



Geosystem Engineering

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tges20>

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Version of record first published: 04 Sep 2012

To cite this article: Moonis Ali Khan, Sang-Hoon Lee, Rajeev Kumar & Byong-Hun Jeon (2010): Adsorptive Removal of Volatile Organic Contaminants from Aqueous Medium by Granular Activated Carbons, Geosystem Engineering, 13:1, 25-34

To link to this article: <http://dx.doi.org/10.1080/12269328.2010.10541306>

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Adsorptive Removal of Volatile Organic Contaminants from Aqueous Medium by Granular Activated Carbons

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ABSTRACT: In order to investigate the adsorption of dichloromethane (DCM) and methyl *tert*-butyl ether (MTBE) from aqueous solution onto granular activated carbons (GACs), kinetics, thermodynamics, and competitive ions studies were carried out. The optimal pH range for the adsorption of DCM and MTBE on GACs was 5.0 to 8.0. Contact time studies showed comparatively lower equilibration time for the adsorption of DCM on GACs. Isotherm studies favored the applicability of Freundlich model. Kinetics studies at different concentrations showed that the adsorption of DCM and MTBE on GACs follow the pseudo-second-order kinetics model. Weber and Morris model showed that the adsorption of MTBE at different concentration on coconut granular activated carbon (CGAC) has intra-particle diffusion as the rate controlling step. The thermodynamics parameters for the adsorption of DCM onto CGAC showed the exothermic nature of the adsorption process. The adsorption of DCM and MTBE on CGAC and wood granular activated carbon (WGAC) was physical adsorption in nature. Competitive ions studies revealed significant potential of CGAC for the removal of DCM even at higher concentrations.

Key words: Dichloromethane, Methyl *tert*-butyl ether, Granular Activated Carbons, Physical adsorption.

INTRODUCTION

Contamination of ground and surface water by volatile organic compounds (VOCs) has been recognized as an issue of growing importance in recent years. These pollutants are ubiquitous in the environment, work place, and consumer products (Baek *et al.*, 1997). 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) are the two most common VOCs of industrial importance. Solvent in paint removers, aerosol propellant, and flammability depressant (in hair sprays, room deodorants, herbicides and insecticides) are some of the uses of DCM (International Agency for Research on Cancer, 1999). However, MTBE has been used as an additive to gasoline replacing tetraethyl lead (Arana *et al.*, 2008).

Mass usage of DCM and MTBE for the industrial applications has raised very serious environmental issue with regard to water quality. The International Agency for Research on Cancer (IARC) classified DCM as 2B class ("possible" human carcinogen) (International Agency for Research on Cancer, 1999). The chronic exposure of humans to MTBE via ingestion of contaminated water had detrimental effects on human health as it is neurotoxic and is catalogued as a suspected human carcinogen (Fiorenza and Rifai, 2003). Concerning the potential hazards caused by DCM and MTBE on human health, the U.S. Environmental Protection Agency (EPA) 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>), while MTBE concentration above 20-40 µg/L may cause adverse health effects (USEPA, 1997).

Air stripping is generally used for the treatment VOCs yielding about 95-99% removal of VOCs (Stenzel and Gupta, 1995). Discharge of VOCs into the atmosphere limits its use. Several studies reported the advanced oxidation techniques like photocatalytic decomposition by UV/TiO₂ (Zang and Farnood, 2005), degradation by Fenton's reagent (Siedlecka *et al.*, 2007), and O₃/H₂O₂ (Mitani *et al.*, 2002) degradation for the removal of VOCs. The removal rate is significantly high by these techniques. 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). Formation of undesirable reaction byproducts is one of the major concerns for using these techniques.

Adsorption is a proven water decontamination technology. Ease of use (Sutherland *et al.*, 2004), applicability even at lower adsorbate concentration (Chong and Volesky, 1995), and

Received June 7, 2010; Revised June 16, 2010;
Accepted June 18, 2010

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avoiding undesirable byproducts in the water (Rossner and Knappe, 2008) are a few of the merits of adsorption process. In recent years use of granular activated carbons (GACs) for the removal of volatile as well as non-volatile compounds is increasing as GACs effectively reduce the organic contaminants to undetectable limits and prevent their discharge into the biosphere. Use of GACs derived from different materials for the removal of DCM and MTBE have been studied (Bansode *et al.*, 2003; Stouffer, 2001). The results showed the significant removal of DCM and MTBE. These studies suggested us to test the feasibility of two commercially available GACs derived from plant materials i.e. Coconut Granular Activated Carbon (CGAC) and Wood Granular Activated Carbon (WGAC) for the adsorption of DCM and MTBE.

