

Removal of Dibenzothiophene from Organic Medium by Modified Zeolite

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Abstract

In this research, adsorption of dibenzothiophene (DBT) as a model of sulfur containing material has been studied by Pb exchanged Y-zeolite under different experimental conditions. The adsorption was kinetically fast and high adsorption capacity was obtained. The equilibrium adsorption data were analyzed using Langmuir and Freundlich isotherm models. The corresponding parameters and correlation coefficients of each model are reported and the data was well fitted by the Langmuir isotherm. Pseudo-first order, pseudo-second order and intra-particle diffusion models were evaluated to examine the kinetic of the adsorption process. It was concluded that removal of DBT obeys the second-order model of kinetic. The adsorbent was tested for five successive regeneration cycles and the considerable capacity of the adsorbent was remained after regeneration.

Keywords: Pb-Y zeolite, Adsorption, Dibenzothiophene, Equilibrium, Kinetic

Introduction

Sulfur content of transportation fuels have been continually regulated around the World due to its environmental effects as well as the effects on engines and catalytic systems. Sulfur removal has also gained prominence in recent years due to the need for sulfur free reformation fuels for various applications including fuel cells [1]. Conventional hydro-desulfurization (HDS) process has been widely used to remove sulfur compounds from the liquid fuels. However, the HDS process which is generally operated at high temperature and pressure decreases octane number of the fuels. It is efficient for removing thiols and sulfides while being less effective for the refractory sulfur compounds such as dibenzothiophene. To reduce the energy needed for desulfurization, a large number of non-HDS processes, such as alkylation, extraction, precipitation, oxidation and adsorption have been investigated. Of these, adsorption process is a promising process. That is because it can be applied at ambient temperature and pressure [2-4]. Many attentions have been focused on novel materials including mesoporous materials, mixed metal oxides, activated alumina, carbon and zeolites as adsorbents [5-7].

Zeolites are efficient and attractive adsorbents for desulfurization of liquid fuel due to their high ion-exchange and size-selective adsorption capacities as well as thermal and mechanical stabilities. During the last decade, zeolites such as 13X [8], ZSM-5 [9] and HY [10] have been studied for desulfurization of transportation fuels. Yang and co-workers [11-14] studied Y-type zeolites ion-exchanged with Cu, Ag, and Ni ions for removal of sulfur compounds in fuels. Song et al. [15-17] reported that cation-exchanged Y zeolites (Cu, Ni, Zn, Pd and Ce) are effective adsorbents for sulfur compounds. Among previous experimental works on zeolite-based desulfurization, no report on application of Pb-exchanged form of Y-zeolite for removal of DBT was observed. Therefore, the objective of this paper is to investigate adsorption of DBT by Pb loaded Y-zeolite. The experimental parameters were systematically investigated and optimized. XRD, FT-IR, and TG/DTG techniques were adopted to characterize the adsorbent before and after adsorption process. The regeneration of the adsorbent was also examined for 5 successive cycles.

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2. Experimental

2.1. Reagents and standards

The refractory sulfur compound, DBT (98%) was obtained from Sigma. Na-Y zeolite used for Pb-exchanged form was purchased from Aldrich. Other chemicals such as n-hexane ($\geq 95\%$) were obtained from Merk.

2.2. Adsorbent preparation

The Pb-Y zeolite used in this work was prepared by liquid-phase ion-exchange method. An amount of 5g zeolite was mixed with 50mL of a 0.1M $\text{Pb}(\text{NO}_3)_2$ solution with constant stirring for 72h and at room temperature, followed by filtration and washing with deionized water. The process was repeated three times, to ensure desired level of the exchange. The adsorbent was dried and stored in air-tight bottles and kept in a desiccator.

2.3. Chemical and physical analyses

The adsorbent was characterized by different techniques including X-ray diffraction (XRD) using a D₈-advanced Bruker diffractometer, FTIR spectrometry by a Perkin-Elmer65 infrared spectrometer and a thermal analysis by a TG-DSC Setaram instrument. UV-Vis spectroscopy was performed on a Perkin Elmer7 spectrometer. The Pb content of the adsorbent was measured by a Perkin Elmer-300 atomic absorption spectrometer.

