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# Adsorption of DCM and MTBE from Aqueous Phase on Granular Activated Carbons: A Comparative Study

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**ABSTRACT:** The laboratory scale batch adsorption studies were conducted to investigate and compare the adsorption potential of granular activated carbons (GACs) for the removal of dichloromethane (DCM) and methyl *tert*-butyl ether (MTBE) from aqueous medium. The effect of various parameters such as solution pH, initial adsorbate concentration, contact time, dose of GACs, and temperature on the adsorption was studied. The optimum adsorption of DCM and MTBE on lignite granular activated carbon (LGAC) was observed at pH 7 while, optimum adsorption on bituminous granular activated carbon (BGAC) was observed in the pH between pH 6 and 8. The equilibrium data was fitted to Langmuir, Freundlich and Temkin models. Freundlich model best described the equilibrium adsorption. Contact time studies showed comparatively lower equilibration time for the adsorption of DCM on GACs. Kinetics modeling was done by applying pseudo-first-order, pseudo-second-order and Elovich models. Good agreement between experimental and theoretical adsorption capacity values along with higher regression coefficient values showed the validity of pseudo-second-order kinetics model. The thermodynamics studies showed endothermic and spontaneous process with randomness at the solid/solution interface. The adsorption of DCM and MTBE on GACs was interpreted to represent a physical adsorption.

**Key words:** Volatile Organic Compounds, Granular Activated Carbons, Physical adsorption

## INTRODUCTION

Over the past few decades, rapid and wide spreading contamination of water resources is an issue of global concern.

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Among these contaminants volatile organic compounds (VOCs) have been recognized as an issue of growing importance. Prolonged exposure to VOCs can cause eye and throat irritation, liver damage, and damage to the central nervous system (Sone *et al.*, 2008). Dichloromethane (DCM) and methyl *tert*-butyl ether (MTBE) belongs to a class of VOCs of industrial importance. Dichloromethane is commonly used in the manufacture of foam polymers, as flammability depressant in various sprays, solvent for paint remover and aerosol propellant (International Agency for Research on Cancer (IARC), 1999). Methyl *tert*-butyl ether has been extensively used as an additive to gasoline to enhance octane ratings and as an "oxygenate" to increase oxygen content for improved combustion efficiency and reduced vehicle emissions (Vainberg *et al.*, 2002).

The chronic effects of DCM and MTBE were well reported. Dichloromethane has been classified as 2B class ("possible" human carcinogen) (International Agency for Research on Cancer (IARC), 1999). Methyl *tert*-butyl ether has been associated with several hazardous effects to human health (e.g. nausea, headache, dizziness and breathing difficulty) (Aivalioti *et al.*, 2010). The United States Environmental Protection Agency (USEPA) classified MTBE as a potential/suspected carcinogen. Concerning the potential hazards caused by DCM and MTBE on human health, the USEPA issued a non-regulatory advisory for DCM and MTBE in drinking water. According to advisory, the maximum permissible level of DCM in drinking water is 5 µg/L (<http://nepis.epa.gov>). The concentration of MTBE above 20-40 µg/L may cause adverse health effects (USEPA, 1997).

The removal of VOCs from ground water has been widely studied. Several researchers reported degradation of VOCs by Fenton's reagent (Siedlecka *et al.*, 2007) and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (Mitani *et al.*, 2002). The advanced oxidation techniques were also reported for the removal of VOCs (Zang and Farnood, 2005). A comprehensive comparison of all these techniques with a major emphasis on cost-effectiveness showed that the performance of all of them depended on site-specific conditions (Melin and Hogan, 2000). The formation of undesirable reaction byproducts is one of the major concerns for using these techniques.

Adsorption is a process that can be applied either *in situ* (with permeable reactive barriers) or *ex situ*, is relatively simple (compared to others) and can achieve quite satisfactory removal

efficiencies. The use of GACs as an adsorbent for the removal of volatile as well as non-volatile organic compounds has been expanded considerably as GACs effectively reduce the concentrations to undetectable limits and prevent their discharge into the biosphere (Bansode *et al.*, 2003). The GACs derived from pecan and almond shells have been successfully tested for the removal of DCM (Bansode *et al.*, 2003). Hung and coworkers had reported adsorptive removal of MTBE onto GAC derived from coconut shell (Hung *et al.*, 2005). These studies motivated us to test and compare the feasibility of two commercially available GACs i.e. lignite granular activated carbon (LGAC) and bituminous granular activated carbon (BGAC) for the adsorptive of DCM and MTBE.

