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The performance of pelletized Ce-Y and Ni-Y zeolites for removal of thiophene from model gasoline solutions

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Abstract−H-Y zeolite was prepared with Na-Y zeolite via ion-exchange method. Ni-Y and Ce-Y zeolites were then prepared with H-Y zeolite via solid-state ion-exchange (SSIE) method. The pellet form of the zeolites was employed for removal of thiophene from samples containing 194, 116 and 72 ppmw sulfur in a batch system at ambient condition. The removal of sulfur over the three types of the adsorbents decreased according to the following order: Ce-Y (81.7%) >Ni-Y (75.2%)>Na-Y (51.7%), indicating that the Ce-Y zeolite was the most effective adsorbent for removing of sulfur compounds from gasoline. Adsorption isotherms of thiophene on Ni-Y and Ce-Y zeolites were obtained and correlated with six well-known isotherms. The equilibrium data of thiophene adsorption were well fitted to the isotherms and the corresponding parameters and fitting error criteria of the isotherm equations were obtained.

Keywords: Adsorption, Zeolite, Thiophene, Gasoline, Isotherm Equations

INTRODUCTION

Sulfur compounds in fuels are generally converted to SO_x during combustion, which results in serious environmental problems such as acid rain. Sulfur compounds also poison catalysts used for reduction of CO and NO_x in catalytic converters. For production of hydrogen for fuel cells applications from transportation fuels in a reforming process, the removal of organic sulfur compounds from the fuels is also essential [1-4]. The sulfur level of the fuels should be further reduced close to zero ppm as the presence of even traces of sulfur poisons the reforming catalysts as well as electrode catalysts [4,5]. In addition, governments worldwide have made increasingly stringent regulations to limit sulfur levels in fuels in recent years [1]. The recent US EPA Tier II regulation mandated a sulfur level of 30 and 15 ppmw in gasoline and diesel, respectively. Likewise, European Union gasoline and diesel fuel specifications call for 10 ppmw sulfur in Euro-IV [6].

Hydrodesulfurization (HDS) is a conventional process being used in refineries worldwide to remove sulfur compounds from liquid fuels by employing $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ catalysts [7,8]. This process can economically reduce sulfur from few thousands to few hundreds ppm level [6]. HDS process is currently employed at elevated temperatures (300-340 °C) and hydrogen partial pressures of 20-100 atm, to convert organosulfur compounds to hydrogen sulfide (H_2S) [9]. This process is very efficient for thiols and sulfides removal, but not for thiophene and thiophene derivatives. The process is also not economical for deep desulfurization (to few tens of ppm level), as a severe process condition (i.e. high hydrogen pressure and temperature) is required for catalytic decomposition of refractory organosulfur compounds [6]. Thus, even after performing the conventional HDS process on a fuel, the refractory sulfur compounds such as thiophene (T), benzothiophene, dibenzothiophene, and their alkylated derivatives remain unconverted [1,10,11].

For production of ultra-clean fuels, adsorption desulfurization has been considered an efficient and an economical technology for removal of thiophene and thiophene derivatives. To develop a proper adsorbent, many studies have been performed using metal oxides, zeolite-based materials, carbon materials, activated alumina, and carbon-based materials [1,7,12]. Among various types of porous materials which have been employed as adsorbents, zeolites have been explored as effective adsorbents due to their high ion-exchange capacity, size-selective adsorption capacity and their thermal and mechanical stabilities. Zeolites are crystalline aluminosilicates of alkali or alkaline earth elements, such as sodium, potassium, and calcium. Various types of zeolites (13X, ZSM-5, H-Y) have been used for desulfurization of transportation fuels [13]. Velu et al. studied the removal of sulfur compounds from model and real jet fuels using Y type zeolites ion-exchanged with Ni, Cu, Zn, Pd and Ce ions [7]. Yang and coworkers performed a research study using ion-exchanged Y zeolites [2]. They reported that, Cu(I)-Y, Ag-Y and Ni-Y zeolites were selective for the removal of sulfur compounds in fuels by providing a π-complexation between sulfur compounds and the transition metal cations loaded on the zeolites. Bhandari et al. also investigated the performance of Ni-Y and Cu-Y zeolites for sulfur removal [11]. King and Li examined the ability of Cu(II)-Y and Cu(I)-Y to remove thiophene from various hydrocarbon mixtures at ambient temperature [14]. Xue et al. studied the Ag+, Cu+, and Ce3+ ion-exchanged Y zeolites as adsorbents specifically for selective adsorption of thiophene and 1-benzothiophene in a model solution of HDS treated gasoline [8]. They reported that the adsorption isotherms for thiophene and 1-benzothiopohene were fitted to the Langmuir isotherm model. Wang et al. investigated adsorptive desulfurization over Ce-Ni-loaded Y type zeolites with an em-