MATERIALS AND METHODS

Adsorbent and adsorbate

Coconut (CGAC) and Wood (WGAC) GACs were purchased from Jarcarbon, S. Korea. The GACs were washed several times with de-ionized (D.I.) water in order to remove dirt and dust. The adsorbents were further washed till they acquired the final pH within the range of 6.8-7.5, and then dried in an oven at 80 to 90 °C for 24 h. To avoid moisture, GACs 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, Japan and Sigma Aldrich, Japan, respectively. The stock solutions of DCM and MTBE (1000 mg/L) were prepared by dissolving the desired quantities of DCM and MTBE in D.I. water. All reagents and chemicals used were of analytical grade or as mentioned.

Apparatus and analysis

The samples were analyzed by Gas chromatography (GC) (DS 6200, Do-nam, Korea) equipped with flame ionization detector (FID). The DB-624 column (30 m, 0.53 mm, 3 μ m) (Agilent, USA) was used for samples analysis. Gas mixture of Air: H₂: N₂ in ratio 10:1:1 was used for analysis. N₂ at 5 cm³/min flow rate was used as a carrier gas for sample analysis. The samples were pretreated by 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 cm³) 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 were measured by the pH meter (HM-20P) (DKK-TOA Corporation, Japan). All experiments except pH experiments were performed in triplicates, and average values were reported.

Effect of pH on adsorption

The influence of hydrogen ion concentration on the adsorption

was studied over a pH range of 2.0 to 10.0. Adsorbate solution (25 mL) with initial concentration of 200 mg/L was taken in 50 mL capped glass bottles. The pH of the solution was then adjusted by adding 0.1N HCl or 0.1N NaOH solution in each bottle. Adsorbent (0.1 g) was added in each bottle and equilibrated in water bath shaker (100 rpm) at 25 ± 2°C. The equilibration time for DCM was 4 h and for MTBE the equilibration time was 24 h.

Point of zero charge (pH_{zpc})

Solid addition method was used to determine the zero surface charge characteristics (pH_{zpc}) of GACs (Lataye *et al.*, 2006). Forty mL DCM and MTBE solutions of desired strength (200 mg/L) were transferred to a series of 50 mL capped glass tubes. The initial pH (pH_i) of the solutions was roughly adjusted between 2.0 to 10.0 by adding 0.1 N HCl and 0.1 N NaOH solutions. The total volume of the solution in each tube was adjusted exactly to 50 mL. The pH_i of the solutions was then accurately noted. 0.5 g of GACs was added to each tube, and the tubes were tightly capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The final pH (pH_f) of the supernatant liquid was noted. The difference between the (ΔpH = pH_i - pH_f) was plotted against the pH_i. The point of intersection of the resulting curve with the abscissa, at which ΔpH = 0, gave the pH_{zpc}.

Adsorption studies

Batch adsorption studies were carried out in 50 mL capped glass bottles. Adsorbate solutions (25 mL) of desired concentrations (0.05 - 500 mg/L) were equilibrated with 0.1 g of adsorbent. The mixtures were shaken in temperature controlled water bath shaker for 24 h at 100 rpm. Ten mL of adsorbate samples after equilibration were taken for GC analysis. The 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* is the equilibrium adsorbate concentration (mg/L), *V* volume of the solution (L), and *W* mass of the adsorbent (g).

Effect of contact time on adsorption

Contact time studies were carried to measure 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 by varying adsorbate concentrations (100 - 300 mg/L) at 25 ± 2°C. To each bottle 0.1 g of adsorbent was added. It was then equilibrated in a temperature controlled water bath shaker 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.