## MATERIALS AND METHODS

### Adsorbent and adsorbate

The adsorbents (LGAC and BGAC) were purchased from Jarcarbon Co, S. Korea. Before the experiments, they were washed several times with deionized water in order to remove dirt and dust. The adsorbents were further washed till they acquire the final pH within the range of 6.8-7.5, then dried in an oven at 80-90°C for 24 h. To avoid moisture, adsorbents were stored in sealed plastic bottles and kept inside a desiccator for further use.

The DCM (98% pure) and MTBE (99.8% pure) were purchased from Junsei Chemicals Co, Japan and Sigma Aldrich, USA, respectively. The stock solutions of DCM and MTBE (1000 mg/L) were prepared by dissolving the desired quantities of DCM and MTBE in deionized water. All reagents and chemicals used were of analytical grade or as mentioned.

### Apparatus and analysis

Dichloromethane and methyl *tert*-butyl ether in the samples were analyzed by Gas chromatography (GC) (DS 6200, Do-nam Co, Korea) equipped with flame ionization detector (FID). The DB-624 column (30 m, 0.53 mm, 3  $\mu$ m) (Agilent, USA) was used for samples analysis. Gas mixture of Air: H<sub>2</sub>: N<sub>2</sub> in ratio 10:1:1 was used for analysis. N<sub>2</sub> at 5 cm<sup>3</sup>/min flow rate was used as a carrier gas for sample analysis. The samples were pretreated by the headspace method (Yoon *et al.*, 2009). The samples of 10 mL volume in 20 mL serum bottles were sealed with rubber corks along with aluminum seal. These bottles were heated at 90°C for 30 min in a water bath. Gas phase sample (1 cm<sup>3</sup>) was collected from the head space and was injected into the GC-FID injector by using a 1 mL syringe. The GC oven temperature was held at 70°C, and the temperature of both the injector and detector was 270°C. The pH values of sorbate solutions were measured by the pH meter (HM-20P) (DKK-TOA Corporation, Japan). All experiments excluding pH experiments were performed in triplicates, and average values were reported.

### Adsorption experiments

The effect of experimental parameters for the adsorption of

DCM and MTBE on GACs was studied in batch mode. Various parameters such as, pH (2-10), sorbate concentration (0.5 - 500 mg/L) and adsorbent dose (0.05 - 1.0 g) were studied. The pH of the experimental solutions was adjusted by adding 0.1M HCl or 0.1M NaOH solutions. Adsorbate solution (25 mL) with initial concentration of 200 mg/L was taken in 50mL capped glass bottles. Adsorbent (0.1 g) was added in each bottle and equilibrated in water bath shaker (100 rpm) at 25±2°C. Preliminary tests showed that the equilibration times were 4h for DCM and 24 h for MTBE. Ten mL of adsorbate samples after equilibration were taken for GC analysis.

The isotherm experiments were carried out in 50 mL capped glass bottles. Adsorbate solutions (25 mL) of desired initial concentrations (0.05 - 500 mg/L) were equilibrated with 0.1 g of adsorbent. The mixtures were shaken in temperature controlled water bath shaker (25±2°C) for 24 h at 100 rpm. The samples were analyzed in triplicates and adsorption capacity values at equilibrium ( $q_e$ ) were calculated by using the following relationship:

$$q_e(\text{mg/g}) = [(C_o - C_e)] \times \frac{V}{W} \quad (1)$$

where  $C_o$  is the initial concentration of adsorbate (mg/L),  $C_e$  the adsorbate concentration at equilibrium (mg/L),  $V$  is the volume of solution (L), and  $W$  is the mass of adsorbent (g).

The kinetics studies were carried out to measure the time dependent uptake of DCM and MTBE on GACs. The studies were done in 50 mL capped glass bottles containing 25 mL of adsorbate solutions ( $C_o = 100$  mg/L). To each bottle 0.1 g of adsorbent was added. It was then equilibrated in a temperature controlled water bath shaker (25±2°C) and at a predetermined time intervals (1 - 1440 min), 10 mL of the adsorbate solution of the specified flask was taken in 20 mL serum bottles for GC analysis.