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phasis on the effect of Ce as a Co-cation on the removal of dibenzothiophene (DBT) from a model transportation fuel [13]. They analyzed the equilibrium adsorption data of DBT on Ni-Ce-Y using Langmuir and Freundlich isotherm models. Although the promising results of these studies are very important, the employed adsorbents were in powder form, which is not suitable for industrial applications. For an efficient adsorption process at industrial scale, adsorbents in the form of macroporous pellets having suitable dimensions, porosity, and mechanical strength are required. To minimize the macropore diffusional resistance of the extra crystalline pores, the pellet size needs to be reduced as much as possible. However, the extent of the size reduction is limited by pressure drop considerations [15]. Generally, a binder is added to help cement the adsorbent particles together in order to achieve satisfactory physical strength. As a result of a poor selection of the binder and the conditions employed for the pelletization process, blinding the crystal surface occurs. This phenomenom leads to a low mass transfer rate, and therefore leads to reduction of the catalytic activity due to occupying some parts of the catalyst surface by the binder [15].

The aim of the present investigation is to study adsorptive properties of metal-ion-exchanged zeolites in pellet form for removal of thiophene from a gasoline model as a model solution of HDS-treated gasoline. For this purpose, Na-form of zeolite Y was synthesized. The acidic form of the zeolite was prepared using liquid ion-exchanged method and Ni-Y and Ce-Y zeolites were prepared via SSIE method. To our knowledge, only a few investigations have been carried out at solid-state exchange of zeolite. The prepared adsorbents were pelletized. To evaluate the performance of the pelletized Ni-Y and Ce-Y zeolites, adsorptive desulfurization of the model fuels was conducted using a batch reactor at ambient temperature and pressure. Additionally, the parameters of the adsorption isotherms for the two adsorbents (Ni-Y and Ce-Y) were obtained.

EXPERIMENTAL

1. Adsorbent Preparation

Na-Y zeolite was synthesized using a hydrothermal synthesis method. Sodium silicate solution (25.5-28.5% SiO_2, 7.5-8.5% Na_2O, 63-67% H_2O, Merck 105621) and sodium aluminate (BDH 1313002-42-7) were used as sources of silicon and aluminum, respectively.

The adsorbent was prepared in three steps. First, Na-Y zeolite was synthesized based on the method reported by Robson [16]. Then, the Na-Y zeolite was ion-exchanged at 55 °C to obtain acidic form using 0.1 M NH_4NO_3 solution. The obtained solution was filtered and washed. The ion-exchange procedure was repeated three times. To convert NH_4-Y to the acidic form (H-Y), the resulting NH_4-Y zeolite was calcined at 500 °C for 5-6 hr in dry air.

In the third step, SSIE method was used to prepare Ni-Y and Ce-Y zeolites. For Ni-Y preparation, H-Y zeolite and $Ni(NO_3)_2\cdot 6H_2O$ (Merck 106721) were manually mixed [8,17]. The amount of salt corresponded to the maximum theoretical cation exchange capacity (CEC) of the zeolite with Ni. Afterward, the zeolite/salt mixture was placed in a furnace at 500 °C for 6 hr. For preparation of Ce-Y, the first two steps were exactly the same, and in the third step, $Ce(NO_3)_3\cdot 6H_2O$ (Merck 102271) was used and the procedure was repeated under the same condition.

SSIE method was selected for the adsorbent preparation, as this method has the following advantages: (i) it is possible to control the metal loading; (ii) the problems caused by the presence of hydrolyzed metal complex resulting from aqueous ion-exchanges are avoided; (iii) the procedure can be accomplished even in the presence of air; (iv) different active sites from those achievable by aqueous exchange, are created; and (v) this method gives better control over crystal size [18]. In addition, Gong et al. noted that metal exchanged zeolite catalysts prepared via SSIE method exhibited more activity in certain catalytic processes than those obtained in aqueous solution [18].

2. Pelletization

Pelletization of the exchanged zeolite samples was performed by adding sodium silicate as a binder to the zeolite powder. The amount of binder was 30 wt% of the total mixture. The required amount of deionized water was added and mixed continuously. The obtained mixture was in paste form. The resultant was dried at ambient temperature. It was then ground to powder form, and the powder was pressed in a press machine (KS, Gemany) to fabricate cylindrical pellets having 8 mm diameter and 5 mm heigh. The obtained pellets were calcined at 500 °C for 3 hr.