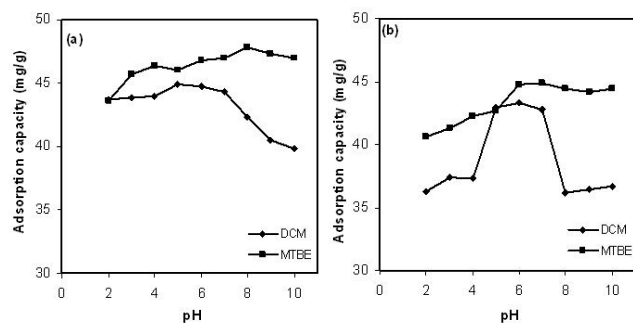


Fig. 1. Effect of initial pH on the adsorption of DCM and MTBE on (a) CGAC, and (b) WGAC.

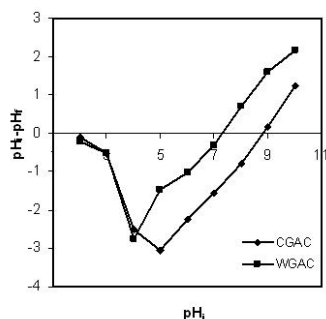


Fig. 2. Determination of point of zero charge (pH_{pzc}) of GACs by solid addition method.

Effect of adsorbent doses

Doses studies were carried out by varying the amount of adsorbents (0.05 - 1.0 g). In 50 mL of glass bottles, 25 mL of adsorbate solution with initial DCM and MTBE concentrations 200 and 100 mg/L, respectively was treated in temperature controlled water bath shaker at $25 \pm 2^\circ\text{C}$ and 100 rpm with varying the doses of adsorbents. The equilibration time was 4 h for DCM and 24 h for MTBE.

RESULTS AND DISCUSSION

Effect of initial pH

The pH of solutions is an important parameter controlling the rate of adsorption. For in-depth analysis of this parameter, the adsorption of DCM and MTBE on GACs was varied over a wide range of initial pH (2.0 to 10.0). At lower pH (i.e. 2.0), the adsorption capacities of DCM and MTBE on CGAC were almost similar (Fig. 1a). The adsorption of DCM on CGAC was maximum in between pH 5.0 to 7.0, while maximum adsorption of MTBE on CGAC was observed in between pH 7.0 to 8.0 (Fig. 1a). The adsorption of DCM and MTBE on WGAC was maximized in between pH 6.0 to 7.0 (Fig. 1b). The observed pH range for maximum adsorption was very near to the pH_{pzc} values of CGAC and WGAC (Fig. 2) indicating that dispersive interactions between graphene layers over the surface of GACs and adsorbate molecules are responsible for the adsorption. The

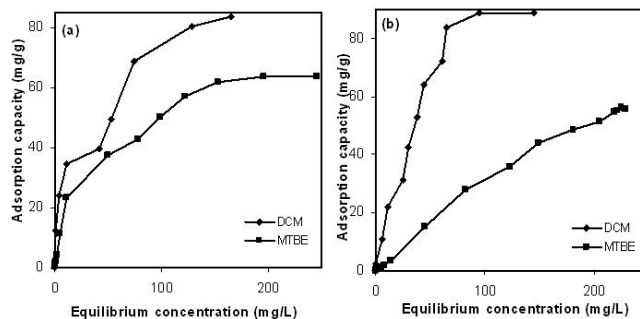


Fig. 3. Effect of initial concentration on the adsorption of DCM and MTBE on (a) CGAC, and (b) WGAC.

dispersive interaction in general are promoted by conduction of experiments at solution pH values near adsorbent's pH_{pzc} , at which repulsive interactions between charged surface groups and uncharged molecules are effectively minimized (Radovic *et al.*, 1997). Compared to DCM, MTBE showed higher adsorption capacities on GACs. The adsorption capacities of MTBE on CGAC and WGAC were 47.82 mg/g at pH 8.0 and 44.89 mg/g at pH 7.0, respectively.

Effect of initial concentration

The effect of concentration on the adsorption on GACs was studied at $25 \pm 2^\circ\text{C}$ over a wide range of initial DCM and MTBE concentrations (0.05 - 500 mg/L). The adsorption was very fast at lower adsorbate concentration, and it gradually slows down with increase in concentration reaching a plateau zone (equilibrium) (Fig. 3a and 3b). 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 increase in 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). The adsorption capacities on CGAC and WGAC at 500 mg/L initial DCM concentration were 83.6 mg/g and 88.67 mg/g, respectively. While for MTBE, the adsorption capacities on CGAC and WGAC at 500 mg/L initial concentration were 63.43 mg/g and 55.25 mg/g, respectively.