2.4. Adsorption experiment

Adsorption of DBT was carried out in a stirred batch system at room temperature. Known amount of adsorbent (0.1g) was added to 10mL n-hexane solutions of DBT and the mixture was shaken at constant temperature. The equilibration time of the system was chosen on kinetic based studies. The adsorbent was then separated from the liquid phase by filtration. The concentration of DBT in the solution was determined by spectrophotometry at the corresponding wavelength. The amount of adsorbed DBT (q) was calculated by the following expressions:

$$q_e = V(C_0 - C_e) / m$$

where V is the volume of the liquid phase, C_0 and C_e are the concentration of the initial and equilibration concentration respectively, and m is the weight of the adsorbent (g).

3. Results and discussion

In order to investigate the structural change of the zeolite structure during ion exchange process, XRD patterns of NaY and Pb-Y zeolites was prepared. The similarity in the patterns of the two zeolites indicated that the original structure was retained without any significant changes in the line position and intensity upon Pb ion exchange (Figure 1).

The exchange capacity of 69.88% was obtained by a repeated ion exchange procedure.

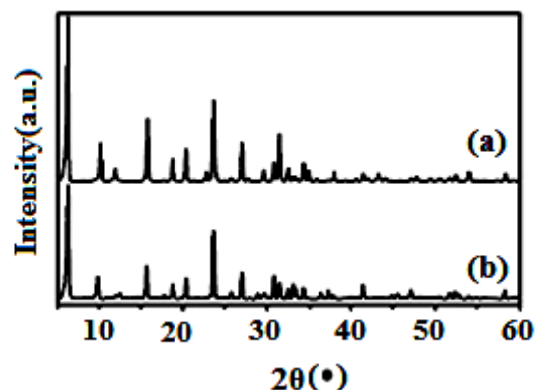


Figure 1: XRD patterns of NaY (a) and Pb-Y (b)

The FT-IR spectrum of the initial and equilibrium Pb-exchanged zeolite provides additional insight into the adsorption of sulfur compound by Pb-Y (Figure 2). It was observed that except for the IR bands of the adsorbent itself, there are a few distinguishable new bands appearing within the range of $1390\text{--}1500\text{ cm}^{-1}$ and 2991 cm^{-1} after DBT adsorption. The band at 2991 cm^{-1} can be assigned to C-H asymmetric stretching vibration of thiophene and the weak bands in the range of $1390\text{--}1500\text{ cm}^{-1}$ can denote to the perturbed symmetric stretching vibration of the C=C bond [18, 19].

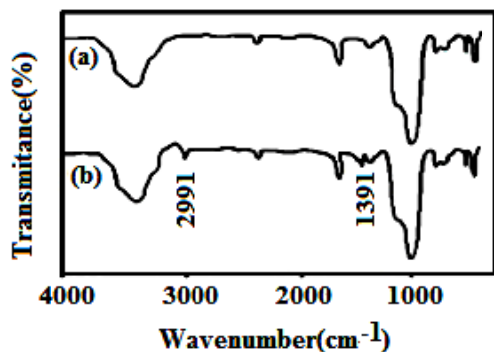


Figure 2: IR spectra of the Pb-Y (a) and after DBT adsorption (b)

The TG/DTG technique was adopted to study the thermal behavior of the adsorbent in N_2 atmosphere. On the thermal curve of Pb-Y sample, a weight loss peak in the range of $40\text{--}150^\circ\text{C}$ which corresponds to the desorption of H_2O molecules; was observed (Figure 3a). After adsorption the thermal curves of Pb-Y (Figure 3b), showed a significant weight loss which is occurred at temperatures of $100\text{--}400^\circ\text{C}$. This can be assigned to the DBT decomposition. Also the possibility of regeneration of adsorbent has been explored using a TG/DTG system. For this purpose, the adsorbent was heated in the TG/DTG system from 50 to 500°C and the curve C shows that it can be regenerated by thermal treatment.

