



Petroleum Research

Petroleum Research 2018 (August-September), Vol. 28, No. 99. 21-25

DOI: 10.22078/pr.2018.2475.2146

Experimental Investigation and Mathematical Modeling of 4,6-DMDBT Adsorption on Modified Activated Carbon

Jaafar Sasanipour, Ahmad Shariati*, Masoud Aghajani, and Mohamadreza Khosravi Nikou

Gas Engineering Department, Ahwaz Faculty of Petroleum, Petroleum University of Technology, Ahwaz, Iran

shariati@put.ac.ir

DOI: 10.22078/pr.2018.3185.2465

Received: February/15/2017

Accepted: May/08/2018

Abstract

In this study, equilibrium and kinetic adsorption of 4,6-DMDBT removal from model fuel, using an acid treated activated carbon is investigated. The equilibrium adsorption capability of this adsorbent is investigated. The equilibrium adsorption data fitted by Freundlich and Toth isotherms. The kinetic adsorption is also investigated by using two kinetic models: intraparticle diffusion model, and homogeneous surface diffusion model (HSDM). The results have shown that the experimental equilibrium adsorption data were fitted very well with both Freundlich and Toth isotherms. Homogeneous surface diffusion model very well fitted kinetic experimental data. Mathematical modeling of the process using HSDM results in values of mass transfer and diffusion coefficients as 2.5558×10^{-2} m/min and 3.4056×10^{-6} m²/min for 4,6-DMDBT adsorption, respectively. HSDM also reveals that both boundary layer diffusion and diffusion into pores of adsorbent are present at the rate-limiting step of the adsorption process.

Keywords: Adsorption Equilibrium; Adsorption Kinetics; Homogeneous Surface Diffusion Model; Mass Transfer Coefficient, 4,6-DMDBT.

INTRODUCTION

Sulfur compounds in the fuels cause many environmental pollution impacts. They also result in acid rains. Usually separation of sulfur compounds in conventional methods including hydrogenation of the fuels with hydrogen gas. But the problem is that the conventional methods are unable to remove all sulfur compounds. For example, strong compounds such as tujene, benzo-tujene, dibenzo-tujene, and their derivatives cannot be separated by conventional methods with hydrogen gas [1]. In order to separate such components, other methods must be used. Adsorption by the porous adsorbent is a method that can be used for such separation. Recently, some studies in the literature investigated the capability of adsorption process for separation of sulfur compounds by zeolite adsorbent, activated carbon and modified activated carbon with copper, nickel, argent, and potassium hydroxide [2-7]. Investigation of theoretical models of adsorption behavior for describing equilibrium and kinetics of the adsorption process is also important. These studies help to understand the mechanism and optimize the process.

In this study, activated carbon for adsorption of sulfur compound from a synthesis fuel was modified and used. In order to obtain the kinetic and isotherm of modified activated carbon, equilibrium, and kinetics experimental adsorption is performed, and different theoretical model is fitted to the experimental model. Finally, with mathematical modeling of the adsorption process, the mass transfer coefficient for sulfur compounds is calculated.

EXPERIMENTAL METHOD

In this study, activated carbon has been employed for sulfur compound adsorption. This activated carbon is charcoal base and the particle diameter is about 1 mm. the BET surface area is 1290 m²/g of adsorbent and micropore diameter is 1.6 nm. At first, in order to remove impurities from the activated carbon, it was washed with acetone several times and dried. For modification, the activated carbon was treated with 4M nitric acid for 24h in lab temperature. After that, the mixture was filtered and successively washed with distilled water until the pH became neutral. Then the adsorbent was dried at 80°C in an oven overnight. For measuring the isotherm, equilibrium adsorption was employed. The synthesis fuel included n-decane as hydrocarbon fuel and 4,6-dimethyldibenzotujene as a sulfur compound. For adsorption equilibrium experiment, 10 ml of synthesis fuel with 0.1g of modified adsorbent was mixed in a sealed bottle and mixed with a magnetic stirrer for 24h at lab temperature (25°C). The initial concentration of sulfur compound was varied from 400-1200 ppm. After equilibrium reached, the final concentration of the sulfur compound in the fuel was measured with a gas chromatograph. For the kinetic experiment, about 0.1 g of adsorbent was contacted with 10 ml of synthesis fuel with an initial concentration of 1200ppm. At a certain time interval, 0.4 µl of the sample withdrawn by a GC syringe and analyzed by GC. In order to investigate the repeatability of the experiment, in some concentrations, the experiments were repeated twice. The repeatability of the experiments revealed that the data are repeatable with a maximum error of ±6%.