Effect of adsorbent doses:

The effect of GACs doses on DCM and MTBE removal is shown in Fig. 4(a-d). It was evident that the percentage adsorption increased significantly with the increase in adsorbent doses. This is due to the fact that a greater amount of adsorbent implies a greater amount of available binding sites. The maximum removal of DCM (97.4%) (Fig. 4a) was observed on CGAC while, the removal of MTBE was maximum (97.7%) on WGAC (Fig. 4d). The adsorption capacity decreases with

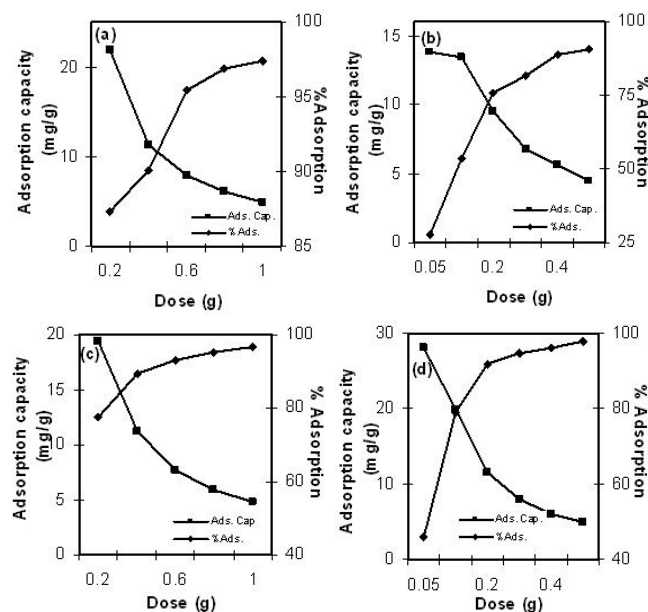


Fig. 4. Effect of adsorbent doses on the removal of (a) DCM on CGAC, (b) MTBE on CGAC, (c) DCM on WGAC, and (d) MTBE on WGAC.

increase in the adsorbent dose (Fig. 4 (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 and initial concentration on adsorption:

The adsorption of DCM and MTBE as a function of contact time was studied at $25 \pm 2^\circ\text{C}$ by varying adsorbate concentrations (100 - 300 mg/L). The adsorption increases with increase in contact time and initial adsorbate concentration (Fig. 5 (a-d)). The adsorption occurred in two phases. An initial phase is an external 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 less than MTBE. The equilibrium attainment times for DCM and MTBE on CGAC at different concentrations were in between 180 to 240 min and 1080 min, respectively. On WGAC, the equilibration times for the adsorption of DCM and MTBE at different concentrations were 180 to 240 min and 720 to 1440 min, respectively. The adsorption capacities of GACs increased to three folds with increase in adsorbate concentration from 100 to 300 mg/L (Fig. 5(a-d)). This is because an increase in initial adsorbate concentration leads to larger mass transfer force which in turn leads to higher adsorption of adsorbate onto GACs (Tan *et al.*, 2008).

Adsorption isotherms

The adsorption isotherms provide vital information in optimizing the use of adsorbents. Descriptions on affinity

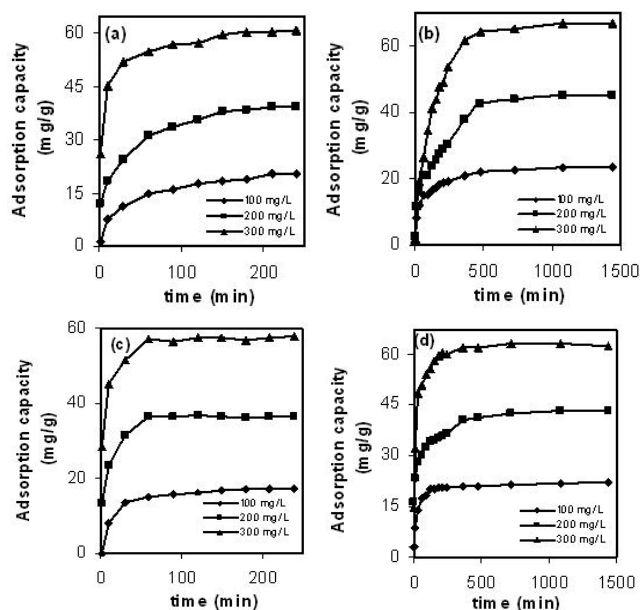


Fig. 5. Effect of contact time on the adsorption of (a) DCM on CGAC, (b) MTBE on CGAC, (c) DCM on WGAC, and (d) MTBE on WGAC.