3. Model Gasoline

The major sulfur compounds remaining in the transportation fuels after performing a conventional HDS process are the refractory sulfur compounds such as thiophene, benzothiophene, dibenzothiophene, and their alkylated derivatives. Since most of these sulfur compounds were commercially not available, the authors used thiophene as model organic sulfur compounds. Thiophene with more than 99% purity, purchased from Merck, was used for preparing the model fuels. The simulated solutions of hydrodesulfurized fuel were prepared by dissolving a certain amount of thiophene in iso-octane. The purity of iso-octane was 99.95%. Three solutions containing thiophene with initial concentrations of 510 ppmw T (194 ppmw S), 305 ppmw T (116 ppmw S) and 189.3 ppmw T (72 ppmw S) were prepared. The selected concentrations of sulfur were close to the concentrations of the sulfur in gasoline produced by Isfahan Oil Refinery in Iran.

4. Adsorption Experiment

Adsorption experiments were carried out at room temperature in a stirred batch system. 10 ml of each solution was added to 1 gr of each ion-exchanged zeolite (almost four pellets of each type). Each mixture was shaken for a desired time. A series of samples of each treated liquid was taken at various times, and the sulfur concentrations of the samples were determined using the UOP method 357-80. This sensitive and precise method is for determination of low concentrations of sulfur, ranging from 0.1 to 200 ppmw, in distillate stocks free of hydrogen sulfide. The method is also limited to samples containing not more than 2% olefins. The organosulfur compounds available in the sample solutions were converted to H_2S by Raney nickel. Oxidized sulfur forms, such as sulfonic acids, are not determined quantitatively; therefore, this method must be applied with discretion to the analysis of stocks which have been treated with sulfuric acid.

The sulfur adsorption capacity (q) and sulfur removal percentage (η, %) were calculated using Eq. (1) and Eq. (2), where V is

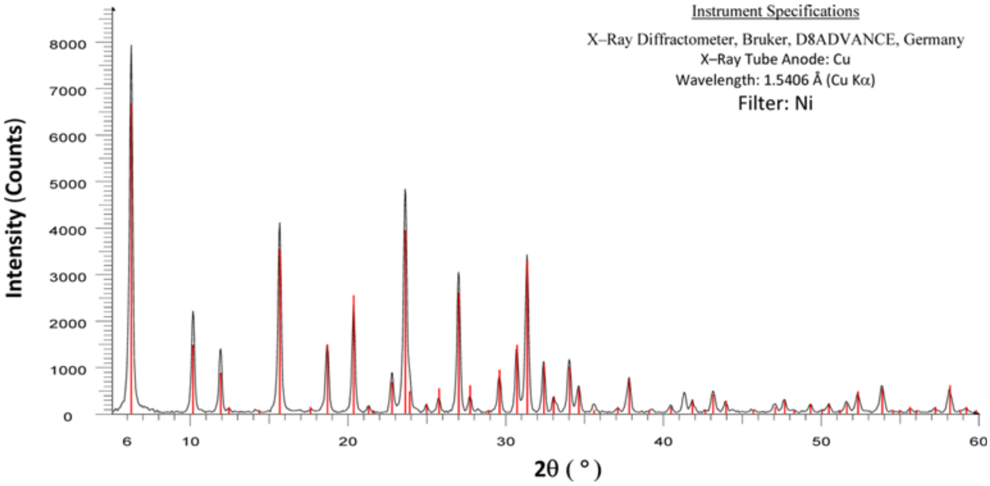

Fig. 1. XRD pattern of Na-Y zeolite.

the volume of the liquid phase, C_o is the concentration of sulfur in the initial solution, C_e is the concentration of sulfur in the solution at equilibrium state and m is the mass (gr) of the composite adsorbent.

