Research note

Adsorption of Volatile Organic Compounds from Aqueous Solution by Granular Activated Carbon (GAC) in Batch System

F. Zeinali, A. A. Ghoreyshi*, G. Najafpour
Chemical Engineering Department, Babol Noshirvani University of Technology, Babol, Iran

Abstract

Chlorinated hydrocarbons and aromatics are the major volatile organic compounds that contaminate the ground water and industrial waste waters. The best way to overcome this problem is to recover the dissolved compounds in water. In order to evaluate the potential ability of granular activated carbon (GAC) for recovery of volatile organic compounds from water, the equilibrium adsorption was investigated. This study deals with the adsorption of dichloromethane as a typical chlorinated volatile organic compound (VOCs) and toluene as the representative of aromatic volatile organic compounds on a commercial GAC. The adsorption isotherms of these two volatile organic compounds on GAC were measured at three different temperatures, toluene at 293, 303 and 313 K and dichloromethane at 298, 303 and 313 K within their solubility concentration range in water. The maximum adsorption capacity of dichloromethane and toluene adsorption by GAC was 4 and 0.2 mol/Kg-1, respectively. The experimental data obtained were correlated with different adsorption isotherm models. The Langmuir model was well adapted to the description of dichloromethane adsorption on GAC at all three temperatures, while the adsorption of toluene on GAC was found to be well described by the Langmuir-BET hybrid model at all three temperatures. The heat of adsorption was also calculated based on the thermodynamic equation of Clausius–Clapeyron, which indicates the adsorption process is endothermic for both compounds.

Keywords: *Adsorption, Dichloromethane, Toluene, Isotherm, GAC*

1. Introduction

The US EPA defined volatile organic compounds (VOC) as stable products exhibiting a vapor pressure above 0.1mmHg (13.332 Pa) at ambient conditions [1]. Chlorinated volatile organic compounds (CVOCs) are a subgroup of VOCs containing some chlorine in the compounds. Their sources in the environment are wastewaters from industries manufacturing herbicide, pesticide, paint, solvent, pharmaceutical, pulp, and paper. The saturated solubility of dichloromethane is considerably higher than other CVOCs [2]. They are toxic, carcinogenic, irritating, and flammable. VOC emissions cause the depletion of the stratospheric ozone layer, photochemical formation of smog, and direct action on

---

∗ Corresponding author: aa_ghoreyshi@nit.ac.ir

human tissues [3]. VOCs are known not only as valuable chemical agents, but also as major pollutants in industrial processes and environmental activities. For this reason, a considerable number of technologies such as combustion, adsorption, absorption, condensation, biofiltration and catalytic oxidation have been extensively used to control, recover and reduce the emissions of VOCs from industrial facilities and also to protect the environmental systems. Among these technologies, the adsorption method has been widely applied in practical applications due to easy operation, low operating cost, high capacity, high selectivity and efficient recovery of most VOCs at low partial pressures [4]. Different types of sorbents have been used in industrial applications, e.g. zeolite, alumina, silica and activated carbon. The latter is an amorphous solid which is exploited in many industrial and environmental applications due to its large internal surface area [5] and its unique mesoporosity and microporosity [6]. The adsorption characteristics of activated carbon depend on the type of starting material, methods and conditions of preparation [7].

In the present study, the equilibrium adsorption of dichloromethane and toluene as two major VOC pollutants of water was experimentally investigated. The experimental data were correlated with different adsorption isotherms models at three different temperatures. A thermodynamic analysis was also conducted to derive a heat of adsorption which gives insight into the thermal nature of adsorption.

2. Experimental
2-1. Materials and methods
The VOCs selected in this study were toluene (mass fraction 0.99 purity) and dichloromethane (mass fraction 0.998 purity). They were purchased from Merck. Coal-based granular activated carbon (GAC) with a size range of 1-3 mm and bulk density of 0.4 g cm^{-3} was purchased from Appli Chem Co. (Germany).

2-2. Equilibrium experiment
Prior to the start of the experiment, GAC was dried in an oven at 115°C to remove all already adsorbed gases and moisture content. The dry based weight of the adsorbent was measured after it was dried for 48 h in an oven at 388 K. The adsorption experiments were carried out by contacting a given amount of adsorbent (3 gr) (weighted by a balance Sartorius Model GE 412, Germany with an accuracy of 0.01 g) with different initial concentrations of adsorbate solutions in an incubator shaker at constant temperature. For each experimental run, 100 ml of toluene and dichloromethane solution of known initial concentration (C_0) and adsorbent dose (3gr) taken in a 250 ml conical flask with a stopper was agitated in a temperature-controlled shaker at a constant speed of 190 rpm. Samples were periodically collected every 15 minutes min and their concentrations were determined by a spectophotometer until the equilibrium was reached (normally after 2 hours). Effect of temperature on toluene and dichloromethane adsorption was studied at three different temperatures.

