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Simulation of a fixed bed adsorber for thiophene removal

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ABSTRACT

Breakthrough adsorption of 2-methyl thiophene on fixed beds of NiY, CeY and CeNiY adsorbents were evaluated at room temperature from a feed containing different concentrations of 2-methyl thiophene in *n*-hexane. The breakthrough curves were simulated by applying an axial dispersed plug flow model, modified to enable use of Langmuir isotherm parameters, for isothermal adsorption of trace systems. The model is able to predict the breakthrough curves fairly accurately. The model parameters include mass transfer coefficients and axial diffusivities. It is shown that the mass transfer parameters can be estimated independently of the experimental data. This improves the versatility of the model for scale up calculations.

1. Introduction

Economical deep desulfurization of petroleum based transportation fuels has become a great challenge in recent years because of the increasingly stringent sulfur specifications imposed world wide by different governmental agencies on gasoline and diesel fuel in order to minimize SO_x pollution [1]. Another reason for lowering sulfur level in reformulated gasoline is the use of noble metal catalysts in the catalytic converters of new generation vehicles. High levels of sulfur in such fuel lead to poisoning of these catalysts which can cause operational failure of catalytic converters and hence increased emission of harmful NO_x and unburned compounds into the environment with tremendous public health hazard [2]. Thus the recent US EPA Tier II regulation mandated a sulfur level of 30 ppmw and 15 ppmw in gasoline and diesel, respectively and like wise European Union gasoline and diesel fuel specifications call for 10 ppmw sulfur in Euro-IV. Another challenge in the near future would be to produce ultra low (<1 ppmw) or zero sulfur bearing liquid hydrocarbon fuels for fuel cell applications [3]. Conventional catalytic hydro desulfurization processes used in the petroleum refinery can economically reduce sulfur from few thousand ppm level to few hundred ppm level but it loses its economic advantage when deep desulfurization to few tens of ppm level is desired. This is because of the requirement of severe process conditions such as high hydrogen pressure and high temperature to catalytically decompose the more refractory organo-sulfur compounds [4]. In this context adsorption is emerging as an important option for ultra deep desulfurization of hydrocarbon fuels since compared to conventional catalytic hydro desulfurization processes, adsorptive desulfurization can be operated under milder process conditions and without or with negligible use of hydrogen, thus having considerable economic advantages [5].

In recent years a great deal of effort has been put both by academia and industry for identifying regenerable adsorbents for sulfur removal and developing adsorptive desulfurization processes based upon these adsorbents. Philips Petroleum, now Conoco Philips achieved a commercial breakthrough by developing and implementing a fluidized bed adsorptive desulfurization process named S-Zorb [6]. This process uses a proprietary mixed oxide based adsorbent and requires low hydrogen pressure. The process is based on reactive adsorption in which sulfur atom is abstracted from the organo-sulfur molecule and retained by the sorbent while the hydrocarbon part is released back into the product stream. The adsorbent gets quickly loaded up with sulfur and needs frequent regeneration under oxidative environment in a FCC type reactor system before reuse. Research Triangle Institute also reported a naphtha deep desulfurization process called TREND that uses a transport reactor and a metal oxide based adsorbent [7]. Limited consumption of hydrogen is also required for this process.

Few research groups have also tried removal of sulfur by physical adsorption of organo-sulfur molecules. Apart from mixed oxide based adsorbents, a group at Pennsylvania State University is working on development of transition metal exchanged zeolites,

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Nomenclature

C	dimensionless fluid phase concentration
C_0	feed concentration (mg/l)
C_i	concentration of thiophene in fluid (mg/l)
D_m	molecular diffusivity (m^2/s)
E_z	axial diffusivity (cm^2/s)
F	volumetric flow rate (cc/s)
K_0	slope of equilibrium isotherm
L	length of adsorbent bed (cm)
M_B	molecular weight of solvent B
Pe	Peclet number
q	dimensionless solid phase concentration
q_m	adsorbent capacity (mg/l)
r	adsorbent particle radius (cm)
Re	Reynolds number
T	temperature (°C)
t	time (s)
u	interstitial velocity (cm/s)
V_A	molal volume of solute A at its normal boiling point