$$q=\frac{V\times(C_o-C_e)}{m} \tag{1}$$

$$\eta=\left[\frac{C_o-C_e}{C_o}\right]\times 100 \tag{2}$$

RESULTS AND DISCUSSION

1. Characterization of the Ion-exchanged Zeolites

XRD technique was employed to characterize the synthesized zeolites using a D8 ADVANCE XRD instrument (Bruker Corporation) equipped with Cu Kα radiation. The XRD pattern of the synthesized Na-Y zeolite is shown in Fig. 1. The XRD patterns of the ion-exchanged zeolites (H-Y, Ni-Y and Ce-Y) are also shown in Fig. 2. As shown, the three samples had identical structures. However, the intensity of the peaks for Ni-Y and Ce-Y zeolites was less than those of the Na-Y zeolite. It seems that the crystallinity of the latter two samples may decrease with a high concentration of the oxides. This also could be due to fewer purities of those samples which occurred by adding new materials, i.e., CeO_2 or Ni [8,9]. As shown in Fig. 2, the broad peaks corresponding to the CeO_2 and NiO phases were also observed in addition to the peaks related to the zeolite structure. Note that the Na-Y zeolite was white, whereas Ni-Y zeolite has a greenish color at the end of ion exchange process. In the case of Ce-loaded zeolite, the white color of the Na-Y zeolite was changed to light yellow, indicating that during the ion-exchange process, the oxidation of cerium ions from trivalent to tetravalent had occurred [9].

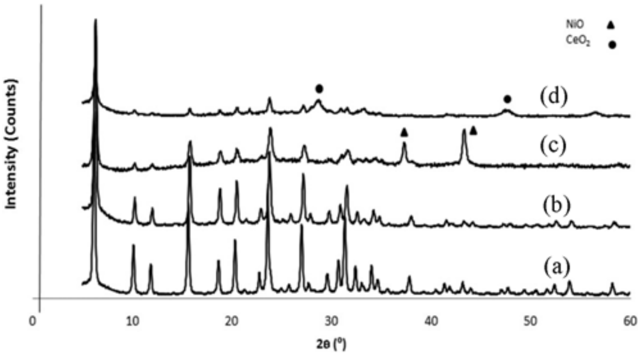

Fig. 2. XRD patterns of (a) Na-Y zeolite, (b) H-Y zeolite, (c) Ni-Y zeolite, (d) Ce-Y zeolite.

A semi-quantitative XRF analysis of Na-Y zeolite was performed using an S4PIONEER XRF instrument (Bruker Corporation) and the results are shown in Table 1. Therefore, the SiO_2/Al_2O_3 ratio of the synthesized zeolite was 2.41.

The pore volumes and BET surface areas of the pelletized zeolites, determined by N_2 adsorption isotherm data at 77.3 K, using a Nova instrument (Quantachrome NovaWin2) are reported in Table 2. The data presented in Table 2 shows that the Ce-Y zeolite may has partially lost the zeolite framework structure.

2. Effect of Contact Time and Initial Concentration

The effects of time and initial concentration on the adsorption of sulfur on Ni-Y and Ce-Y zeolites are shown in Fig. 3 and Fig. 4,

Table 1. Semi quantitative XRF analysis results of Na-Y zeolite (concentration, %w/w)

SiO_2	Al_2O_3	Na_2O	Fe_2O_3	TiO_2	CaO	ZrO_2	CuO	LOI*
45.08	18.6	11.60	0.043	0.033	0.015	0.008	0.005	24.47

*Loss on Ignition

Table 2. Porosity, BET surface area, porosity and pore volume of Na-Y, Ni-Y and Ce-Y zeolites

Adsorbent	BET surface area (m^2/g)	Porosity [-]	Pore volume (cm^3/gr)
Na-Y	405	0.55	0.20
Ni-Y	625	0.45	0.22
Ce-Y	128	0.51	0.04

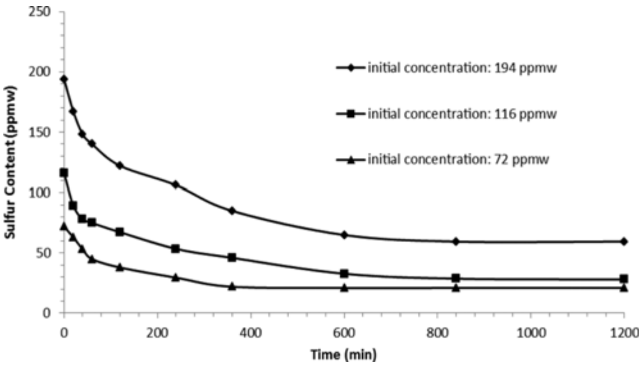

Fig. 3. Effect of contact time and initial concentration on uptake of thiophene from thiophene/iso-octane solution.