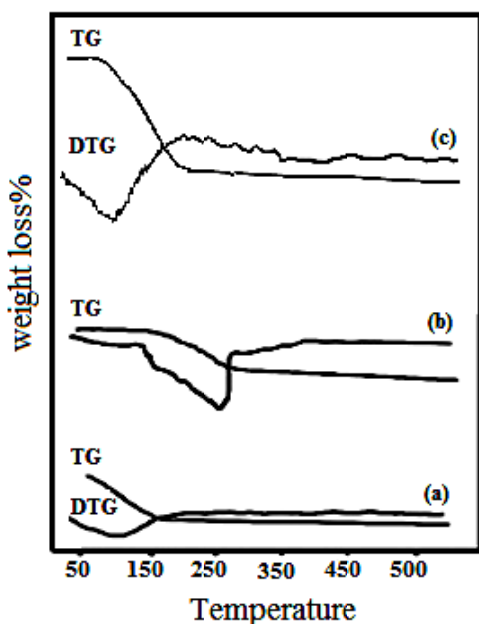


Figure 3: TG/DTG curve of the Pb-Y (a), after DBT adsorption (b) and after first regeneration (c)

3.1. Effect of contact time

The effect of contact time on DBT adsorption by Pb-Y zeolite at ambient temperature is shown in Figure 4. It was concluded that the adsorption process is very fast and the equilibrium is achieved after 10min. Under the experimental conditions, the adsorption capacity of 7.94 mg S/g was obtained.

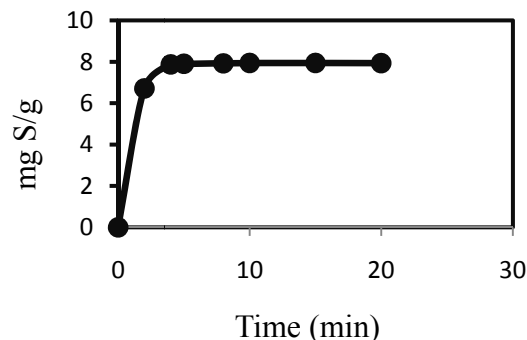


Figure 4: Effect of contact time on DBT adsorption. Temperature: 25°C , initial DBT concentration: 80 mg/L , adsorbent to solution ratio: $0.1\text{g}/10\text{ mL}$

3.2. Effect of initial DBT concentration

The sulfur adsorption capacity of the adsorbent increased to a maximum amount of 108.77 mg S/g as the initial DBT concentration increased from 100 mg/L to 1500 mg/L (Table 1).

Table 1: The effect of initial DBT concentration on DBT adsorption. Temperature: 25°C , contact time: 10 min , adsorbent to solution ratio: $0.1\text{g}/10\text{ mL}$

Initial DBT concentration (mg/L)	Adsorption capacity (mg/g)
100	9.91
500	48.8
800	72.98
1000	85.12
1200	91.53
1500	108.77
1800	108.76
2000	108.74
2200	108.76

The adsorption of DBT by Pb-Y zeolite can be explained in terms of the hard and soft acids and bases, which states that hard acids prefer to associate with hard bases, and soft acids prefer soft bases. Since Pb^{2+} is a soft acid, it prefers soft bases such as

DBT. Because of desirable capacity and reaction kinetic, the removal of DBT from the fuels by column operation is feasible.

The effect of contact time and initial DBT concentration was studied by Zhang and his co-workers. They reported DBT removal using Ag-Y sorbent. A capacity of 45mg S/g for DBT concentration 1500mg/L and equilibration time of 1h were obtained [20].

Wang reported the DBT adsorption to be 11mg/g, using NiCe-Y with DBT content of 500mg/L and at equilibration time of 2 h [21].

3.3. Adsorbent regeneration

The equilibrium adsorbent was regenerated by thermal treatment in the atmosphere at 450°C for 6 h [20]. Small reduction in the adsorption capacity was observed after the first regeneration (Table 2). The adsorption capacity of the adsorbent decreased within 17% after 5 successive regeneration cycles. The reduction in removal capacity can be attributed to the deposition of decomposed products on the adsorbent surface. However the adsorbent can be used at least for 3 regeneration cycles with 90% capacity.