Greek letters

α	mass transfer parameter
ε	bed voidage
η_B	viscosity of solvent
φ	association factor for solvent B
ρ_B	fluid density (g/cc)
τ	dimensionless time
τ_p	tortuousity
ψ	parameter defined in Eq. (2)

supported mixed metal oxides and mesoporous solid based adsorbents for deep desulfurization of diesel, gasoline, and jet fuels mainly for fuel cell applications [8]. Their adsorbents work on the principle of selective adsorption of organo-sulfur molecules, in presence of aromatic and polar species, by direct interaction between sulfur atom and the active metal sites present in the adsorbent. Another group at Michigan State University is working on Cu(I), Ni(II) and Ag(I) exchanged X and Y type zeolites which separate organo-sulfur molecules from gasoline, diesel and jet fuels by a completely different mechanism. The interaction between these metal ions inside the zeolitic channel with thiophenic molecules is suggested to be based on π-complexation, which allows higher selectivity and capacity for such molecules in comparison to a normal physi-sorption process [9]. At the same time, these bonds are still weak enough to be broken by raising temperature or decreasing pressure of the system thus allowing better regeneration of the adsorbents.

Transition metal exchanged zeolites being investigated by the above mentioned groups are showing promising results in adsorptive desulfurization of gasoline range hydrocarbons which may lead to commercial scale desulfurization processes based on adsorption in the future. However, there is no report so far in literature of a simulation study of the dynamic behavior of sulfur adsorption from liquid phase on a fixed bed of these zeolites. Such a study will be important for predicting scale up characteristics of a fixed bed adsorptive desulfurization process. In this paper, we have evaluated breakthrough adsorption of 2-methyl thiophene on fixed beds of three different metal exchanged zeolite adsorbents at room temperature from a feed containing different concentrations of 2-methyl thiophene in *n*-hexane and we have simulated the breakthrough curves by a mathematical model.

2. Experimental

2.1. Preparation of adsorbent

Three different metal exchanged zeolite adsorbents namely NiY, CeY and CeNiY have been investigated for their 2-methyl thiophene adsorption behavior in this study. The starting material used for preparation of these three adsorbents was NaY zeolite (Si/Al = 2.5) from M/s Süd Chemie India Ltd. Prior to ion exchange the NaY zeolite was calcined at 500 °C for 5 h. NiY adsorbent was prepared by ion exchanging NaY zeolite with required amount of 1.72 M aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$, under reflux conditions at 120 °C for 3 h. The amount of Ni^{2+} ion kept in exchange solution was four times the calculated ion exchange capacity of NaY. This exchange procedure was repeated two more times under same conditions. After each exchange, the solid was separated from the exchange solution by filtration and then washed with copious amount of distilled water. The solid was next dried at ambient temperature for 4 h followed by drying in an air oven at 120 °C for 12 h. Finally, after the completion of 3rd exchange, the zeolite was calcined at 500 °C in a furnace for 5 h.

For preparing CeY and CeNiY, the NaY zeolite was first converted to NH_4Y by ion exchange with 1 M NH_4Cl solution (the amount of NH_4^+ ions in the exchange solution was equivalent to five times the ion exchange capacity of NaY) for 48 h at room temperature followed by filtration, washing with distilled water and drying at 120 °C in an air oven. The NH_4Y thus formed was calcined at 500 °C for 5 h to form HY. CeY was prepared by ion exchanging this HY with required amount of 1 M $Ce(NO_3)_3$ aqueous solution (keeping the amount of Ce^{3+} equal to 2.5 times the theoretical proton exchange capacity of HY) for 24 h at 80 °C. The solid was recovered by filtration, washed with distilled water and dried at 120 °C for 12 h. The above exchange procedure was repeated one more time under same condition. The final solid was calcined at 500 °C for 5 h.

In the case of CeNiY, ion exchange of HY was first done with 1 M $Ce(NO_3)_3$ solution (Ce^{3+} = 0.5 times of the proton exchange capacity of HY) for 24 h at 80 °C followed by further exchange of the CeHY with 1 M aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ (amount of Ni^{2+} was equal to 1.5 times proton exchange capacity) at room temperature for 24 h. The final solid, CeNiY, was calcined at 500 °C for 5 h.