The adsorption capacity of the granular activated carbon was determined according

to the following equation:

$$q_e = \frac{V(C_0 - C_e)}{w} \qquad (1)$$

Where C_0 and C_e are the initial and equilibrium liquid phase concentrations (molm^{-3}), respectively, V is the volume of solution (m^3), and w is the weight of dry sorbents (kg).

3. Results and discussion

3-1. Adsorption equilibrium

Adsorption isotherm is the most fundamental and informative data on an adsorption system. It is also very important in model prediction for analyzing and designing an adsorption process. Adsorption onto a sorbent is generally driven by the force dispersed between the adsorbate and adsorbent. Thus, the adsorption capacity depends on the properties of both the sorbate and the sorbent. By investigating the effect of contact time, it was found that the adsorption of toluene and dichloromethane is fast in the first 30 min, thereafter, the toluene and dichloromethane removal become very slow. Fig. 1 shows the adsorption isotherms of toluene on GAC at three different temperatures, i.e. 293, 303 and 313 K and Fig. 2 depicts the adsorption isotherms of dichloromethane on GAC at temperatures of 298, 303 and 313 K. Several equilibrium isotherm equations, namely, Langmuir, Freundlich, Redlich–Peterson and Langmuir-BET hybrid isotherm have been tested to represent the experimental sorption isotherm data.

Langmuir model can be described by the following equation:

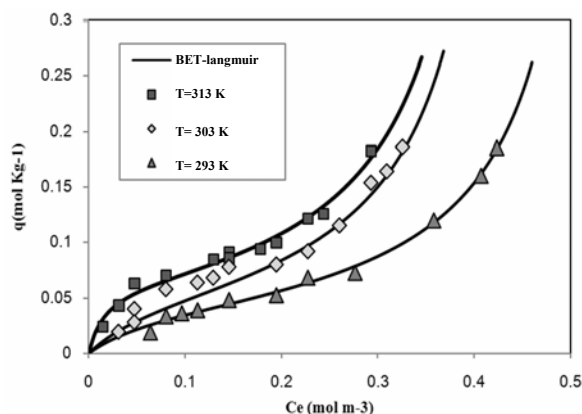$$q_e = \frac{q_m \, b \, C_e}{1 + b \, C_e} \qquad (2)$$

Figure 1. Adsorption isotherms of toluene on GAC at T= 298, 303, and 313 K. symbols=experimental data, line=model
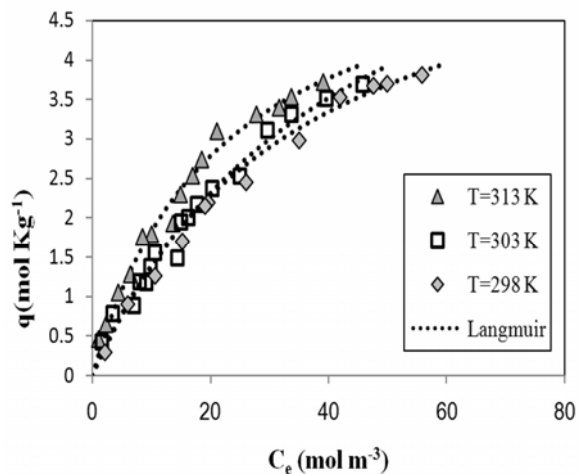

Figure 2. Adsorption isotherms of dichloromethane on GAC at T= 298, 303, and 313 K, symbols= experimental data, line=model

Where C_e is the equilibrium concentration of the adsorbate (molm^{-3}), q_e is the amount of adsorbate adsorbed per unit weight of the adsorbent (molkg^{-1}), and q_m and b are the Langmuir isotherm constants related to

maximum adsorption capacity and energy of adsorption, respectively. The Langmuir-BET model is described by the equation:

$$q_e = \frac{q_m b C_e}{1+b C_e} + \frac{q_m K_{BET} C_s C_e}{(C_s - C_e)[C_s + (K_{BET} - 1) C_s]} \quad (3)$$

Where K_{BET} is the BET isotherm model parameter and C_s is the saturated solubility of the compound in water.

Matlab 7.5 (2007) has been employed to recover isotherm equation parameters through a nonlinear fit to the experimental data. By comparing the experimental results with equilibrium isotherm equations, it is found that Langmuir-BET hybrid isotherm represents the toluene-GAC data, while the Langmuir isotherm best represents well the dichloromethane-GAC data. The Freundlich model and the Redlich–Peterson model were not satisfactory.