## RESULTS AND DISCUSSION

### Effect of initial pH

The effect of solution pH on the adsorption of DCM and MTBE on GACs was studied over a wide range of initial pH (2 - 10). The optimum adsorption capacities of DCM and MTBE on LGAC were observed at pH 7 (Fig. 1a), while those on BGAC were observed at pHs between 6 and 8 (Fig. 1b). The observed pH range for maximum adsorption was very near to the point of zero charge ( $\text{pH}_{\text{zpc}}$ ) values of LGAC and BGAC (i.e. 8.0 and 6.8, respectively) (Lataye *et al.*, 2006). The adsorption near  $\text{pH}_{\text{zpc}}$  indicates the involvement dispersive interactions between graphene layers over the surface of GACs and adsorbate molecules. The dispersive interaction in general are promoted by conduction of experiments at solution pH values near adsorbent's  $\text{pH}_{\text{zpc}}$ , at which repulsive interactions between charged surface groups and uncharged molecules can be effectively minimized (Radovic *et al.*, 1997). The adsorption of MTBE was maximum (46.84 mg/g) on LGAC, while, the adsorption of DCM was maximum (39.5 mg/g) on BGAC.

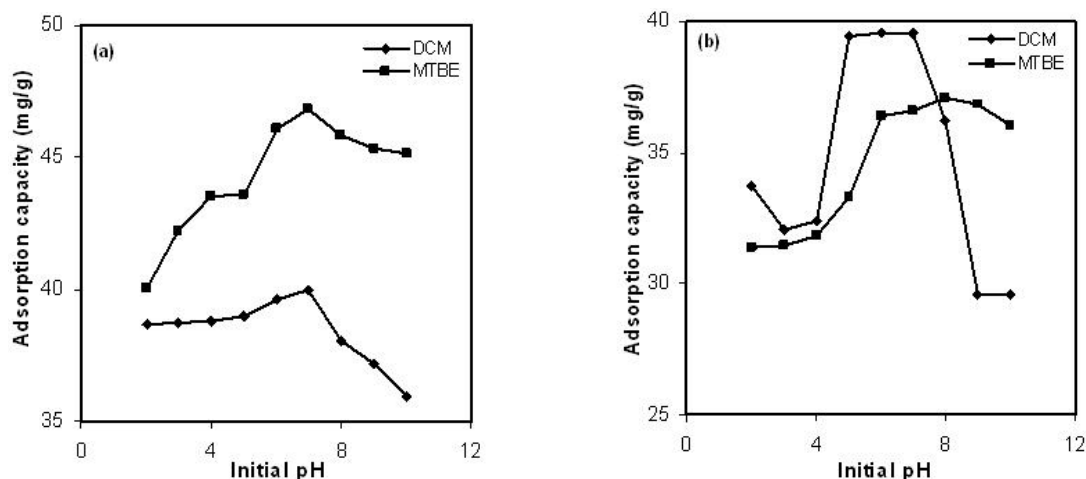


Fig. 1. Effect of initial pH on the adsorption of DCM and MTBE on (a) LGAC and (b) BGAC.

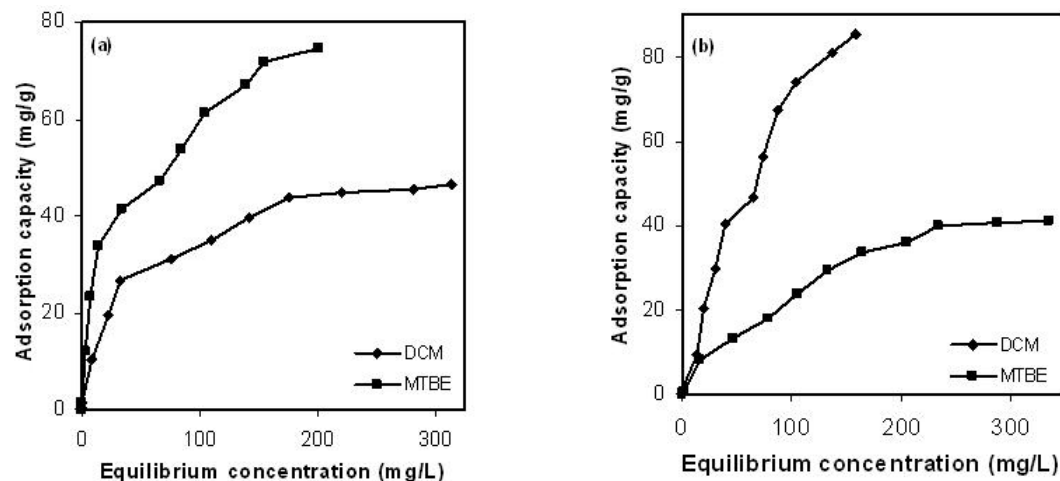


Fig. 2. Effect of initial concentration on the adsorption of DCM and MTBE on (a) LGAC and (b) BGAC.