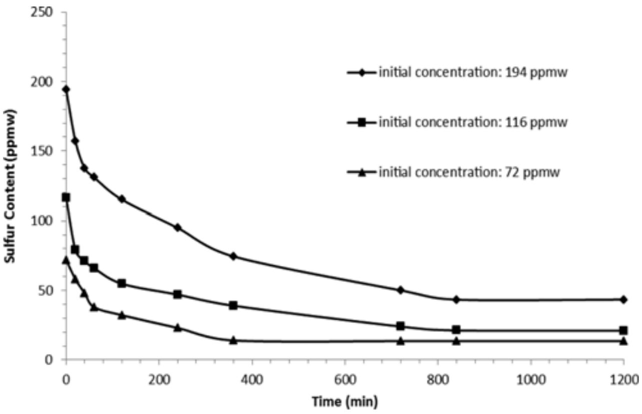

Fig. 4. Effect of contact time and initial concentration on uptake of thiophene from thiophene/iso-octane solution.

respectively. For this purpose, three sulfur model solutions with initial sulfur concentrations of 194, 116 and 72 ppmw were employed. As it is shown, the adsorption processes were initially rapid, which could be due to a large mass transfer driving force, but decreased with the time and leveled off at the equilibrium concentration of the sulfur in the solution. Velu et al. also used the Ni-Y and Ce-Y zeolites to uptake the sulfur compounds from the jet fuel using a batch system as well as a packed column [7]. They pointed out that most of the sulfur compounds were adsorbed on Ce-Y zeolite within the first 1 hr of the experiment. This remark was similar to what we observed in this research work.

It is also shown that the sulfur uptake increased by decreasing sulfur initial concentration. The sulfur concentrations leveled off at 59.5, 28.0 and 21.0 ppmw for Ni-Y zeolite; and at 43.4, 21.0 and 16.0 ppmw for Ce-Y zeolite for the aforementioned three sulfur concentrations, respectively. It seems that at this stage, the adsorption sites were saturated and the system reached equilibrium state, at which the rate of adsorption was equal to the rate of desorption. After 2 hr, the entire sulfur uptakes by Ni-Y zeolite were 46.8%, 53.5% and 70.8% using the solutions containing 194, 116 and 72 ppmw sulfur, respectively. These values were increased to 56%, 64.4% and 71% when Ce-Y zeolite was employed for the same period of time, indicating that Ce-Y zeolite was more effective than Ni-Y zeolite for almost all initial sulfur concentrations. It seems that the interaction of thiophene with Ce-Y zeolite is stronger than the interaction with Ni-Y zeolite. Also, adsorption equilibrium for the solutions containing 194 pmmw and 116 ppmw of sulfur was achieved after 14 hr, whereas for the solution with initial concentration of 72 ppmw of sulfur, it was achieved after 6 hr.

Hernandez et al. used Ni-Y zeolite for desulfurization of diesel fuel (297.2 ppmw S) [17,19]. They reported that the Ni-Y prepared via SSIE method was capable of removing 0.16 mmol S/g of adsorbent, at breakthrough. They pointed out that the high uptake of sulfur was related to the formation of π-complexation between Ni cations and sulfur compounds. Xue et al. studied the adsorption of thiophene and 1-benzothiophene from an organic model solution of hydrodesulfurized gasoline using Ce-Y zeolite powder in a batch system [9]. They also reported that the thiophene adsorption was initially rapid and decreased by increasing the time.

Wang et al. investigated the selective adsorption of dibenzothiophene from model transportation fuels over Ce/Ni-Y zeolite powder in a batch reactor [13]. They also indicated that the adsorption process was fast and most of the sulfur compounds were adsorbed within 1 hr. Although, they employed powder form and we used the pellet form of the adsorbent, the trend of the adsorption was the same.

3. Comparison of the Performance of the Adsorbents

Desulfurization of sulfur solution containing 116 ppmw of sulfur was performed over Na-Y, Ni-Y and Ce-Y zeolites for 14 hr. The results are presented in Fig. 5. As it is shown, the desulfurization performance of the adsorbents decreased as follows: CeY> NiY>NaY. It can be seen that the SSIE of Na-Y zeolite with Ni- and Ce-cations was very effective for desulfurization of the sulfur solution, as the adsorption capacity of NaY is the lowest. It can be postulated that the low performance of Na-Y zeolite for sulfur removal relies on the physical adsorption, whereas Ni-Y zeolite can adsorb thiophene by π-complexation between Ni^{2+} ions and thiophene aromatic rings. For the case of Ce-Y zeolite, thiophene was adsorbed over the adsorbent via a direct S-adsorbent interaction or direct S-M bond (donating the lone pair of electrons of the sulfur atom to the adsorbent by thiophene) rather than π-complex-