Table 1 reports data on the extent of metal ion exchange in the exchanged zeolites, determined from elemental analysis by ICP-AES, following dissolution of the zeolite matrix by HF and aqua-regia. BET Surface areas of the exchanged zeolites, determined from N_2 adsorption isotherm data at 77 K, are also reported in Table 1.

Extrudate of these exchanged zeolites was formed by adding calcined zeolite powder with γ-alumina powder as binder. The amount of binder added was 30 wt% of the total mixture. A thick paste was then formed by pouring required amount of 3 vol% acetic acid drop wise into the above mixture with continuous mixing. This paste was then pressed through a hand extruder to form cylindrical extrudates. The extrudates formed were dried at ambient temperature for 2 h and were then calcined at 500 °C for 5 h.

2.2. Adsorption breakthrough experiments

For fixed bed adsorption breakthrough experiment 6 g metal exchanged zeolite extrudate was packed inside a stainless steel column (19 mm internal diameter) which was positioned inside a three-zone tubular furnace. The inlet of the column was connected to a feed reservoir through a HPLC pump and the outlet was

Table 1
Extent of metal ion exchange and BET surface area of the adsorbents studied

Adsorbent	Metal ion exchanged	%Exchange[a]	BET surface area (m^2/g)
NiY	Ni(II)	97.2	362.3
CeY	Ce(III)	67.5	280.0
CeNiY	Ce(III)	18	243.6
	Ni(II)	13	

[a] Percentage of theoretical exchange capacity.

connected to a liquid collection unit through a condenser. The position of the adsorbent bed was kept in the middle position with respect to the furnace heating zone. Any dead space present inside the column was filled with inert alumina balls having no sulfur adsorption capacity. The adsorber column had the provision for measuring internal temperatures at three axial positions with the help of K type thermocouples placed suitably inside a thermocouple well, in-built with the column. Prior to the first adsorption experiment the adsorber column was heated at 350 °C in presence of flowing dry nitrogen for 2 h in order to remove any moisture present in the adsorbent bed. Next the adsorber was cooled down to room temperature under nitrogen, and a feed of 2-methyl thiophene in *n*-hexane was pumped in absence of any nitrogen flow. Column effluents were collected at different time intervals and absorbance values of 2-methyl thiophene in the effluents were recorded by UV spectroscopy at λ_{max} 233 nm. Concentration in terms of sulfur was then determined from a linear calibration curve prepared earlier by plotting absorbance versus concentration value of 2-methyl thiophene in calibration samples at the same wavelength. Adsorption breakthrough experiments were performed with each exchanged zeolite adsorbent with feeds having three different concentrations of 2-methyl thiophene varying from 150 mg/L to 1000 mg/L sulfur in hexane respectively. The feed flow rate was maintained at 4.0 ml/min throughout each adsorption experiment.

2.3. Regeneration experiments

After each adsorption experiment the bed was regenerated by following a two-step procedure. In the first step, the bed was purged by dry nitrogen at 350 °C for 1 h at ambient pressure. Next, a mixture of air and nitrogen containing 1–4% oxygen was passed through the bed at the same temperature and pressure for 1 h.

3. Modelling of thiophene adsorption in a fixed bed adsorber

The axial dispersed plug flow model as described by Raghavan et al. [10] for isothermal adsorption for trace systems was used to simulate the experimental breakthrough data. The model equations were modified to enable the Langmuir form of isotherm to be used and the modified mass balances are given below:

$$\frac{\partial C}{\partial \tau} = \frac{1}{Pe}\frac{\partial^2 C}{\partial x^2} - \frac{\partial C}{\partial x} - \psi\alpha\left[\frac{\beta C}{1+\beta C} - q\right]. \quad (1)$$

The parameters ψ and α are defined as follows:

$$\psi = \frac{(1-\varepsilon)q_m}{\varepsilon C_0} \quad (2)$$

$$\alpha = \frac{Lk}{u}. \quad (3)$$

The particle mass balance is:

$$\frac{\partial q}{\partial \tau} = \alpha\left[\frac{\beta C}{1+\beta C} - q\right]. \quad (4)$$

The above equations were discretized by the method of orthogonal collocation using shifted Legendre polynomials [11]. The resulting system of ordinary differential equations was solved by a fourth order Gear algorithm with a variable step size strategy [12].