### Effect of initial concentration

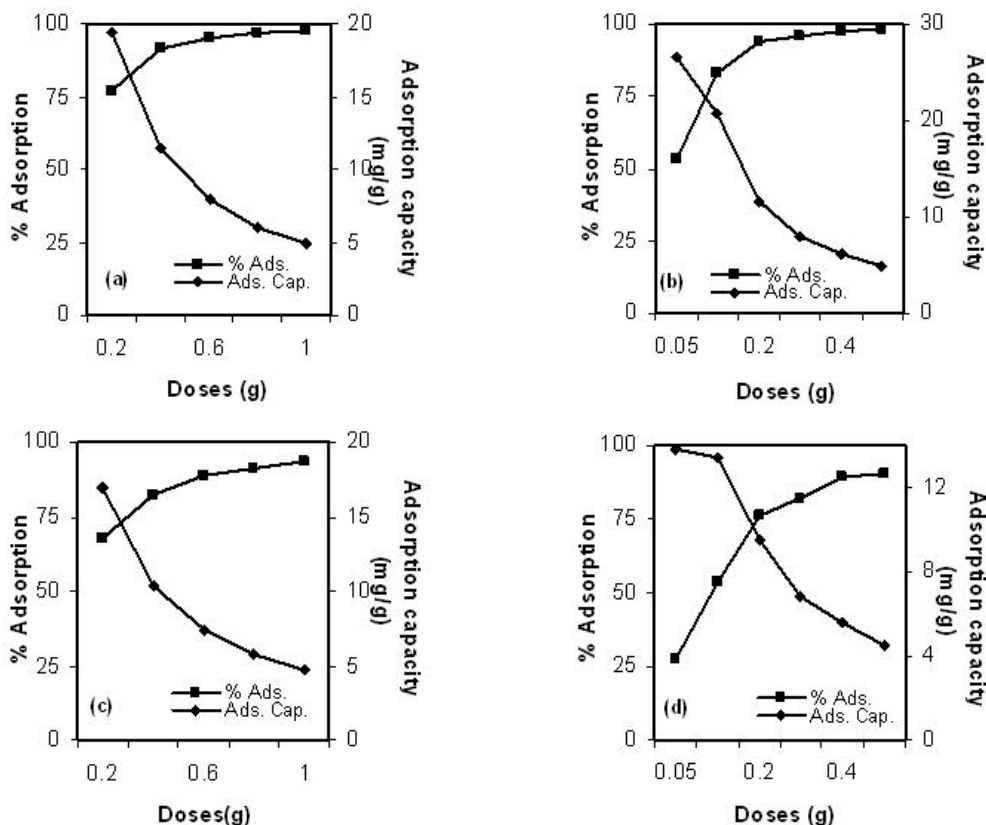
The concentration studies were carried out at  $25 \pm 2^\circ\text{C}$  over a wide range of initial DCM and MTBE concentrations (0.5 - 500 mg/L). The adsorption was very fast at lower adsorbate concentration, it gradually slows down with the increase in concentration, ultimately reaching a plateau zone (i.e., equilibrium). The fast adsorption at lower concentration indicates higher affinity towards the solute. Hydrophobicity and large pore size of GACs plays an important role to obtain high capacity at higher adsorbate concentrations, while at low adsorbate concentrations the small hydrophobic pores were the dominant factor for achieving high adsorption (Abu-Lail *et al.*, 2010). The adsorption capacity increases with increasing initial adsorbate concentration. This is because the transfer of adsorbate from bulk to the surface of the adsorbent increases with the increase in adsorbate concentration (Rao and Khan, 2009). On LGAC, MTBE showed maximum adsorption capacity (74.56 mg/g) (Fig. 2a) while, on BGAC, DCM showed maximum adsorption capacity (85.33 mg/g) (Fig. 2b).

### Effect of adsorbent doses

The effect of GACs doses on DCM and MTBE removal is shown in Fig. 3(a-d). The percentage adsorption increased significantly with the increase in GACs dose. This is due to the fact that a greater amount of adsorbent implies a greater amount of available binding sites. Compared to BGAC, the adsorption of DCM and MTBE was maximized on LGAC (97.7 and 98.2%, respectively) (Fig. 3a and 3b). The adsorption capacity decreases with the increase in GACs dose (Fig. 3 (a-d)). This may be due to the fact that some of the adsorption sites remain unsaturated during the adsorption process (Sharma and Forster, 1993).