Table 2: Effect of regeneration cycles on adsorption capacity. Adsorption conditions: Temperature: 25°C, initial DBT concentration: 1500 mg/L

Adsorption(%)	Adsorption capacity(mg/g)	Recycle No.
100	108.77	0
96.99	105.5	1
94.41	102.7	2
91.2	99.2	3
87.7	95.4	4
83.84	91.2	5

3.4. Adsorption isotherms

The equilibrium adsorption isotherm is important for the design and operation of adsorption systems. By plotting solid phase concentration against liquid phase concentration at the equilibrium condition, it is possible to depict the equilibrium adsorption isotherm. Here, the adsorption isotherm was studied by fitting experimental

data to Langmuir and Freundlich isotherms. The Langmuir model is developed to represent adsorption sites having the same sorption energies which are independent of surface coverage and have no interaction between adsorbed molecules. The Langmuir equation is represented in the linear form [22]:

$$\frac{C_e}{q} = \frac{C_e}{q_m} + \frac{1}{bq_m}$$

where q is the amount of DBT adsorbed at equilibrium (mg/g), C_e is the equilibrium DBT concentration in solution (mg/L), q_m is the maximum adsorption capacity (mg/g), and b is the Langmuir adsorption equilibrium constant (L/mg). Maximum sorption capacity (q_m) represents monolayer coverage of adsorbent and b represents the affinity between the adsorbent and the sorbate [23]. As shown in (Figure 5), the plot of C_e/q versus C_e yielded a straight line. From the slope and intercept, the values of q_m and b for the DBT adsorption are determined as 125 mg S/g and 0.03 respectively, with a correlation coefficient of 0.9982. It demonstrates that the DBT adsorption onto Pb-Y can be well explained by the Langmuir monolayer adsorption model.

The Freundlich isotherm gives an empirical model that assumes heterogeneous adsorption due to the diversity of adsorption sites. This isotherm does not predict any saturation of the adsorbent by the sorbate thus infinite surface coverage is mathematically predicted indicating a multilayer sorption of the surface. The linear form of Freundlich sorption is [24]:

$$\log q = \log k_f + \frac{1}{n} \log C_e$$

where K_f and n are equilibrium constants indicative of adsorption capacity and adsorption intensity, respectively. Using the experimental data, a log scale plot of q against C_e is performed and the values of K and n were estimated as 14/92 L/mg and 3/17, respectively, with a correlation coefficient of 0.8976. This result is

graphically depicted in (Figure 6). The numerical value of $1/n < 1$ ($1/n = 0.31$) indicates that sorption capacity is only slightly suppressed at lower equilibrium concentration. The adsorption equilibrium analysis (Figure 5 and 6) showed that Langmuir model gives a better fit to the adsorption isotherms - in the investigated concentration range - than that of the Freundlich model.

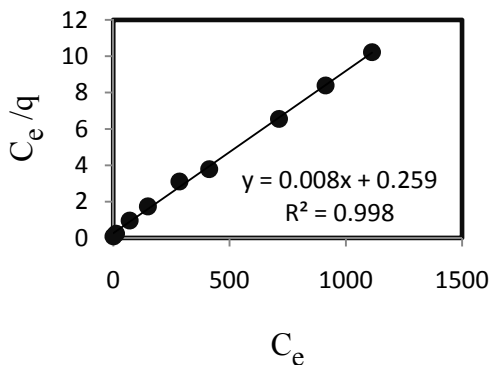


Figure 5: Langmuir isotherm at 25°C. Adsorbent to solution ratio: 0.1g/10mL; contact time= 10 min

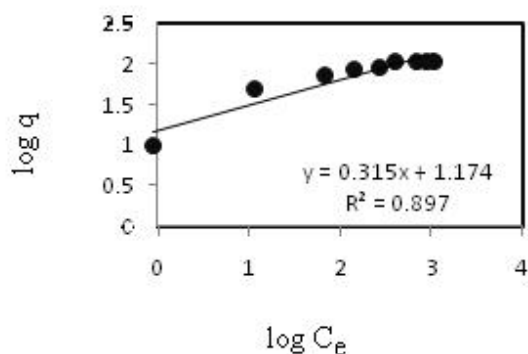


Figure 6: Freundlich isotherm at 25°C. Adsorbent to solution ratio: 0.1g/10mL; contact time= 10 min

3.5. Kinetic analysis

In order to gain a better understanding of the adsorption process, the kinetic models are used to test the experimental data. Adsorption kinetics were investigated by applying pseudo-first order, pseudo-second order and intra particle models.

