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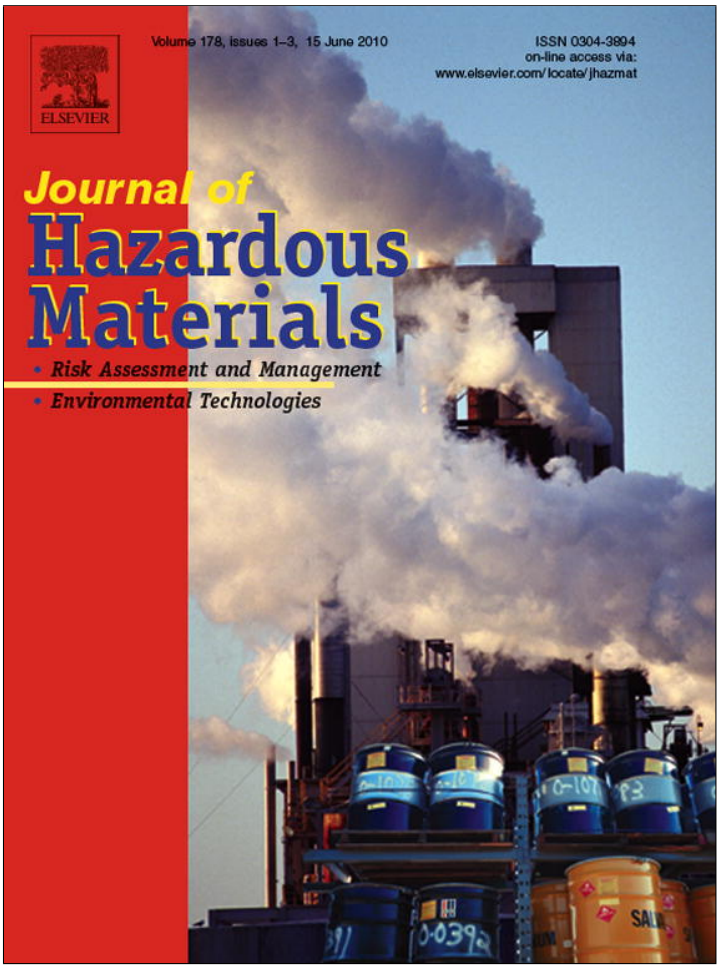


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# Adsorption studies of Dichloromethane on some commercially available GACs: Effect of kinetics, thermodynamics and competitive ions

Moonis Ali Khan[a], Seong-wook Kim[a], Rifaqat Ali Khan Rao[b], R.A.I. Abou-Shanab[a,c], Amit Bhatnagar[a], Hocheol Song[d], Byong-Hun Jeon[a,*]

[a] Department of Environmental Engineering, Yonsei University, Wonju, Gangwon-do 220-710, South Korea
[b] Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh, 202002, India
[c] Department of Environmental Biotechnology, Mubarak City for Scientific Research, Alexandria, Egypt
[d] Geologic Environment Division, KIGAM, Daejeon 305-350, South Korea

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ABSTRACT

The objective of this work was to compare the effectiveness of four commercially available granular activated carbons (GACs); coconut (CGAC), wood (WGAC), lignite (LGAC) and bituminous (BGAC) for the removal of dichloromethane (DCM) from aqueous solution by batch process. Various parameters such as thermodynamics, kinetics, pH, concentration of adsorbate, dosages of adsorbent and competitive ions effect on DCM adsorption were investigated. Maximum adsorption capacity (45.5 mg/g for CGAC) was observed at pH 6.0–8.0. The kinetics data indicate better applicability of pseudo-second-order kinetics model at 25 and 35 °C. Freundlich model was better obeyed on CGAC, WGAC, and BGAC, while LGAC followed Langmuir model. The adsorption process for 100 mg/L initial DCM concentration on CGAC was exothermic in nature. The adsorption of DCM on various adsorbents involves physical adsorption process. The adsorption of DCM over a large range of initial concentration on CGAC and LGAC is effective even in presence of ionic salts.