### Effect of contact time

The contact time studies for the adsorption of DCM and MTBE on GACs were carried out at 100 mg/L initial adsorbate concentration and  $25 \pm 2^\circ\text{C}$  temperature. The adsorption increases with the increase in contact time (Fig. 4a and 4b). The adsorption possibly occurred in two phases. An initial phase is an external



**Fig. 3.** Effect of doses on the adsorption of (a) DCM on LGAC, (b) MTBE on LGAC, (c) DCM on BGAC and (d) MTBE on BGAC.

surface adsorption. This phase is rapid and significantly contributes to equilibrium uptake. The other phase is the internal surface adsorption which is relatively slower and comparatively smaller adsorption occurred in this phase. The equilibrium attainment time for the adsorption of DCM on GACs was comparatively shorter than that for MTBE. The equilibration time for DCM on GACs was 240 min (Fig. 4a and 4b). For MTBE, the equilibrium attainment times were 1080 min on LGAC (Fig. 4a) and 1440 min on BGAC (Fig. 4b). Among the two GACs, the maximum adsorption capacities for DCM (18.79 mg/g) and MTBE (23.43 mg/g) at equilibrium were observed on LGAC.

## Adsorption modeling

### Isotherm modeling

The adsorption isotherms provide vital information in optimizing the use of adsorbents. Descriptions on affinity between adsorbates and adsorbents, bond energy, and adsorption capacity can be extracted from isotherm equilibrium models applicable to adsorption processes (Ijagbemi *et al.*, 2009). The experimental data in this study have been analyzed by Langmuir, Freundlich and Temkin isotherm models. The Langmuir adsorption model is based on the sorption on a homogeneous surface by monolayer sorption without interaction between sorbed species. Langmuir model assumes that the adsorptive forces are similar

to the forces in the chemical interaction. The linearized form of Langmuir model is given by Eq. (2)

$$\frac{C_e}{q_e} = \frac{1}{bqm} + \frac{1}{qm} \times C_e \quad (2)$$

where  $qm$  shows the monolayer adsorption capacity (mg/g),  $b$  is Langmuir constant (L/mg),  $C_e$  is the concentration of adsorbate in the solution at equilibrium (mg/L) and  $q_e$  represents amounts of adsorbates adsorbed on GACs at equilibrium (mg/g). The values of Langmuir constants  $b$  and  $qm$  for GACs were calculated from the slope and intercept of the linear plot of  $C_e/q_e$  vs.  $C_e$  (Figures not shown). The higher values of  $b$  for the adsorption of DCM and MTBE on BGAC (Table 1a) showed strong affinity of BGAC than LGAC to adsorb DCM and MTBE (Ajmal *et al.*, 2006).

The essential feature of Langmuir model can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter ( $R_L$ ) given by relation:

$$R_L = \frac{1}{1 + bC_o} \quad (3)$$

where  $C_o$  is the initial adsorbate concentration (mg/L) and  $b$  is the Langmuir constant (L/mg). The values of  $R_L$  for the

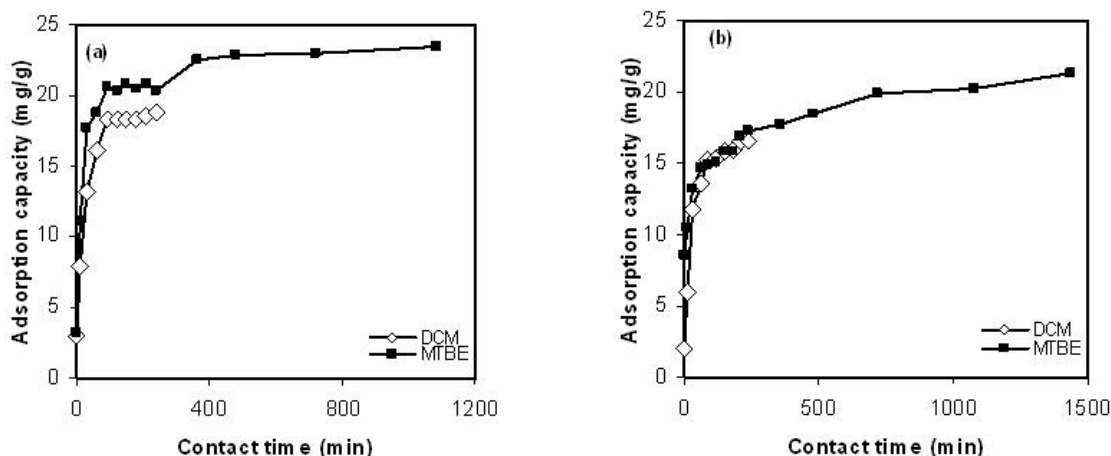


Fig. 4. Effect of contact time on the adsorption of DCM and MTBE on (a) LGAC and (b) BGAC.