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 and Freundlich 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). Higher values of b for the adsorption of DCM on GACs (Table 1) compared to MTBE showed strong affinity of GACs to adsorb DCM (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:

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

Table 1. Langmuir and Freundlich constants for the adsorption of DCM and MTBE on GACs

Adsorbates	Adsorbents	Langmuir constants			Freundlich constants			
		qm (mg/g)	b (L/mg)	R^2	R_L	K_f (mg/g)(L /mg) ^{1/n}	n	R^2
DCM	CGAC	2.364	47.00	0.853	0 - 0.68	2.339	1.259	0.924
	WGAC	2.079	80.17	0.683	0 - 0.55	2.188	1.185	0.944
MTBE	CGAC	0.058	1.855	0.615	0 - 0.35	2.993	1.577	0.971
	WGAC	2.377	0.013	0.001	0 - 0.99	1.407	1.472	0.993

Table 2a. Pseudo-first-order and pseudo-second-order kinetics constants for the adsorption of DCM at different concentrations on GACs

Adsorbents	Conc. (mg/L)	$qe_{(exp)}$ (mg/g)	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
			$qe_{(theo)}$ (mg/g)	$K1$ (1/min)	R^2	$qe_{(theo)}$ (mg/g)	$K2$ (g/mg-min)	R^2
CGAC	100	20.3	15.28	0.014	0.981	22.22	0.0017	0.994
	200	39.4	26.67	0.018	0.983	41.67	0.0017	0.993
	300	60.9	22.65	0.018	0.911	62.99	0.0770	0.998
WGAC	100	17.2	10.91	0.021	0.937	18.52	0.0042	0.999
	200	36.5	23.66	0.051	0.995	40.00	0.0052	0.999
	300	57.5	19.19	0.046	0.687	58.82	0.0072	0.999

where, C_0 is the initial adsorbate concentration (mg/L) and b is the Langmuir constant (L/mg). The values of R_L for the adsorption of DCM and MTBE of GACs lie in between 0 and 1 indicating the favorable nature of the adsorption process (Table 1) (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 equation (4):

$$\log qe = \log Kf + \frac{1}{n} \log Ce \quad (4)$$

where, C_e is adsorbate concentration at equilibrium (mg/L), qe the amount of adsorbate adsorbed per unit weight of GACs (mg/g), Kf and n are the Freundlich constants. Kf indicates the adsorption capacity of adsorbent. The constant n is a measure of deviation from linearity of the adsorption. The values of Kf and n were calculated from the slope and intercept of linear plot of $\log qe$ vs. $\log Ce$ (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 CGAC and WGAC were found to be $n > 1$ indicating favorable nature of adsorption process (Ozcan *et al.*, 2005). Higher regression coefficient (R^2) values (Table 1) for the adsorption of DCM and MTBE on GACs showed better applicability of Freundlich model. These results indicate that the adsorption of DCM and MTBE on GACs was multilayer adsorption. The results were in good agreement with the results reported elsewhere (Hung *et al.*, 2005).

Adsorption kinetics

The rate constants for the adsorption of DCM and MTBE at different concentrations onto GACs were determined by pseudo-first-order and pseudo-second order kinetics equations. The pseudo-first-order kinetics equation was given by Langergren and Svenska (1898) as:

$$\log (qe - qt) = \log qe - \frac{K1}{2.303} \times t \quad (5)$$

where, qe 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 . $K1$ is the rate constant for pseudo-first-order model.

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

$$\frac{t}{qt} = \frac{1}{K2 qe^2} + \frac{1}{qe} \times t \quad (6)$$

where, $K2$ is the pseudo-second order rate constant (g/mg-min).