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## 1. Introduction

Contamination of ground water by volatile organic compounds (VOCs) has been recognized as an issue of growing importance in recent years. These pollutants must be controlled under increasingly stringent environmental regulations as they are toxic, carcinogenic, irritating, and flammable [1]. These compounds are also responsible for the depletion of stratospheric ozone layer, formation of photochemical smog, and for direct action on human tissues [2]. Chlorinated volatile organic compounds (CVOCs) form the sub group of VOCs containing chlorine. Dichloromethane (DCM), a CVOC commonly used as solvent in paint removers, aerosol propellant, degreaser agent, flammability depressant (hair sprays, room deodorants, herbicides and insecticides), and in the manufacture of foam polymers [3].

Ground water pollution by DCM causes numerous health hazards [4]. The International Agency for Research on Cancer (IARC) classified DCM as 2B class ("possible" human carcinogen) [3]. The maximum permissible level set by USEPA for DCM in drinking water is 5 μg/L [5].

There are various treatment technologies available for the treatment of effluents containing DCM. Air stripping is generally used for the treatment yielding about 95–99% removal of VOCs [6]. However, because of the environmental issues, discharge of VOCs into the atmosphere limits its use. Hydrophobic polymer resins [1], Lees materials such as wheat bran, rape seed, linseed, okara, and sakekasu [7] were reported for the removal of DCM from wastewater.

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 back into the biosphere. Adsorption of DCM on GACs prepared from pecan shell and almond shell was reported elsewhere [8]. The results showed that pecan shell and almond shell GACs could be the better alternative adsorbents.

These studies prompted us to study the adsorption potential of four commercially available GACs coconut granular activated carbon (CGAC), wood granular activated carbon (WGAC), lignite granular activated carbon (LGAC) and bituminous granular activated carbon (BGAC) for DCM removal from aqueous solution. Kinetics, thermodynamics parameters along with the effect of ionic salts on the adsorption were studied to justify the results.

* Corresponding author. Tel.: +82 33 760 2446; fax: +82 33 760 2571.
*E-mail address:* bhjeon@yonsei.ac.kr (B.-H. Jeon).

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## 2. Materials and methods

### 2.1. Adsorbent

Granular activated carbons (CGAC, LGAC, WGAC and BGAC) were purchased from Jarcarbon, S. Korea. Virgin 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 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 the adsorbents were stored in sealed plastic bottles inside a desiccators for further use.

### 2.2. Characterization of adsorbent

Perkin Elmer Spectrum (100 FT-IR Spectrometer) with PIKE MIRacle ATR (attenuated total reflection) attachment was used for the analysis of adsorbent samples before and after DCM adsorption. The MIRacle ATR is a unique optical design providing high throughput of the IR beam and thereby provides the ability to collect high quality spectral data within a minute or less.

### 2.3. Adsorbate solution

DCM (98% pure) was purchased from Junsei chemicals, Japan. The stock solution of DCM (1000 mg/L) was prepared by dissolving the desired quantity of DCM in D.I. water. All reagents and chemicals used were of analytical grade or as mentioned.

### 2.4. 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 mm) (Agilent, USA) was used for DCM samples analysis. Gas mixture of air:$H_2$:$N_2$ in ratio 10:1:1 was used for analysis. $N_2$ at 5 $cm^3$/min flow rate was used as a carrier gas for sample analysis. The samples were pretreated by the headspace method [9]. 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 $cm^3$) 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 were performed in triplicates, and average values were reported.

### 2.5. Adsorption studies

Adsorption studies were carried out by batch process. Adsorbate solutions (25 mL) of desired concentrations (0.01–500 mg/L) were equilibrated with 0.1 g of adsorbent in 50 mL capped glass bottle. The mixtures were shaken in temperature controlled water bath shaker for 24 h at 100 rpm. Ten milliliters of adsorbate samples after equilibration were taken for GC analysis. The samples were analyzed in triplicates and adsorption capacity values at equilibrium ($q_e$) were calculated by using the following relationship:

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

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

### 2.6. Effect of pH on DCM adsorption

The influence of hydrogen ion concentration on the adsorption was studied over a pH range of 2.0–10.0. 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 0.1 M HCl or 0.1 M NaOH solution in each bottle. Adsorbent (0.1 g) was added in each bottle and equilibrated for 4 h in water bath shaker at 25 °C.