RESULTS

MODIFICATION OF ADSORBENT

The BET surface area measurement revealed that the surface area of the modified adsorbent reduced to 830 m²/g of adsorbent. Also, it was revealed that the total pore volume of the adsorbent reduced from 0.55 cm³/g to 0.37 cm³/g. In addition, it was determined that the mean pore diameter of the adsorbent has not changed by acid modification. The energy dispersive X-ray (EDX) analysis showed that the initially activated carbon is just carbon, but modification of the adsorbent introduced oxygen atoms to the structure of the adsorbent by 9 wt%. This oxygen introduced in form of carbonyl and hydroxyl group to the surface of the adsorbent.

EQUILIBRIUM AND KINETIC OF 4,6-DMDBT

Figure 1 shows the 4,6-DMDBT concentration variation with time in the liquid phase at lab temperature (25°C). As Figure 1 shows, at the beginning the kinetic is rapid and after 250 min the equilibrium is reached.

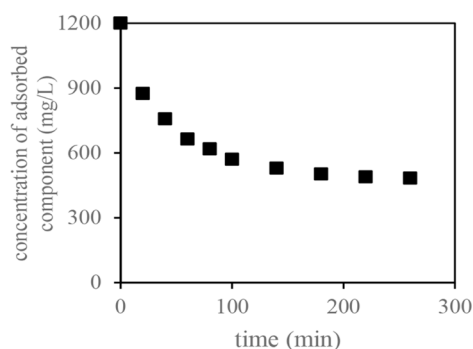


Figure 1: Concentration change of 4,6-DMDBT at 25°C.

The adsorbed amount can be calculated according to the following equation:

$$q = \frac{V(C_0 - C_e)}{M} \quad (1)$$

where q is the amount of adsorbed, V is the initial volume of the liquid, C_0 is the initial concentration of the sulfur compound in the liquid phase, C_e is the equilibrium concentration of the sulfur compound and the M is the mass of adsorbent used.

In Figure 2, the fitted Freundlich and Toth isotherms with experimental data are presented. As it can be seen, both isotherms predicted experimental data very well. The value of $1/n$ in Freundlich showed the intensity of the adsorption which higher value shows favorable adsorption (Table 1). As Figure 2 shows, at 550 ppmw the amount of 4,6-DMDBT adsorption is near its saturation. At higher concentration, the amount of adsorption did not increase significantly. The isotherm is type I which indicated single layer adsorption. The results showed that the sulfur compounds adsorption on activated carbon is irreversible where increasing the temperature of the adsorbent to 850 K, the amount of adsorbed sulfur on the surface of the adsorbent is near 70 % of its initial amount. This can be attributed to the chemical interaction of the sulfur with the oxygen on the surface of the adsorbent.

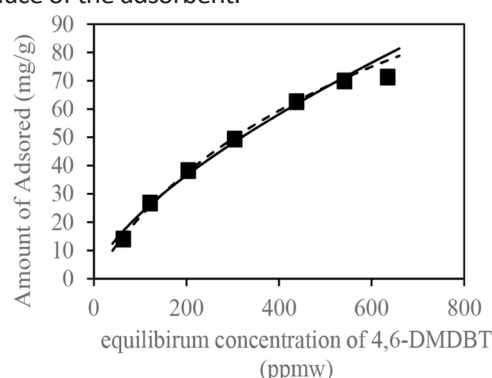


Figure 2: Equilibrium adsorption isotherm, ■ experimental data, - - Toth isotherm, __ Freundlich isotherm.

Table 1. The fitted value of both isotherms is presented in table 1.

Isotherm	Parameter	value
Freundlich	$K (L/g)^n$	0.9154
	$n/1$	0.7312
	R^2	0.9949
Toth	$(q_m (mg/g)$	182.7039
	$(b (l/mg)$	0.00197
	t	0.8476
	R^2	0.9996

MATHEMATICAL MODELING OF THE ADSORPTION PROCESS

In order to investigate the kinetics of adsorption, two models including homogenous surface diffusion (HSDM) and pore diffusion model (PDM) were employed. The predicted amount of adsorption and the relative error of both model are presented in Table 2. The relative error was calculated according to the following equation.

$$RE = 100 \times \left(\frac{|q_{cal} - q_{exp}|}{q_{exp}} \right) \quad (2)$$

The higher relative error value for the pore diffusion model compared to the homogenous surface diffusion indicates that this model cannot predict the kinetic behavior of the present system. It can be concluded that the homogenous surface diffusion model is a proper model for prediction

of the kinetic behavior of sulfur compound adsorption on activated carbon.