Table 1a. Equilibrium sorption constants for the adsorption of DCM on GACs at 25°C

Langmuir	$q_m(\text{mg/g})$	$b(\text{L/mg})$	$R^2$	$R_L$
LGAC	2.19	22.85	0.991	0 - 0.81
BGAC	1.60	78	0.707	0 - 0.56
Freundlich	$K_f(\text{mg/g})(\text{L/mg})^{1/n}$	$n$	$R^2$	
LGAC	1.83	1.54	0.896	
BGAC	4.15	1.71	0.974	
Temkin	$A_T(\text{L/mg})$	$b_T(\text{J/mol})$	$R^2$	
LGAC	6.61	448.38	0.915	
BGAC	4.90	216.37	0.731	

Table 1b. Equilibrium sorption constants for the adsorption of MTBE on GACs at 25°C

Langmuir	$q_m(\text{mg/g})$	$b(\text{L/mg})$	$R^2$	$R_L$
LGAC	18.34	0.03	0.805	0 - 0.99
BGAC	0.20	1.02	0.630	0 - 0.98
Freundlich	$K_f(\text{mg/g})(\text{L/mg})^{1/n}$	$n$	$R^2$	
LGAC	5.54	1.94	0.993	
BGAC	1.02	1.49	0.990	
Temkin	$A_T(\text{L/mg})$	$b_T(\text{J/mol})$	$R^2$	
LGAC	28.22	350.39	0.915	
BGAC	3.48	518.20	0.731	

adsorption of DCM and MTBE of GACs lie in between 0 and 1 indicating the favorable nature of the adsorption process (Tables 1a and 1b) (Poots *et al.*, 1978).

The Freundlich adsorption isotherm gives an expression on the surface heterogeneity and exponential distribution of the active sites and their energies. The widely used empirical Freundlich model can be expressed by Eq. (4)

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where  $C_e$  is adsorbate concentration at equilibrium (mg/L),  $q_e$  the amount of adsorbate adsorbed per unit weight of GACs (mg/g),  $K_f$  and  $n$  the Freundlich constants.  $K_f$  indicates the adsorption capacity of adsorbent. The constant  $n$  is a measure of deviation from linearity of the adsorption. The values of  $K_f$  and  $n$  were calculated from the slope and intercept of linear plot of  $\log q_e$  vs.  $\log C_e$  (Figure not shown) (Table 1). The constant  $n$  is not only a measure of the deviation from linearity, but inform about the degree of heterogeneity on the adsorption sites. As  $n$  approaches zero, the surface site heterogeneity increase. The values of  $n$  for the adsorption of DCM and MTBE on GACs were found to be  $n > 1$  indicating favorable adsorption (Ozcan *et al.*, 2005).

Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm (Temkin and Pyzhev, 1940) has generally been applied in the following Eq. (5)

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad (5)$$

where  $A_T$  (L/g) and  $b_T$  (J/mol) are the Temkin constants,  $T$  is the absolute temperature in K and  $R$  is the universal gas constant, 8.314 J/mol-K. Temkin constants,  $A_T$  and  $b_T$  were determined from the slope and intercept of the plot between  $q_e$  vs.  $\ln C_e$  (Figure not shown). The calculated parameters at 25°C were listed in Tables 1a and 1b. Based on the regression coefficient ( $R^2$ ) values for the adsorption of DCM on LGAC obeyed Langmuir model while, the adsorption of DCM on BGAC obeyed Freundlich model (Table 1a). The adsorption of MTBE on GACs showed better applicability of Freundlich model. These results were in good agreement with the results reported elsewhere (Hung *et al.*, 2005).