### 2.7. Point of zero charge ($pH_{zpc}$)

Solid addition method was used to determine the zero surface charge characteristics ($pH_{zpc}$) of GACs using 0.01 M, 0.1 M KCl solutions along with 200 mg/L DCM and a blank [10]. Forty milliliters of KCl and DCM solutions of desired strengths 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 and 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 by adding KCl and DCM solution of the same strength. The $pH_i$ of the solutions was then accurately noted. 0.5 g of different GACs was added to each tube, and the tubes were tightly capped immediately. The suspension 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 ($\Delta$pH) = $pH_i - pH_f$ was plotted against the $pH_i$. The point of intersection of the resulting curve with the absicca, at which $\Delta$pH = 0, gave the $pH_{zpc}$.

### 2.8. Effect of contact time on DCM adsorption

Contact time studies were carried out in 50 mL capped glass bottles containing 25 mL of adsorbate solutions by varying adsorbate concentrations (100–300 mg/L) at different temperatures (10–35 °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 (1–240 min), 10 mL of the adsorbate solution of the specified flask were taken in 20 mL serum bottles for GC analysis.

### 2.9. Effect of adsorbent dosages on DCM removal

Dosages studies were carried out by varying the adsorbent dosages from 0.2 to 1.0 g. In 50 mL glass bottles, 25 mL of adsorbate solution with initial concentration 200 mg/L were treated in temperature controlled water bath shaker at 25 °C with varying the dosages of adsorbent for 4 h. Ten milliliters of the solution were taken in 20 mL serum bottles for GC analysis.

## 3. Results and discussion

### 3.1. ATR-FT-IR characterization of adsorbents

Fig. 1 showed the ATR-FT-IR spectra of (a) CGAC, (b) BGAC, (c) LGAC, and (d) WGAC before (A) and after (B) the adsorption of DCM. Weak bands at 2970 $cm^{-1}$ were aroused due to –$CH_2$ asymmetric stretching vibrations. The band at 1737 $cm^{-1}$ was ascribed to stretching vibration of aryl ketone and the C=O stretching of carbonyl group generally present on GACs derived from natural materials. The bending vibrations at 1365–1366 $cm^{-1}$ occurred because of the ethylene group. The bands at 1216–1217 $cm^{-1}$ were the characteristics peaks of the condensed C–C–C bending vibrations. The FT-IR spectra showed that the transmittance of methylene bending vibrations peaks decreased after the adsorption of DCM. It is evidenced that the adsorption of DCM occurred

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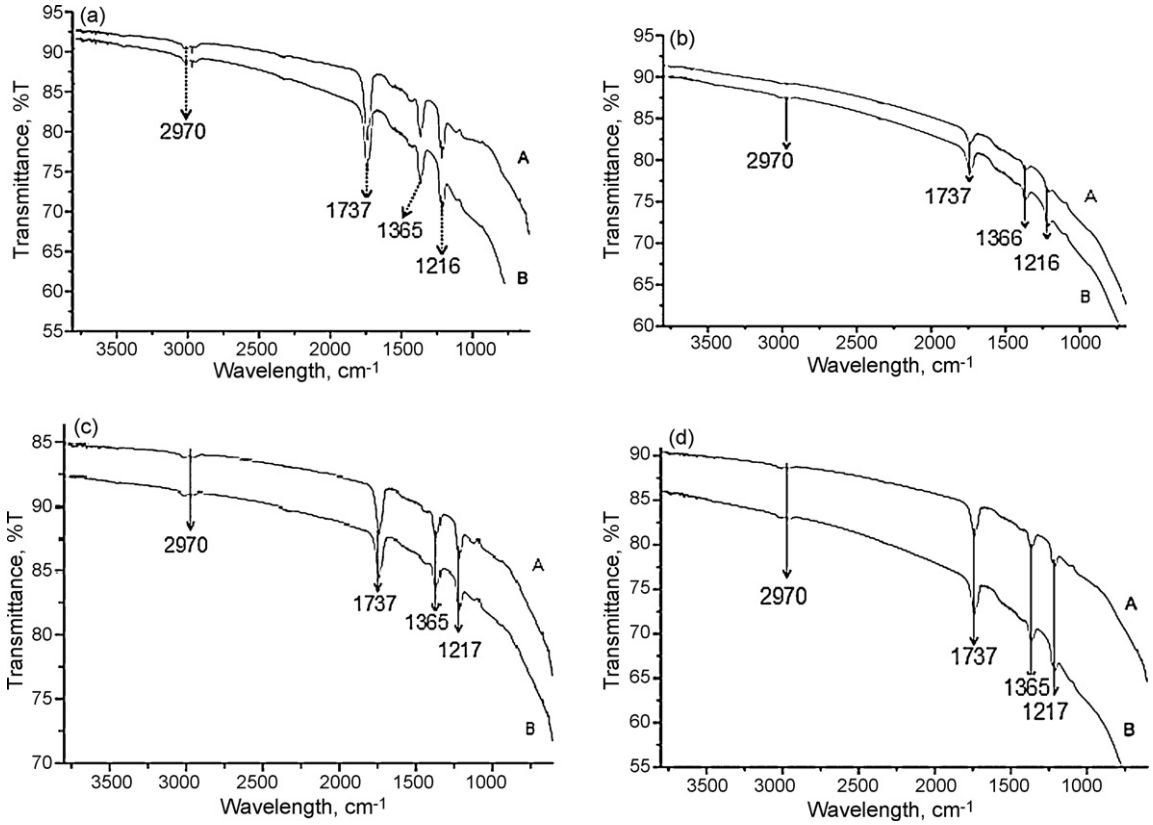