The values of $K1$ for pseudo-first-order kinetics model were obtained from the slopes of the linear plots of $\log (qe - qt)$ vs. t (figure not shown). The correlation coefficient (R^2) values for pseudo-first-order kinetics model were very low (Table 2a and 2b). The experimental qe values for the adsorption of DCM and MTBE of CGAC and WGAC did not agree with the theoretical qe values obtained for pseudo-first-order kinetics model. The values of correlation coefficient (R^2) for pseudo-second-order kinetics model were obtained by plotting t/qt vs. t (figure not shown). Relatively higher correlation coefficient (R^2) values

which approached unity and good agreement between the experimental and the theoretical q_e data (Table 2a and 2b) indicates that for the adsorption of DCM and MTBE on CGAC and WGAC pseudo-second-order kinetics model was better applicable. Similar kinetics results were reported for the adsorption of MTBE on GAC and diatomite (Gonzalez-Olmos and Iglesias, 2008; Aivalioti *et al.*, 2010).

To verify the mechanism involved for the adsorption of DCM and MTBE of GACs Weber and Morris model (Weber and Morris, 1962) was adopted. The mechanism in general involve three steps, one or any combination of which can be the rate-controlling mechanism: (i) mass transfer across the external boundary layer film of liquid surrounding the outside of the particle; (ii) adsorption at a site on the surface (internal or external) and the energy will depend on the binding process (physical or chemical); this step is often assumed to be extremely rapid; (iii) diffusion of the adsorbate molecules to an adsorption site either by a pore diffusion process through the liquid filled pores or by a solid surface diffusion mechanism. The model can be expressed by equation (7)

$$qt = Kid t^{1/2} + C \quad (7)$$

where, qt is the adsorption capacity at time t , Kid is the intra-particle diffusion rate constant ($\text{mg/g min}^{1/2}$) and C is the intercept, which represents the thickness of the boundary layer.

The plots of qt vs. $t^{1/2}$ for the adsorption of DCM and MTBE on GACs showed multi-linearities (Fig. 6 (a-d)). The first, sharper portion was attributed to the diffusion of DCM and MTBE through the solution to the external surface of GACs, or the boundary layer diffusion of solute molecules. The second portion described the gradual adsorption stage, where intra-particle diffusion was rate limiting. The third portion was attributed to the final equilibrium stage for which the intra-particle diffusion started to slow down due to the extremely low adsorbate concentration left in the solution. If intra-particle diffusion occurs, then qt vs. $t^{1/2}$ will be linear and if the plot passes through the origin, then the rate-limiting process is only due to the intra-particle diffusion. Otherwise, some other mechanism along with intra-particle diffusion is also involved (Cheung *et al.*, 2007). As stated, the plots were not linear over the whole time range, implying that more than one process affected the adsorption (Fig. 6 (a-d)). The multiple natures of these plots could be explained by boundary layer diffusion, which gave the first portion and the intra-particle diffusion that gave further two linear portions. If the intra-particle diffusion was the only rate-controlling step, the plot passed through the origin; if not, the boundary layer diffusion controlled the adsorption to some degree (Cheung *et al.*, 2007). As observed, the plot for the adsorption of MTBE at different concentrations on CGAC passes through the origin showing intra-particle diffusion as the rate limiting process (Fig. 6b). The plots for the adsorption of DCM on both CGAC and WGAC and for the

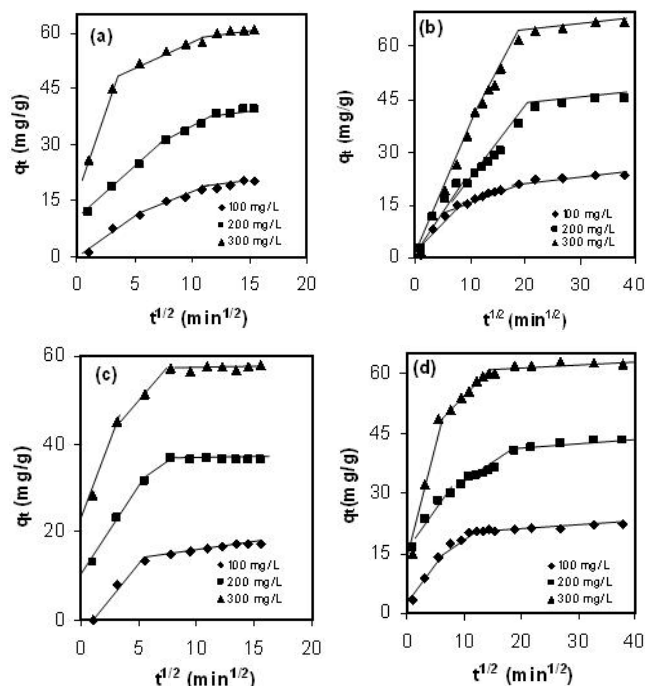


Fig. 6. Weber and Morris plots for the adsorption of (a) DCM on CGAC, (b) MTBE on CGAC, (c) DCM on WGAC, and (d) MTBE on WGAC.