#### Kinetics modeling

The rate constants for the adsorption of DCM and MTBE onto GACs were determined by pseudo-first-order kinetics,



**Table 2a.** Kinetics parameters for the adsorption of DCM on GACs at 25°C ( $C_0=100\text{mg/L}$ )

<i>Pseudo-first-order</i>	$q_{e(\text{theo})}(\text{mg/g})$	$K1(1/\text{min})$	$R^2$		
LGAC	14.86	0.032	0.940		
BGAC	12.16	0.028	0.978		
<i>Pseudo-second-order</i>	$q_{e(\text{theo})}(\text{mg/g})$	$K2(\text{g/mg-min})$	$h(\text{mg/g-min})$	$t_{1/2}(\text{min})$	$R^2$
LGAC	20.41	0.0040	1.667	12.25	0.984
BGAC	17.24	0.0043	1.278	13.49	0.997
<i>Elovich</i>	$a(\text{mg/g-min})$	$\beta(\text{g/mg})$	$R^2$		
LGAC	7.00	0.32	0.964		
BGAC	4.77	0.35	0.970		

pseudo-second-order kinetics and Elovich equations. The pseudo-first-order kinetics equation was given by Lagergren and Svenska (Lagergren and Svenska, 1898) as:

$$\log(q_e - qt) = \log q_e - \frac{K_1}{2.303} \times t \quad (6)$$

where  $q_e$  is the amount of adsorbate adsorbed per unit weight of GACs at equilibrium or adsorption capacity (mg/g),  $qt$  the amount of adsorbate adsorbed per unit weight of GACs at any given time  $t$ .  $K_1$  is the rate constant for pseudo-first-order model. The correlation coefficient ( $R^2$ ) values for pseudo-first-order model do not represent a good fit with experimental data (Tables 2a and 2b).

The pseudo-second-order kinetics rate equation is expressed as (Ho and McKay, 1998)

$$\frac{t}{qt} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \times t \quad (7)$$

where  $K_2$  is the pseudo-second order rate constant (g/mg-min). The higher values of correlation coefficient ( $R^2$ ) along with good agreement between  $q_{e(\text{theo})}$  (Tables 2a and 2b) and  $q_{e(\text{exp})}$  values (Figs. 4a and 4b) implies the validity of pseudo-second-order kinetics model.

The initial rate of sorption was estimated from pseudo-second-order kinetic model from the below equation:

$$h = K_2 q_e^2 \quad (8)$$

The highest initial sorption rates for DCM and MTBE were obtained on LGAC (Tables 2a and 2b)

The half-sorption time,  $t_{1/2}$  known as the time required for the adsorption to take up half as much adsorbate as its equilibrium value. This time is often used as a measure of the adsorption rate (Dogan *et al.*, 2009)

$$t_{1/2} = \frac{1}{K_2 q_e} \quad (9)$$

**Table 2b.** Kinetics parameters for the adsorption of MTBE on GACs at 25°C ( $C_0=100\text{mg/L}$ )

<i>Pseudo-first-order</i>	$q_{e(\text{theo})}(\text{mg/g})$	$K1(1/\text{min})$	$R^2$		
LGAC	9.79	0.0083	0.888		
BGAC	8.89	0.0041	0.949		
<i>Pseudo-second-order</i>	$q_{e(\text{theo})}(\text{mg/g})$	$K2(\text{g/mg}\cdot\text{min})$	$h(\text{mg/g}\cdot\text{min})$	$t_{1/2}(\text{min})$	$R^2$
LGAC	22.99	0.0030	1.586	14.50	0.996
BGAC	19.84	0.0019	0.748	26.53	0.994
<i>Elovich</i>	$a(\text{mg/g}\cdot\text{min})$	$\beta(\text{g/mg})$		$R^2$	
LGAC	25.21	0.37		0.907	
BGAC	93.21	0.55		0.965	

The half-sorption time values for the adsorption of DCM and MTBE on GACs were given in Tables 2a and 2b. The lowest half-sorption time for both DCM and MTBE was observed on LGAC.

The Elovich model is known for describing adsorption on highly heterogeneous adsorbents (Bulut *et al.*, 2008). It is generally represented as (Chien and Clayton, 1980)

$$qt = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (10)$$

where  $\alpha$  is the initial adsorption rate (mg/g-min) and  $\beta$  is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The values of correlation coefficient ( $R^2$ ) for Elovich model were comparatively lower than those for pseudo-second-order model (Tables 2a and 2b). The kinetics modeling results brings us to the conclusion that the adsorption of DCM and MTBE on GACs obeys pseudo-second-order kinetics model. Similar kinetics results were reported for the adsorption of MTBE on GAC and diatomite (Gonzalez-Olmos and Iglesias, 2008; Aivalioti *et al.*, 2010).