**Fig. 1.** ATR-FT-IR spectra of (a) CGAC, (b) LGAC, (c) WGAC, (d) BGAC before (A) and after (B) the adsorption of DCM.

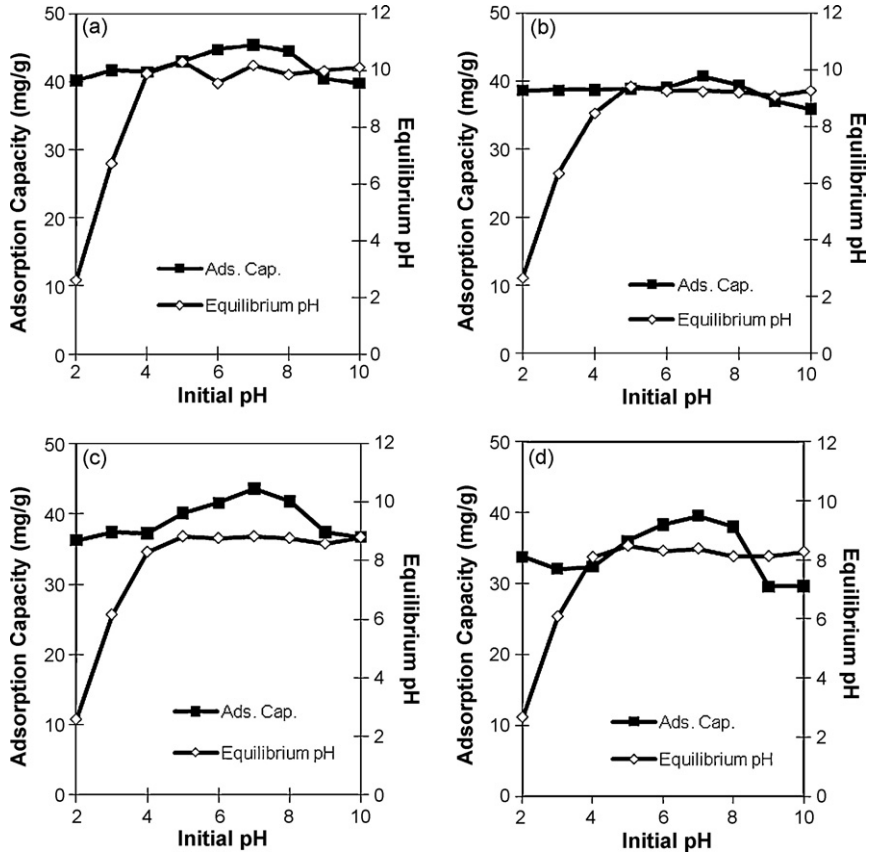


**Fig. 2.** Effect of initial pH on the adsorption of DCM on (a) CGAC, (b) LGAC, (c) WGAC, and (d) BGAC.

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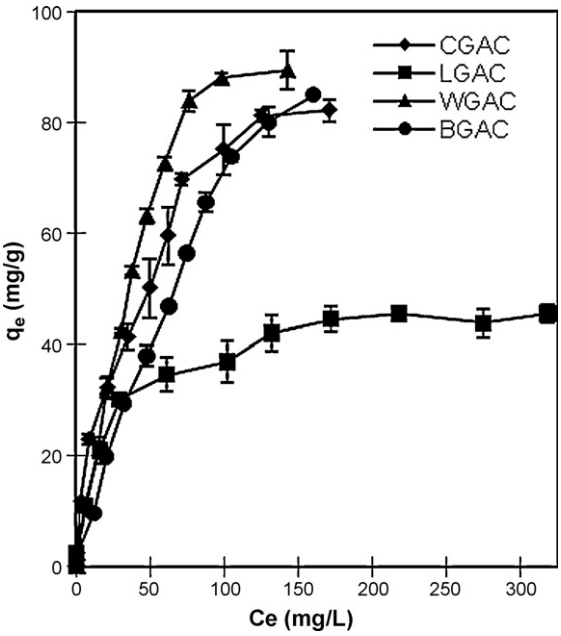


**Fig. 3.** Effect of DCM concentration on the adsorption on different adsorbents.

on available active sites of the adsorbents through physical interactions i.e. hydrogen/coordinate bond.

### 3.2. Effect of initial pH

The effect of initial pH on the adsorption of DCM on GACs along with the variation in equilibrium pH is shown in Fig. 2(a–d). Increase in $pH_i$ causes an increase in the $pH_f$ till equilibrium (equilibrium pH values for CGAC, LGAC, WGAC and BGAC were 10, 9.4, 9.0 and 8.4, respectively). The maximum adsorption of DCM on CGAC, LGAC, WGAC and BGAC was observed in between pH 6.0 and 8.0 which is very near to the point of zero charge ($pH_{pzc}$) values of CGAC, LGAC, WGAC and BGAC (8.6, 8.5, 7.5 and 7.5, respectively). Further increase or decrease in pH leads to decrease in adsorption capacity. Maximum adsorption near pH = $pH_{pzc}$ showing dispersive interactions between the DCM molecules and graphene layers over the surface of activated carbon. The surface chemistry of activated carbons showed the involvement of hydrophobic graphene layers for the adsorption of organic compounds [11]. The dispersive interactions in general are promoted by conduction of experiments at solution pH values near adsorbate's $pH_{pzc}$, at which repulsive interactions between charged surface groups and uncharged molecules are effectively minimized. [12]. The adsorption capacity was maximum for CGAC (45.4 mg/g) followed by WGAC, LGAC and BGAC (Fig. 2(a–d)).