4. Results and discussion

The breakthrough curves obtained with the model feed mixtures of 2-methyl thiophene in hexane are shown in Figs. 1–9. The

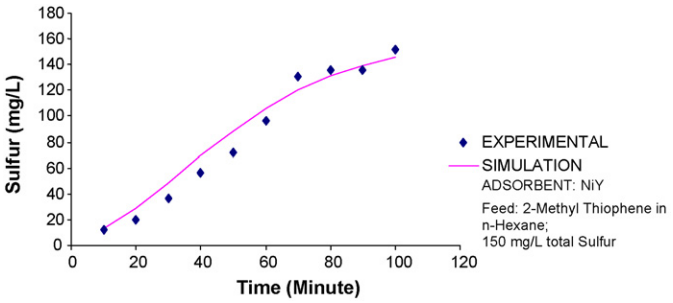

Fig. 1. Simulation of breakthrough data.

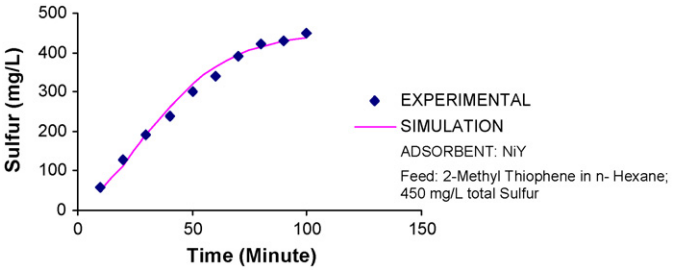

Fig. 2. Simulation of breakthrough data.

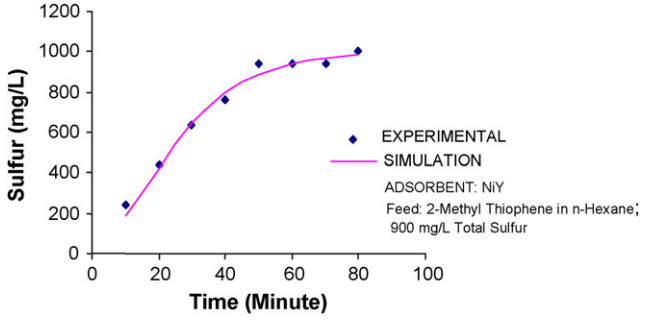

Fig. 3. Simulation of breakthrough data.

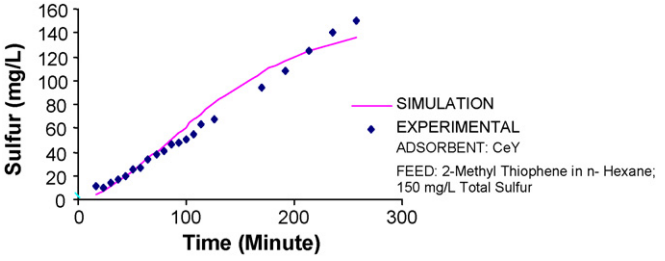

Fig. 4. Simulation of breakthrough data.

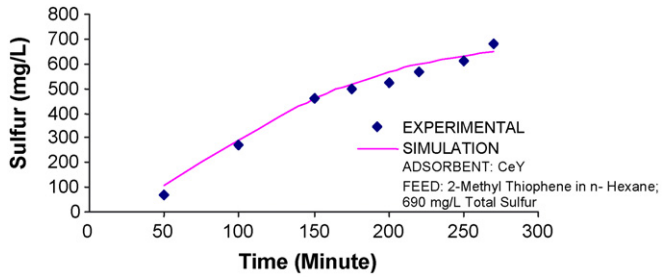

Fig. 5. Simulation of breakthrough data.