The pore diffusion model prediction is less accurate compared to HSDM model which can be attributed to the hard adsorption of 4,6-DMDBT compound on the adsorbent sites. The pore diffusion model assumes that the rate controlling step is the diffusion of the particle on the pore while in HSDM it is assumed that the rate controlling step is the adsorption of adsorbate on the surface of the adsorbent. 4,6-DMDBT molecule is a hard adsorbed molecule, and therefore diffusion inside pores is difficult. Therefore, the rate controlling step is adsorption on the surface which is predicted in the HSDM model. Therefore, the HSDM has a better prediction of the amount of adsorption.

Table 2: Kinetic experimental value and mathematical model prediction with relative error.

Time (min)	Experimental value (mg/g)	Calculated value (mg/g)		Relative error (%)	
		PDM	HSDM	PDM	HSDM
20	30.5939	30.9426	30.4165	1.32	0.4
40	44.2360	38.9607	43.9228	12.54	0.71
60	51.6272	44.6361	51.0318	13.54	1.15
80	56.1856	49.6482	55.8405	11.64	0.61
100	59.9167	54.0640	59.4462	9.77	0.79
140	65.0877	61.7274	64.4952	5.16	0.91
180	67.7543	68.3538	67.7975	0.88	0.06
220	69.2411	74.2670	70.0931	7.27	1.23
260	69.6662	79.6810	71.7116	14.38	2.94
Mean relative error	-	-	-	8.50	0.98

CONCLUSIONS

Investigation of equilibrium and kinetic adsorption of 4,6-DMDBT from synthesis fuel on modified activated carbon revealed that the Freundlich and Toth isotherms can predict the experimental isotherm data. Also, mathematical modeling of adsorption kinetic with PDM and

HSDM models has revealed that the HSDM model has a better prediction of kinetics adsorption . In addition, the mass transfer coefficient and mass transfer diffusion of $2.5558 \times 10^{-2} \text{ m}^2/\text{min}$ and $3.4056 \times 10^{-6} \text{ m}^2/\text{min}$ for 4,6-DMDBT adsorption was calculated respectively.

REFERENCE

- [1]. Xue M., Chitrakar R., Sakane K., Hirotsu T., Ooi K., Yoshimura Y., Feng Q. and Sumida N., "*Selective adsorption of thiophene and 1-benzothiophene on metal-ion-exchanged zeolites in organic medium,*" J. Colloid Interface Sci., Vol. 285, No. 2, pp. 487–492, 2005.
- [2]. Ahmed I. and Jhung S. H., "*Adsorptive desulfurization and denitrogenation using metal-organic frameworks,*" J. Hazard. Mater., Vol. 301, pp. 259–276, 2016.
- [3]. Jung B. K. and Jhung S. H., "*Adsorptive removal of benzothiophene from model fuel, using modified activated carbons, in presence of diethylether,*" Fuel, Vol. 145, pp. 249–255, 2015.
- [4]. Khan N. A., Kim C. M. and Jhung S. H., "*Adsorptive desulfurization using Cu–Ce/metal-organic framework: Improved performance based on synergy between Cu and Ce,*" Chem. Eng. J., Vol. 311, pp. 20–27, 2017.
- [5]. Shi Y., Zhang X. and Liu G., "*Activated carbons derived from hydrothermally carbonized sucrose: remarkable adsorbents for adsorptive desulfurization,*" ACS Sustain. Chem. Eng., Vol. 3, No. 9, pp. 2237–2246, 2015.
- [6]. Ishaq M., Sultan S., Ahmad I., Ullah H., Yaseen M. and Amir A., "*Adsorptive desulfurization of model oil using untreated, acid activated and magnetite nanoparticle loaded bentonite as adsorbent,*" J. Saudi Chem. Soc., Vol. 21, No. 2, pp. 143-151, 2015.
- [7]. Jin T., An S., Yang X., Hu J., Wang H., Liu H., Tian Z., Jiang D., Mehio N. and Zhu X., "*Efficient adsorptive desulfurization by task-specific porous organic polymers,*" AIChE J., Vol. 62, No.6, pp. 1740-1746, 2016.