### Thermodynamics modeling

The thermodynamics parameters were evaluated to determine the feasibility and spontaneity of the process for adsorption of DCM and MTBE on GACs. Various thermodynamics parameters such as standard free energy change ( $\Delta G^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ), and standard entropy change ( $\Delta S^\circ$ ) were determined. The equation given below was used to determine the standard free energy change of adsorption ( $\Delta G^\circ$ )

$$\Delta G^\circ = -RT \ln K_c \quad (11)$$

where  $R$  is the gas constant, 8.314 J/mol-K,  $T$  is absolute temperature, K,  $K_c$  is the adsorption equilibrium constant, given by Eq. (12)

$$K_c = \frac{C_{As}}{C_s} \quad (12)$$

**Table 3a.** Thermodynamics parameters for the adsorption of DCM on GACs ( $C_0=100\text{mg/L}$ )

Temperature (K)	$\Delta S^\circ$ (J/K-mole)	$\Delta H^\circ$ (kJ/mole)	$\Delta G^\circ$ (kJ/mole)
LGAC			
283			-2.369
298	65.08	16.122	-3.749
308			-3.992
BGAC			
283			-0.369
298	106.74	30.252	-1.667
308			-3.331

**Table 3b.** Thermodynamics parameters for the adsorption of MTBE on GACs ( $C_0=100\text{mg/L}$ )

Temperature (K)	$\Delta S^\circ$ (J/K-mole)	$\Delta H^\circ$ (kJ/mole)	$\Delta G^\circ$ (kJ/mole)
LGAC			
288			-4.511
298	177.65	46.63	-6.499
308			-7.973
BGAC			
283			-1.202
298	291.84	85.74	-0.376
308			-4.617

where  $C_{Ae}$  and  $C_e$  are equilibrium concentrations of DCM and MTBE on the GACs and in the solution, respectively.

Van't Hoff equation was used to calculate standard enthalpy change ( $\Delta H^\circ$ ), and standard entropy change ( $\Delta S^\circ$ )

$$\log K_c = \frac{\Delta S^\circ}{2.303 R} - \frac{\Delta H^\circ}{2.303 RT} \quad (13)$$

The thermodynamics parameters for the adsorption of DCM and MTBE on LGAC and BGAC are given in Table 3a and 3b. As observed the standard enthalpy change ( $\Delta H^\circ$ ) for the adsorption of DCM and MTBE on GACs was positive indicating endothermic nature of the adsorption. The endothermic nature of the adsorption of MTBE on GAC was also reported by Gonzalez-Olmos and Iglesias (2008). The positive values of standard entropy change ( $\Delta S^\circ$ ) indicate randomness at the solid/solution interface during the adsorption process (Namasivayam and Ranganathan, 1995). The standard free energy change ( $\Delta G^\circ$ ) values for the adsorption of DCM on GACs and MTBE on LGAC decreases with the increase in temperature, reflecting energetically favorable adsorption process. The values of  $\Delta H^\circ$  for the adsorption of DCM and MTBE on GACs were well in the range of physical adsorption (i.e.  $< 84 \text{ kJ/mol}$ ) (Faust and Aly, 1987). Similar result for the adsorption of MTBE on GAC was reported elsewhere (Gonzalez-Olmos and Iglesias, 2008).

## CONCLUSIONS

The adsorption performance was significantly influenced by temperature, concentration of adsorbate, contact time, pH, and adsorbent dose. The optimum adsorption of DCM and MTBE on LGAC was observed at pH 7, while, that on BGAC was observed in the pH range of 6 to 8. The adsorption increases with the increase in adsorbate concentration. The maximum adsorption of MTBE (74.56 mg/g) was observed on LGAC, while, on BGAC, DCM showed a maximum adsorption (85.33 mg/g). Compared to MTBE, the equilibration time for the adsorption of DCM on GACs was 4 to 6 folds lesser. Isotherm studies showed the applicability of Freundlich model. The values of separation factor ( $R_L$ ) for the adsorption of DCM and MTBE on GACs were in the range of favorable adsorption. Kinetics data showed validity of pseudo-second-order kinetics

model over other models. The adsorption of DCM and MTBE on GACs was endothermic and spontaneous, and the spontaneity of adsorption reaction increases with the increase in temperature. The positive values of standard entropy change showed the randomness at the solid/solution interface.

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