The parameters of model isotherm for adsorption of dichloromethane and toluene on activated carbon (GAC) at three different temperatures are listed in Table1.

3-2. Effect of temperature
The effect of temperature on the equilibrium

uptake of toluene and dichloromethane by GAC was studied. As Fig. 1 and Fig. 2 show, it is evident that the sorption of toluene and dichloromethane, and hence the toluene and dichloromethane removal from the solution, increases with an increase in temperature, which shows that the sorption of both adsorbates (toluene and dichloromethane) is an endothermic process.

3-3. Estimation of heat of adsorption
Apparent isosteric heat of adsorption ($\Delta H_{st,a}$) at different constant equilibrium uptake (q_e = 0.05mol kg^{-1}, 0.1 mol kg^{-1}, 0.15 mol kg^{1}, and 0.18 mol kg^{-1} for toluene and q_e =1.5 mol kg^{-1}, 2.5 mol kg^{-1}, 3 mol kg^{-1}, and 3.95 mol kg^{-1} for dichloromethane) was calculated using the Clausius–Clapeyron equation [7]:

$$\frac{d \ln C_e}{dT} = \frac{-\Delta H_{st,a}}{RT^2}$$

$$\frac{d \ln C_e}{dT} = \frac{-\Delta H_{st,a}}{RT^2} \quad (4)$$

Table 1. The fitting parameters of Langmuir and Langmuir–BET equations for dichloromethane and toluene at three different temperatures.

Isotherms	Constants	Dichloromethane			Toluene		
		Temperature(K)					
		298	303	313	293	303	313
Langmuir	B	7.12	7.3382	5.8510	_	_	_
	q_m	0.02166	0.0230	0.04565	_	_	_
	R^2	0.9821	0.9849	0.9881	_	_	_
Langmuir-BET	B	_	_	_	13.03	22.98	58.01
	q_m	_	_	_	0.04391	0.05631	0.06287
	K_{BET}	_	_	_	0.2444	0.4614	0.2763
	R^2	_	_	_	0.9956	0.9856	0.9869

For this purpose, C_e at constant q_e was obtained from the Langmuir-BET adsorption isotherm equation for toluene and from the Langmuir adsorption isotherm equation for dichloromethane at different temperatures. $\Delta H_{st,a}$ is calculated from the slope of the $\ln(C_e)$ versus $(1/T)$ plot (Fig. 3a and 3b). Fig. 3 (a) and (b) show that $\Delta H_{st,a}$ decreases as the equilibrium uptake increases. The positive value for heat of adsorption (positive slope) reconfirmed that the sorption of toluene and dichloromethane on GAC is an endothermic process. The calculated heat of adsorption at different constant equilibrium uptakes have been shown in Tables 2 and 3 for toluene and dichloromethane, respectively. However, the low values obtained for $\Delta H_{st,a}$ for both components (maximum 6.64 $KJ.mol^{-1}$ in Table 2) indicated that the adsorption of both components onto GAC adsorbent was dominated by physisorption.
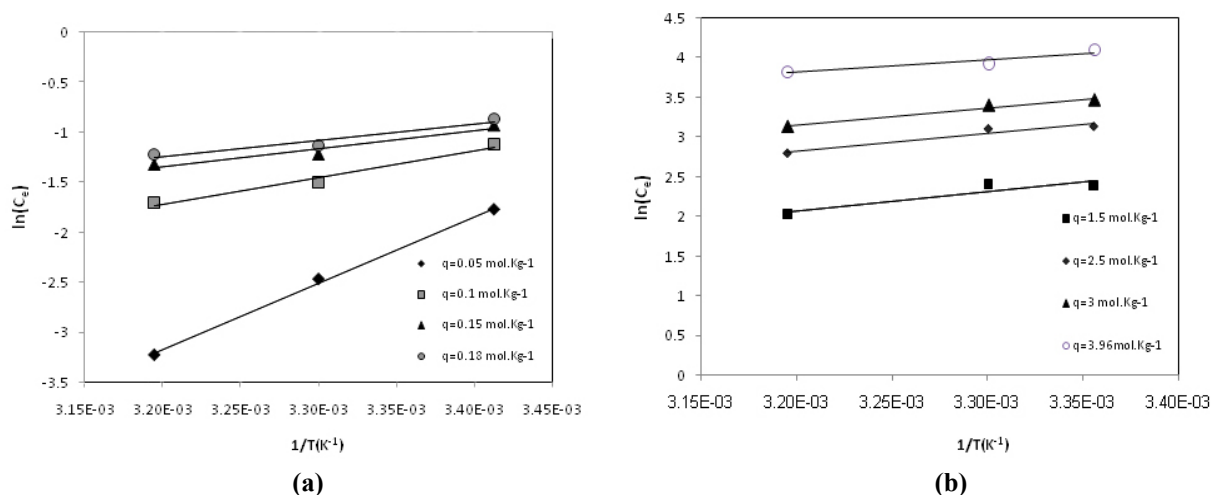

Figure 3. Adsorption isotherm for determining heat of adsorption for
(a) toluene on GAC. (b) dichloromethane on GAC.