The pseudo-first order model indicates that adsorption of adsorbate is a diffusion based process. The linearized form of pseudo-first order Lagergren model is [25]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

where q_t (mg /g) is the amount of adsorbed DBT on the adsorbent at time t (min), k_1 (min^{-1}) is the rate constant of the pseudo-first order adsorption and q_e (mg/g) is the equilibrium sorption uptake. Consistency of the experimental data with the pseudo-second order kinetic model indicated that adsorption is controlled by chemical process. The equation of pseudo-second order model is [25]:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where k_2 (g/mg.min) is the rate constant of pseudo-second order adsorption. q_e and k can be determined by plotting t/q versus t . The intra particle diffusion model which is written as:

$$q = K_i t^{1/2} + C$$

Where K_i is the intra particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$) and C (mg g^{-1}) is a constant related to the adsorption energy that is also examined [26]. Intra particle diffusion model constants can be determined as slope and intercept of linear plot of q versus $t^{1/2}$, respectively. If the regression of q versus $t^{1/2}$ is linear and passes through the origin, then intra particle diffusion is the proper rate-limiting step.

Because of the regression for intra particle diffusion, the model was not linear and did not pass through the origin (table 3), suggesting that the adsorption is not influenced by the intra particle diffusion and that it was not the rate controlling step.

The results of kinetic analysis are given in (Table 3). According to such data, the equilibrium sorption uptake value calculated from pseudo-first order model differ substantially from measured adsorption capacity while the q_e value attained from pseudo-second order model are only slightly lower. This result together with the fact that the points on the graphic interpretation of pseudo-second order model lies on the straight line and the correlation coefficient, R^2 value is close to 1; suggest that the

kinetic of adsorption of DBT on Pb-Y zeolite is described by the pseudo- second order model.

Table 3: Kinetic parameters of adsorption

	K_1	q_e	R^2
pseudo-first order	0.021	0.079	0.2908
	K_2	q_e	R^2
pseudo-second order	4.07	7.93	0.9998
	K_i	C	R^2
intra particle	0.0485	7.58	0.1449

Table 4: Experimental and calculated values of q_e and the relative error of kinetic models

	q_e (exp)	q_e (cal)	RE%
pseudo-first order	7.94	0.079	-99.005
pseudo-second order	7.94	7.93	-0.12

3.6. Comparison of accuracy of models

The above two mentioned kinetic models were used for modeling the adsorption kinetic of dibenzothiophene on Pb-Y zeolite. Statistical parameters such as the correlation coefficient (r^2) and relative error (RE) are evaluated as guiding parameters to find out the condition of best fit. The relative error is defined as:

$$RE = \frac{q_{cal} - q_{exp}}{q_{exp}} \times 100$$

Where q_{exp} and q_{cal} are the experimental and calculated values of q at equilibration time respectively. The experimental value of q_e , calculated value of q_e and the relative error (RE) for both models are listed in Table 4. The low relative error for pseudo-second order model indicates that this

model is a suitable model for description of adsorption kinetic.

4. Conclusion

In the present study, the adsorptive removal of DBT from organic medium by Pb-Y zeolite was systematically studied. The effects of experimental parameters such as initial DBT concentration and adsorption time were investigated and optimized. The optimal conditions were recognized as: contact time of 10 min and DBT concentration of 1500 mg.L^{-1} . The maximum adsorption capacity of $108.77 \text{ mg S.g}^{-1}$ was obtained. The large adsorption capacity of the adsorbent was attributed to the high specific surface area of zeolite (Table 5).

Equilibrium studies showed that the experimental data were fitted to Langmuir isotherm. The equilibrium adsorbent can be effectively regenerated by air-calcinations at 450°C . As the reaction kinetic was fast and desirable adsorption capacity was obtained, it is assumed that the prepared adsorbent could be used for removal of DBT at an ambient temperature and pressure.

Table 5: Surface area and pore volume data of ion exchanged Y zeolite

sample	Surface area (m^2/g)	Pore volume (ml/g)
HY	546	0.3045
NaY	540	0.3021
FeY	529	0.2982
CoY	532	0.2986
NiY	528	0.2974
CuY	530	0.2983
PdY	500	0.2870

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