adsorption of MTBE on WGAC at different concentration did not pass through the origin (Fig. 6a, c, and d) indicating the involvement of some other mechanism along with intra-particle diffusion for the adsorption. These results were similar to that observed in previous works on adsorption (Al-Ghouti *et al.*, 2009; Nasuha *et al.*, 2010).

Adsorption thermodynamics

To evaluate the effect of temperature on the adsorption of DCM and MTBE on GACs thermodynamic parameters, standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy (ΔS°) were determined. The equation given below was used to determine the Gibbs free energy of adsorption (ΔG°)

$$\Delta G^\circ = -RT \ln Kc \quad (8)$$

where, R is the gas constant, $8.314 \text{ J/mol}\cdot\text{K}$, T is absolute temperature, K , Kc is the adsorption equilibrium constant, given by equation (9).

$$Kc = \frac{CAe}{Ce} \quad (9)$$

where, CAe and Ce 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 (ΔH°), and standard entropy (ΔS°)

Table 2b. Pseudo-first-order and pseudo-second-order kinetics constants for the adsorption of MTBE at different concentrations on GACs

Adsorbents	Conc. (mg/L)	$q_{e(\text{exp})}$ (mg/g)	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
			$q_{e(\text{theo})}$ (mg/g)	K_1 (1/min)	R^2	$q_{e(\text{theo})}$ (mg/g)	K_2 (g/mg-min)	R^2
CGAC	100	23.36	12.93	0.0044	0.943	23.58	0.0010	0.943
	200	45.2	38.54	0.0048	0.972	47.39	0.0002	0.961
	300	67.05	53.21	0.0055	0.968	72.99	0.0002	0.991
WGAC	100	21.87	5.64	0.0044	0.660	21.69	0.0038	0.999
	200	43.4	19.01	0.0046	0.975	43.29	0.0009	0.995
	300	62.9	21.89	0.0081	0.895	63.29	0.0014	0.999

Table 3a. Thermodynamics parameters for the adsorption of DCM and MTBE on CGAC

Temperature (°C)	ΔS° (J/K-mole)	ΔH° (kJ/mole)	ΔG° (kJ/mole)
DCM			
10			-3.746
25	-4.33	-5.04	-3.749
35			-3.582
MTBE			
15			-4.807
25	45.05	8.19	-5.193
35			-5.703

Table 3b. Thermodynamics parameters for the adsorption of DCM and MTBE on WGAC

Temperature (°C)	ΔS° (J/K-mole)	ΔH° (kJ/mole)	ΔG° (kJ/mole)
DCM			
10			-2.369
25	65.08	16.12	-3.749
35			-3.992
MTBE			
15			0.005
25	179.50	53.44	3.749
35			-3.874

$$\log Kc = \frac{\Delta S^\circ}{2.303 R} - \frac{\Delta H^\circ}{2.303 RT} \quad (9)$$

The thermodynamics parameters for the adsorption of DCM and MTBE on CGACs and WGAC are given in Table 3a and 3b. As observed the adsorption of DCM on CGAC was exothermic in nature (Table 3a). Endothermic process was observed of the adsorption of DCM and MTBE on WGAC (Table 3b) and for the adsorption of MTBE on CGAC (Table 3a). 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 (ΔS°) indicate randomness at the solid/solution interface during the adsorption process (Namasivayam and Ranganathan, 1995). The value of ΔS° for the adsorption of DCM on CGAC was negative (Table 3a) indicating an increase in the state of orderliness at solid/solution interface during the adsorption process (El Bakouri *et al.*, 2009). The Gibbs free energy (ΔG°)

values for the adsorption of MTBE on CGAC and DCM on WGAC decreases with increase in temperature reflecting energetically favorable adsorption process. The values of ΔH° for the adsorption of DCM and MTBE on GACs were well in the range of physisorption (i.e. < 84 kJ/mol) (Faust and Aly, 1987).