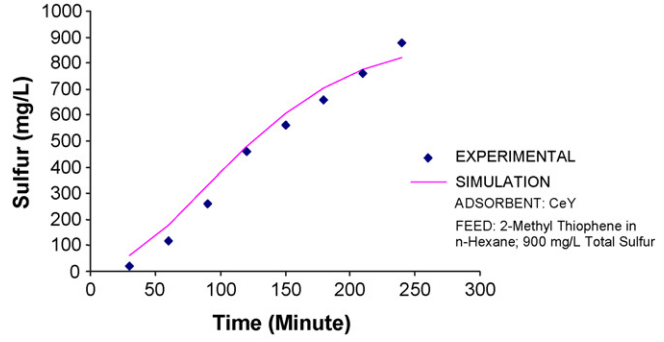

Fig. 6. Simulation of breakthrough data.

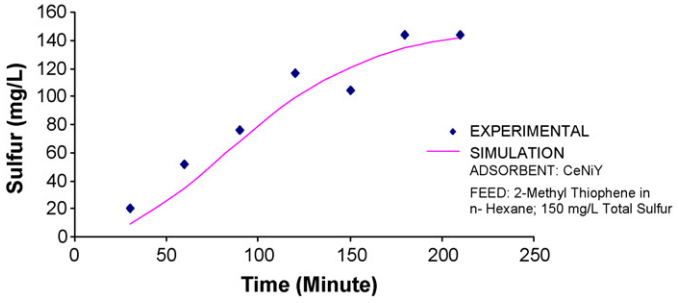

Fig. 7. Simulation of breakthrough data.

thiophene adsorption capacities at the experimental temperature (30 °C) on each adsorbent corresponding to the three feed concentrations could be estimated by integration of the time versus concentration breakthrough data using the following relation:

$$Q = FtC_{\text{feed}} - F\int C_{\text{i}}\,\mathrm{d}t. \tag{5}$$

The adsorption capacities corresponding to each feed concentration for the three adsorbents thus obtained are given in Table 2. The Langmuir isotherm parameters could be extracted from this

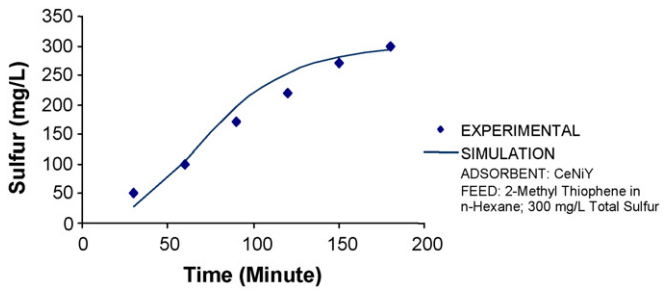

Fig. 8. Simulation of breakthrough data.

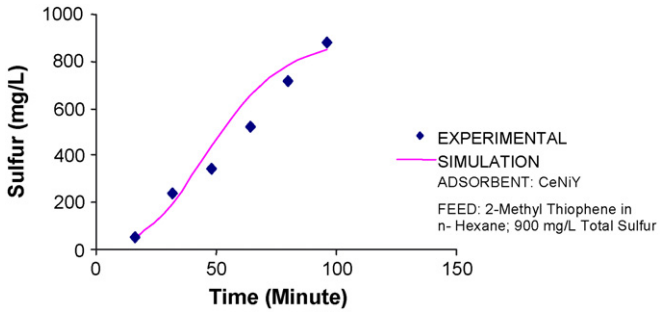

Fig. 9. Simulation of breakthrough data.

Table 2
Equilibrium capacities and Langmuir isotherm parameters from breakthrough measurements

Adsorbents	Equilibrium sulfur concentration in liquid phase (mg/L)	Equilibrium sulfur concentration in adsorbent phase (mg/g)	Langmuir constant, q_m (mg/L)	Langmuir constant, b (L/mg)
NiY	150	6.39		
	450	13.8	2,50,000	1.47×10^{-3}
	1000	19.19		
CeY	150	13.33		
	690	60.2	10,00,000	6.76×10^{-5}
	900	72		
CeNiY	150	9.87		
	300	18.29	50,000	1.17×10^{-3}
	900	32.47		

data and are also given in Table 2. The column dimensions, fluid and adsorbent properties required in the simulations are summarized in Table 3.