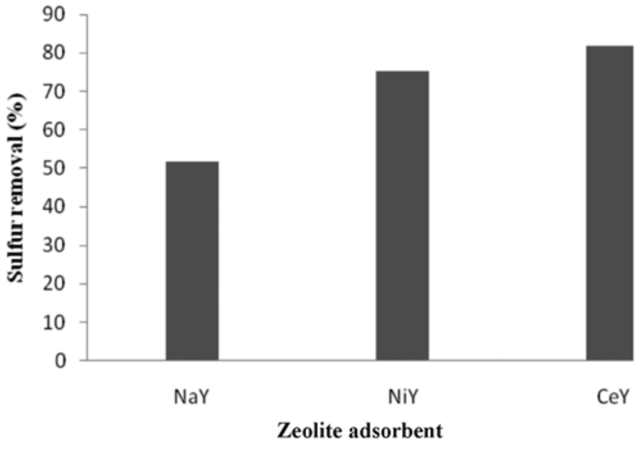

Fig. 5. Thiophene uptakes by metal-ion-exchanged zeolites; contact time=14 hr; concentration of sulfur=116 ppmw; adsorbent-to-solution ratio=1 g/10 ml.

ation [7,20]. It seems that the aromatic ring in thiophene made their C-S bonds quite stable. The higher performance of Ce-Y compared to Ni-Y zeolite in the adsorption of thiophene might be due to the high polarizability of Ce^{4+} ions [7,9,13].

4. Adsorption Isotherms

The equilibrium isotherms were determined for the two experimental systems. The first requirement in the design of any adsorption processes is to determine the equilibrium adsorption capacity. In other words, the successful representation of the dynamic adsorptive separation of a solute from a solution on an adsorbent depends upon a good description of the equilibrium separation between the two phases. By plotting solid phase adsorbate concentration against liquid phase adsorbate concentration, it is possible to depict graphically the equilibrium adsorption isotherm [20]. To optimize the design of an adsorption system, it is important to establish an appropriate correlation for the equilibrium curve. As mentioned before, there is no published work on adsorption equilibrium of sulfur onto ion-exchanged zeolites in pellet form. Thus, one objective of the present study was to investigate the thiophene adsorption onto Ni-Y and Ce-Y zeolites in pellet form.

There are many theories relating to adsorption equilibrium. Six isotherm equations were examined in the present research: Langmuir, Freundlich, Sips, Toth, Temkin and Jovanovich. The adsorption data were analyzed using the aforementioned isotherm models. A comparison among the fit error criteria (FEC) of the isotherms discloses the applicability of each isotherm model.

The Langmuir model is probably the best known and most widely applied adsorption isotherm. It has produced good agreement with a wide variety of experimental data and may be represented in the form of Eq. (3). This equation can be linearized to the form of Eq. (4).

$$\frac{q}{q_m}=\frac{bC_e}{1+bC_e} \tag{3}$$

$$\frac{C_e}{q}=\frac{1}{q_m b}+\frac{C_e}{q_m} \tag{4}$$

where C_e is the equilibrium concentration (ppmw), q is the amount of sulfur adsorbed (mg/g), q_m is q for a complete monolayer (mg/g) and b is a adsorption equilibrium constant ($ppmw^{-1}$) [21]. The Langmuir constants, q_m and b, are calculated from the isotherm and their values are given in Table 3. Fig. 6 and Fig. 7 show the adsorption equilibrium data fitted to the non-linear form of the Langmuir isotherm for sulfur adsorption on Ni-Y and Ce-Y zeolites.

The Freundlich isotherm empirical model can be applied to nonideal adsorption on heterogeneous surfaces as well as to multilayer adsorption and is expressed by Eq. (5) [20]. This equation is frequently used in the linear form by taking the logarithm of both sides (Eq. (6)). The isotherm constants, k and n, are given in Table 3. Fig. 6 and Fig. 7 show the experimental data of adsorption equilibrium fitted to Freundlich isotherm for Ni-Y and Ce-Y zeolite, respectively.

$$q=kC_e^{2/n} \tag{5}$$

$$\log q=\log k+\frac{1}{n}\log C_e \tag{6}$$

The Toth isotherm is another empirical model that is efficient in describing the data of hydrocarbons and carbon oxides on activated carbon and zeolite [22]. Being a three-parameter model, the Toth equation can describe many adsorption data. This isotherm model is presented in the form of Eq. (7). When t=1, the Toth isotherm reduces to the famous Langmuir equation. The Toth constants, q_m, b and t, are calculated from this isotherm and their values are reported in Table 3. The adsorption equilibrium data fitted to Toth isotherm are shown in Fig. 6 and Fig. 7 for Ni-Y and Ce-Y zeolites, respectively.

