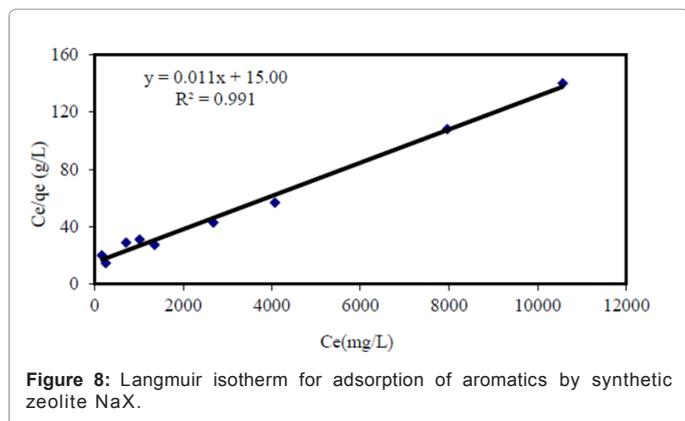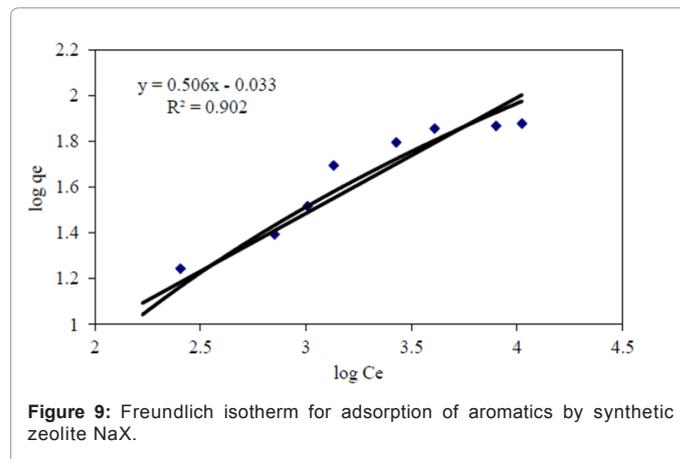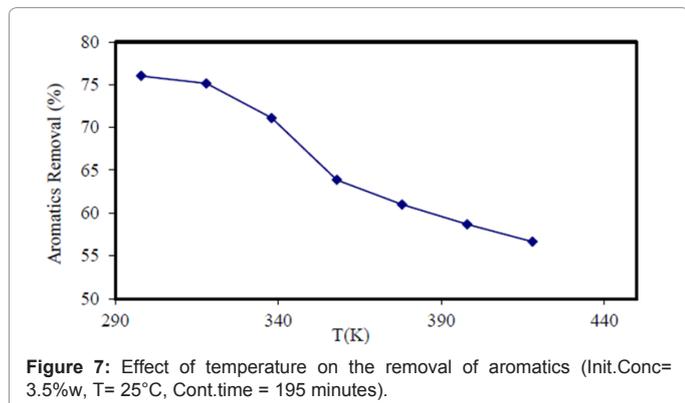$$K_d = \frac{C_i - C_e}{C_e} \times \frac{V}{m} \qquad (4)$$

C_i and C_e are respectively initial and equilibrium concentration (mg/L), V is volume of the solution (ml) and m is the adsorbent weight (g). ΔH°, ΔS° were calculated from the slope and intercept of linear plot of 1/T versus lnK_d, according to equation (5), where T is the solution temperature (K) and R is the gas constant and is equal to 8.314 J/mol K (Figure 10).

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

Values of the Gibbs free energy change for the adsorption process was obtained from equation 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 were negative, the indication of an exothermic process and their magnitudes (<40 kJ/mol) showed a physical adsorption process. The negative value of ΔG° indicated the spontaneous nature of the adsorption process. Finally, the negative values of the adsorption entropy were consistent

Figure 7: Effect of temperature on the removal of aromatics (Init.Conc= 3.5%w, T= 25°C, Cont.time = 195 minutes).

Figure 9: Freundlich isotherm for adsorption of aromatics by synthetic zeolite NaX.

Figure 8: Langmuir isotherm for adsorption of aromatics by synthetic zeolite NaX.

Figure 10: Equilibrium constant as a function of temperature.

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

Table 2: Isotherm parameters for removal of aromatics by-products.

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

Table 3: Thermodynamic parameters of the reaction.