Effect of competitive ions

To study the hindrance caused by ionic salts generally abundant in wastewater competitive ions studies were performed. Strong affinity of GACs to adsorb DCM and comparatively shorter equilibration time for DCM prompted us to select DCM for competitive ions studies. Various salt solutions (NaCl, KCl, MgCl_2 , and CaCl_2) of different concentrations (0.1 and 0.5M) were added to different concentrations (50–200 mg/L) of DCM and the influence of various ionic salts on the adsorption capacities were compared with that in D.I. water. The adsorption capacities at 50 and 100 mg/L initial DCM concentrations on CGAC and WGAC remain almost unchanged in the presence

Table 4. Effect of competitive ions on the adsorption of DCM on GACs

Adsorbents	Conc. of DCM (mg/L)	Adsorption capacity (q_e)(mg/g)								
		D.I	NaCl		KCl		CaCl ₂		MgCl ₂	
			0.1M	0.5M	0.1M	0.5M	0.1M	0.5M	0.1M	0.5M
CGAC	50	12.24	11.09	12.03	10.90	11.68	11.61	11.60	11.28	11.92
	100	24.06	22.03	22.82	22.72	22.64	22.64	23.30	22.50	22.88
	200	39.65	44.30	43.03	41.98	43.97	43.97	43.63	43.63	43.79
WGAC	50	12.23	10.80	11.76	10.78	11.03	11.72	11.40	11.44	11.46
	100	24.35	21.30	22.71	22.57	22.90	23.32	22.10	23.10	22.88
	200	42.82	42.23	42.80	42.08	42.71	42.78	41.21	43.55	42.20

of ionic salts solutions compared to D.I. water (Table 4) showing the effectiveness of these adsorbents with no hindrance caused on the adsorption even in the presence of ionic salts. Increase in the adsorption capacities was observed on CGAC in presence of ionic salts with increase in DCM concentration to 200 mg/L. This is because the presence of ionic salts nullifies the repulsive forces leading to an increase in the adsorption. Similar results for the adsorption of phenol on activated charcoal in presence of NaCl were reported (Halhouli *et al.*, 1995). Studies showed the effectiveness of CGAC for the removal of DCM from wastewater even at higher concentrations.

CONCLUSIONS

This study showed the influence of temperature, concentration, contact time, pH and adsorbent dose on the adsorption. The pH studies showed 5.0 to 8.0 as an optimum pH range for the adsorption of DCM and MTBE on GACs. At higher initial DCM concentrations (500 mg/L) the adsorption capacities on CGAC and WGAC were 83.6 mg/g and 88.67 mg/g, respectively. These values were comparatively higher than the values obtained for MTBE at 500 mg/L initial concentration. The equilibration time for the adsorption of DCM at different initial concentrations on GACs was in range of 180 to 240 min. The equilibration time for DCM was about 4 to 6 folds less than the equilibration time for MTBE on GACs. Isotherm studies showed better applicability of Freundlich model, with strong affinity of GACs to adsorb DCM. Kinetics studies showed better applicability of pseudo-second-order kinetics model. Weber and Morris plot showed that the adsorption of MTBE on CGAC occurred by intra-particle diffusion. While for DCM on GACs and MTBE on WGAC, intra-particle diffusion along with some other diffusion process was the rate limiting steps. Thermodynamics studies showed endothermic and spontaneous nature of the adsorption process. Reverse trend was observed for the adsorption of DCM on CGAC where the adsorption process is exothermic. The adsorption of DCM and MTBE on GACs was physical adsorption in nature. Competitive ions studies showed CGAC was a better choice for the adsorption of DCM even at higher concentrations.

ACKNOWLEDGEMENT

This work was supported by the 21st Frontier research project (Sustainable Water Resources Research Center 3-4-3), Global Research Laboratory project (Korea Institute of Geosciences and Mineral Resources NP2008-019). We are also thankful to Brain Korea-21(BK-21) program of Ministry of Education, Science & Technology (MEST) in 2009 (K20815000002) for financial support.

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