$$q=q_m\frac{bC_e}{(1+(bC_e)^t)^{2/t}} \tag{7}$$

The Sips isotherm (Langmuir-Freundlich) is a three-parameter equation similar to the Freundlich equation. This isotherm model (Eq. (8)) was proposed by Sips in 1948 [22]. In this type of isotherm also when n=1, it reduces to the famous Langmuir equation. The constants, q_m, b and n, were determined for the Sips isotherm for Ni-Y and Ce-Y zeolites; and are presented in Table 3. As shown in Fig. 6 and Fig. 7, the adsorption equilibrium data are fitted to the Sips model, which combines the Langmuir and Freundlich models for Ni-Y and Ce-Y zeolites, respectively.

$$q=q_m\frac{(bC_e)^{2/n}}{1+(bC_e)^{2/n}} \tag{8}$$

Empirical Eq. (9), the Temkin isotherm equation, was proposed originally by Slygin and Frumkin (1935). Although this equation is not commonly used for physical adsorption, it is more popular for describing chemisorption systems.

$$q=b\ln(aC_e) \tag{9}$$

where a and b represent isotherm constants, respectively [21]. To obtain the isotherm constants for the Temkin model, the adsorp-

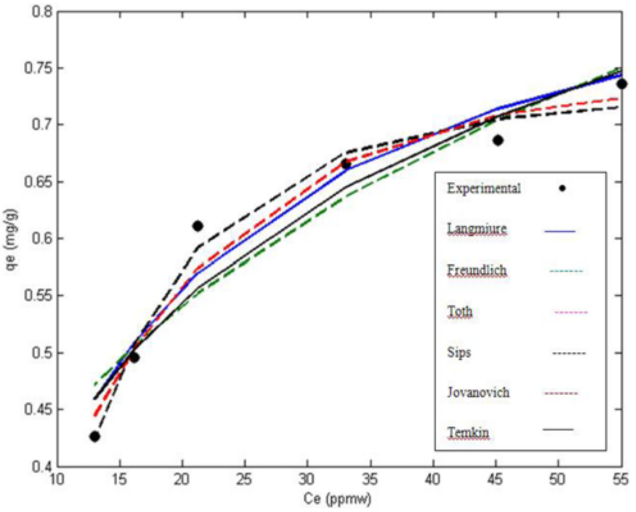

Fig. 6. Equilibrium isotherms of thiophene on Ni-Y zeolite; contact time=14 hr; concentration of sulfur=116 ppmw; mass of adsorbent=0.1-1.5 g; solution volume=10 ml; temperature=25 °C.

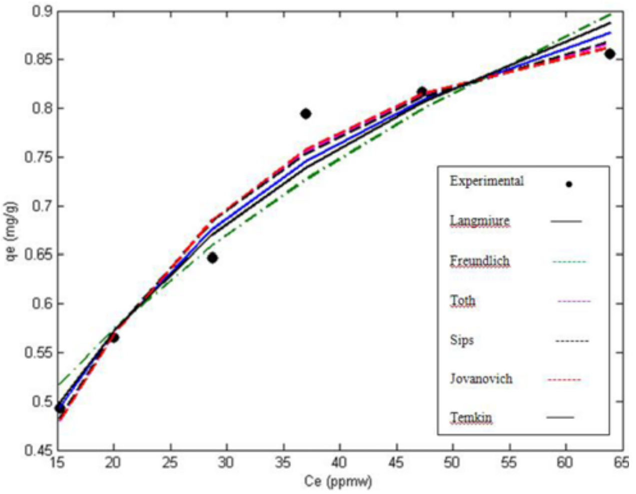

Fig. 7. Equilibrium isotherms of thiophene on Ce-Y zeolite; contact time=14 hr; concentration of sulfur=116 ppmw; mass of adsorbent=0.1-1.5 g; solution volume=10 ml; temperature=25 °C.

tion equilibrium data were fitted to the Temkin model as shown in Fig. 6 and Fig. 7. The Temkin constants are also reported in Table 3.