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

Kinetic of adsorption

In order to investigate the mechanism of sorption process, various kinetic models were examined. The rate constant for the apparent adsorption of aromatics was obtained from the pseudo second-order equation [20]:

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

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.
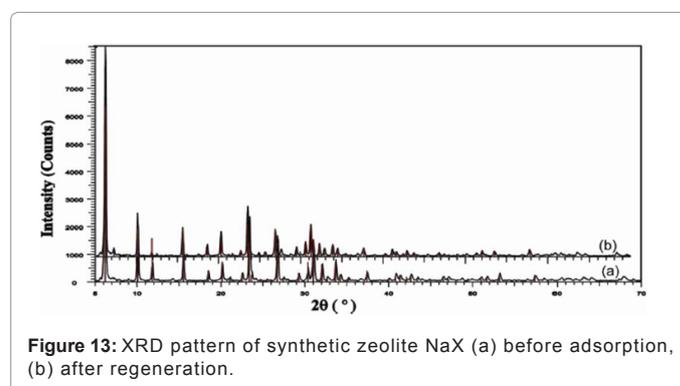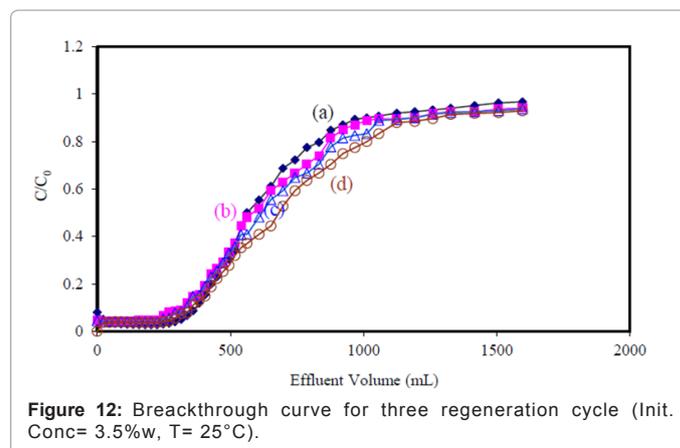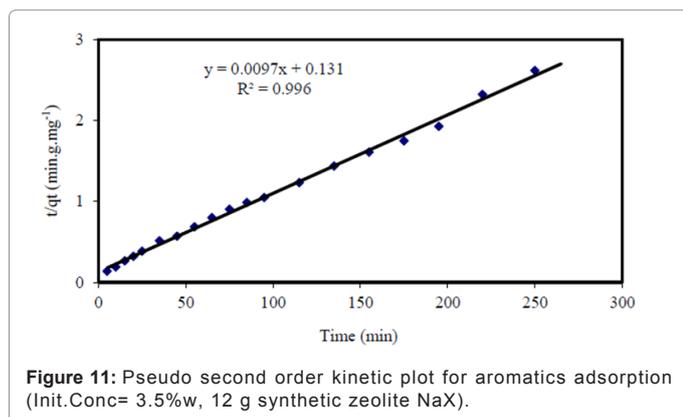
When t/q_t was plotted against t, a straight line was fitted to the data (Figure 11), the obtained correlation factor ($R^2 = 0.9965$) suggested that aromatic adsorption by NaX zeolite followed pseudo second order kinetics.

Adsorbents regeneration

One of the challenging problems on adsorptive process is the regeneration of the adsorbents. Generally, there are two techniques for regeneration of the adsorbents, the thermal treating and the solvent elution. Zeolites based adsorbents are usually regenerated by solvent washing at ambient temperature but effective removal of the solvent is difficult. Therefore solvent washing is suitable for certain applications involving heat sensitive materials (i.e. active carbon). In this study, the thermal treatment was adopted and the adsorbent was regenerated by flowing nitrogen at 500°C for 15 h. The breakthrough curve of the regeneration step was constructed (Figure 12). It was concluded that after three regeneration cycles, the adsorption capacity remained unchanged. The XRD pattern of the regenerated adsorbent showed that the structure of zeolite was not affected by thermal treatment (Figure 13).

Conclusion

Characterization of the synthesized NaX zeolite by XRD, XRF and FT-IR confirmed that the pure phase of zeolite had been prepared. Experimental data fitted well with Langmuir model. It was also concluded that the aromatics adsorption was an spontaneous and exothermic process. The negative value of the standard entropy change ($\Delta S°$) indicated that randomness decreased with the uptake of the

Figure 11: Pseudo second order kinetic plot for aromatics adsorption (Init.Conc= 3.5%w, 12 g synthetic zeolite NaX).

Figure 12: Breackthrough curve for three regeneration cycle (Init. Conc= 3.5%w, T= 25°C).

Figure 13: XRD pattern of synthetic zeolite NaX (a) before adsorption, (b) after regeneration.

aromatics. The high correlation coefficient value (R2=0.9965) indicated that the adsorption followed pseudo second-order model. The adsorbent was throughly regenerated with flowing nitrogen at 500°C and the initial adsorption capacity was kept after three sucsecive 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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