Table 2. *$\Delta H_{st,a}$* calculated from the slope of the *$\ln(C_e)$* versus *(1/T)* and the values of *C_e*
at different temperatures for toluene

q_e (mol. Kg^{-1})	C_e (mol. m^{-3}), at T=293 K	C_e (mol. m^{-3}), at T=303 K	C_e (mol. m^{-3}), at T=313 K	$\Delta H_{st,a}$, (J. mol^{-1})
0.05	0.17	0.085	0.0399	6640
0.1	0.327	0.223	0.182	2694
0.15	0.396	0.295	0.266	1833
0.18	0.42	0.321	0.296	1628

Table 3. $\Delta H_{st,a}$ calculated from the slope of the $ln(C_e)$ versus $(1/T)$ and the values of C_e at different temperatures for dichloromethane

q_e (mol/Kg)	C_e (molm^{-3}), at T=298 K	C_e (molm^{-3}), at T=303 K	C_e (molm^{-3}), at T=313 K	$\Delta H_{st,a}$, (J/mol)
1.5	10.97	11.16	7.55	2505
2.5	23.16	22.44	16.34	2279
3	32.07	30.02	23.05	2113
3.95	60.04	50.9	45.87	1583

4. Conclusions

In this study adsorption of dichloromethane and toluene on a commercial coal-based granular activated carbon were investigated at three different temperatures. Adsorption equilibrium data of dichloromethane on GAC were fitted with Langmuir isotherm, while it was found that Langmuir-BET model describes, satisfactorily, the isotherms of toluene adsorption by GAC at all three temperatures. The sorption of toluene and dichloromethane increases with an increase in temperature, showing that the sorption of both adsorbates (toluene and dichloromethane) is an endothermic process. $\Delta H_{st,a}$ was calculated from the slope of the $ln(C_e)$ versus $(1/T)$ at constant q_e. The positive value of $\Delta H_{st,a}$ which denotes the adsorption of toluene and dichloromethane on GAC is an endothermic process. However, the low heat of adsorption calculated for both components demonstrated that the prevailing mechanism of adsorption onto GAC is physisorption for both components.

5. Acknowledgments

6. Nomenclature

b Langmuir constant (m^3. mol^{-1})

C_0 inlet (feed) or initial phenol concentration (mg. l^{-1})

C_e concentration in equilibrium with the adsorbed phase (mol. m^{-3})

C_s saturated solubility of the compound in water (mol. m^{-3})

K_{BET} equilibrium constant (–)

w adsorbent dose (kg)

q_e amount of adsorbate adsorbed per unit weight of the adsorbent (mol. kg^{-1})

q_m Langmuir constant (mol. kg^{-1})

T temperature (K)

V volume (m^3)

$\Delta H_{st,a}$ isosteric heat of adsorption (J. mol^{-1})

References

[1] Giaya, A. and Thompson Jr., R.W., "Liquid and vapor phase adsorption of chlorinated volatile organic compounds on hydrophobic molecular sieves", Micropor. Mesopor. Mater., 40 (14), 205 (2000).

[2] Rexwinkel, G., Heesink, B.B.M. and van Swaaij, P.M., "Adsorption of halogenated hydrocarbons from aqueous solutions by wetted and nonwetted hydrophobic and hydrophilic sorbents: equilibria", J. Chem. Eng., Data 44 (7), 1139 (1999).

[3] Pires, J., Carvalho, A. and Carvalho de, M. B., "Adsorption of volatile organic compounds in Y zeolites and pillared clays", Micropor. Mesopor. Mater., 43 (11), 277 (2001).

[4] Shim, W. G., Moon, H. and Lee, J. W., "Performance evaluation of wash-coated MCM-48 monolith for adsorption of volatile organic compounds and water vapors", Micropor. Mesopor. Mater., 94 (14), 15 (2000).

[5] Kirk-Othmer, J., Concise encyclopedia of chemical technology, 4th ed., John Wiley & Sons, New York, USA, p. 1724 (1999).

[6] Wartelle, L., Marshall, W., Toles, C. and Johns, M. "Comparison of nutshell franular activated carbons to commercial adsorbents for he purge-and-trap gas chromatographic analysis of volatile organic compounds", J. Chromatogr. A., 879 (7), 169 (2000).

[7] Young, D.M. and Crowell A.D., Physical Adsorption of Gases, Butterworths, London, p. 162 (1962).