The simulation requires knowledge of two parameters, the mass transfer parameter α and the column Peclet number, *Pe*. In the first instance the simulation was run using these as adjustable parameters. The best fit estimates for the mass transfer parameter and the column Peclet number for each adsorbent are given in Table 4. A comparison of experimental and model predicted breakthrough curves with these values of α and *Pe* are shown in Figs. 1–9. As can be seen, the model is able to predict the thiophene breakthrough curves fairly well with a Peclet number of 10 and mass transfer parameter ranging from 0.055 to 0.08.

An attempt was also made to estimate the dimensionless mass transfer parameter α and Peclet number from correlations

Table 3
Parameters used in simulation

Parameters	Adsorbents		
	NiY	CeY	CeNiY
Molecular diffusivity of 2-methyl thiophene in hexane ($m^2\ s^{-1}$)	4.8×10^{-9}	4.8×10^{-9}	4.8×10^{-9}
Adsorbent particle radius (m)	1.4×10^{-3}	0.8×10^{-3}	0.9×10^{-3}
Fluid viscosity (kg/m s)	0.278×10^{-3}	0.278×10^{-3}	0.278×10^{-3}
Adsorbent density (kg/m^3)	750	750	750
Tortuosity	1.4	1.4	1.4
Particle porosity [16]	0.45	0.45	0.45
Bed voidage	0.3	0.3	0.3
Column length (m)	0.04	0.04	0.035
Column diameter (m)	0.019	0.019	0.019

Table 4
Comparison of calculated values of simulation parameters with best fit estimates

Adsorbent	Peclet number *Pe*		Mass transfer parameter α	
	Best fit estimate	Calculated	Best fit estimate	Calculated
NiY	10	4.0	0.07	0.051
CeY	10	6.7	0.05	0.052
CeNiY	10	6.7	0.08	0.077

available in literature. Thus the mass transfer coefficient, k was calculated by Linear Driving Force model using the Gleuckauf relationship [13]:

$$k = \frac{15\varepsilon_p D_m K_0}{r^2 \tau_p}. \quad (6)$$

The molecular diffusivity of thiophene in hexane was estimated by the Wilke Chang equation [14]:

$$D_m = \frac{7.4e^{-8}(\varphi M_B)^{0.5} T}{\eta_B V_A^{0.6}}. \quad (7)$$

A tortuousity of 1.4 was assumed for the Y zeolite in these calculations.

The column Peclet number *Pe* was estimated from the correlation of Chung and Wen [15]:

$$\frac{E_z \rho_B}{\eta_B} = \frac{Re}{0.20 + 0.011 Re^{0.48}} \quad (8)$$

$$Pe = \frac{Lu}{E_z}. \quad (9)$$

The calculated value of mass transfer coefficient using Eqs. (6) and (7) was used to estimate α for each adsorbent and the values are given in Table 4. It is seen that the predicted values of α are fairly close to the best fit estimates. However, the column Peclet number was found to be lower than the best fit estimate. It is likely that the correlations of axial diffusivity estimation in fixed beds are not applicable in the present case as our L/D ratio is very much smaller since our experiments were at a preliminary screening level. Further breakthrough measurements are required in adsorber columns of higher bed length to firm up the axial diffusivity.

5. Conclusion

Breakthrough measurements have been made in the liquid phase adsorption of 2-methyl thiophene from mixtures in hexane on three different exchanged Y-zeolite adsorbents. The experimental breakthrough curves have been simulated by a mathematical model which assumes isothermal adsorption of thiophene on the Y-zeolite. The model is able to predict the breakthrough curves fairly accurately. The model parameters include mass transfer coefficients and axial diffusivities. It is shown that the mass transfer parameters can be estimated independently of the experimental data. This improves the versatility of the model for scale up calculations. However, the axial diffusivities as estimated from correlations available in literature are not able to give simulations to a satisfactory degree and have to be estimated as a fitting parameter. This could probably be due to the very low L/D ratio of the adsorber column used in the present study which is at a preliminary screening level. Further work on adsorber columns with larger L/D ratios wherein the available correlations are expected to be applicable, are warranted to firm up the axial diffusivity estimation procedures.

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