The Jovanovich isotherm (Eq. (10)) is more popular in the description of chemisorption systems. Although not as popular as the other empirical equations proposed so far, it is nevertheless a useful empirical equation [22]. The Jovanovich constants, q_m and b, are listed in Table 3. The adsorption equilibrium data were fitted to Jovanovich isotherm as shown in Fig. 6 and 7 for Ni-Y and Ce-Y zeolites.

$$q = q_m[1 - e^{-bC_e}] \tag{10}$$

The equilibrium data for adsorbents tested in this work were fitted to the above isotherm models, using home-made fitting software. Fig. 6 and Fig. 7 show the comparative fit of various isotherms with the equilibrium data plotted as q_e versus C_e. In addition, these figures indicate the equilibrium adsorption capacity for pellet form of Ce-Y and Ni-Y zeolites. The equilibrium adsorption capacity of Ce-Y and Ni-Y adsorbents is experimentally obtained 0.86 and 0.74 mg/g, respectively.

The fitting error criteria (FEC,%) are also calculated using Eq. (11), where N is the number of data points, q_{exp} and q_{cal} are the measured value of adsorbed thiophene and calculated one at equilibrium (mg/g), respectively.

$$\mathrm{FEC}(\%) = \frac{\sqrt{\sum (q_{exp} - q_{cal})^2}}{N} \times 100 \tag{11}$$

The calculated values of FECs are listed in Table 3. The lower the value of FEC, the better the goodness of fit. As seen, the adsorption behavior is described better by Sips, Toth and Jovanovich type isotherms. The high value of FEC indicates that the Freundlich model cannot be used to describe thiophene adsorption onto Ce-Y and Ni-Y zeolites. Since the b value in the Langmuir isotherm reflects the strength of the adsorption, the larger b value suggests that Ce-Y interacts with thiophene stronger than Ni-Y zeolite in spite of the fact that the former has a smaller q_m value [9].

Table 3. Constant parameters and FEC calculated for various adsorption models

Isotherm equations	CeY	NiY
Langmuir		
q_m (mg/g)	0.9127	1.1589
b (1/ppmw)	0.0765	0.0488
SE (%)	1.0197	1.0247
Freundlich		
k (mg Sol/gr Ads)	0.2071	0.1827
n	3.1127	2.6129
SE (%)	1.4050	1.4252
Sips (L-F)		
q_m (mg/g)	0.7361	1.0201
b (1/ppmw)	0.0880	0.0605
n	0.4409	0.7738
SE (%)	0.6210	0.9699
Toth		
q_m (mg/g)	0.7226	0.9772
b (1/ppmw)	0.0486	0.0412
t	3.2107	1.6012
SE (%)	0.6611	0.9535
Temkin		
a (1/ppmw)	0.1993	0.2710
b (mg/g)	0.7722	0.4138
SE (%)	1.1971	1.1510
Jovanovich		
q_m (mg/g)	0.7388	0.8995
b (1/ppmw)	0.0709	0.0501
SE (%)	0.8252	0.9179

CONCLUSION

From the results obtained in this study, it was concluded that pellet form of Ni-Y and Ce-Y zeolites were suitable candidates for removal of thiophene from gasoline. The Ce-Y zeolite exhibited higher performance for adsorption of thiophene than Ni-Y and Na-Y zeolites. Naturally, the powder form of the adsorbent is more effective than the pellet form. The adsorption processes were initially rapid, which could be due to the large mass transfer driving force, but decreased with the time and leveled off at the equilibrium concentration of the sulfur in the solution. It was also observed that the thiophene uptake increased by decreasing sulfur initial concentration.

Thiophene adsorption onto ion exchanged zeolites was investigated, and the equilibrium adsorption capacity was determined for pellet form of Ce-Y and Ni-Y zeolites.

The six well-known isotherm models were used to describe thiophene adsorption on Ni-Y and Ce-Y zeolite in pellet form at equilibrium. The results obtained demonstrated that Sips, Toth and Jovanovich isotherm models showed goodness-of-fit for both Ni-Y and Ce-Y zeolite adsorbents.

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NOMENCLATURE

a : constant parameter of isotherm
b : constant parameter of isotherm
C_0 : the concentration of sulfur in the initial solution [ppmw]
C_e : the concentration of sulfur at equilibrium state [ppmw]
k : constant parameter of isotherm
m : mass of adsorbent [gr]
n : constant parameter of isotherm
q : the sulfur sorbed per unit mass of adsorbent [mg g^{-1}]
q_m : constant parameter of Langmuir isotherm [mg g^{-1}]
q_{exp} : measured value of adsorbed thiophene [mg g^{-1}]
q_{cal} : calculated value of adsorbed thiophene [mg g^{-1}]
t : constant parameter of isotherm
V : volume of the liquid phase [m^3]

Greek Symbols

η : sulfur removal percentage [%]

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