### 3.3. Effect of initial DCM concentration

The effect of initial DCM concentration on the adsorption onto different GACs was investigated (Fig. 3). Adsorption increased with increase in initial DCM concentration. The adsorption capacity of DCM was maximum on WGAC (89.4 mg/g) and minimum on LGAC (45.5 mg/g) at 500 mg/L initial DCM concentration. It was observed that adsorption capacity increased up to 500 folds for all the adsorbents when initial concentration of DCM increased from 0.01 to 1 mg/L. This shows steep increase in the adsorption at lower concentrations, indicating higher affinity towards the solute. When the initial DCM concentration increases from 1 to 100 mg/L, the increase in adsorption capacity was reduced to 100 folds for all the adsorbents. It was further reduced to 5 folds with the increase in concentration from 100 to 500 mg/L showing almost horizontal plateaus. This is the usual phenomenon observed on various adsorbents for the adsorption of organic and inorganic pollutants since the transfer of adsorbate from bulk to the surface of the adsorbent increases with the increase in adsorbate concentration [13].

### 3.4. Effect of contact time

The removal of DCM by CGAC, LGAC, WGAC and BGAC as a function of contact time was studied by varying initial DCM concentration (100–300 mg/L) and temperature of adsorbate solution (10–35 °C) (Figs. 4–7). The adsorption capacity of DCM on CGAC at 200 and 300 mg/L initial concentrations increases with increase in temperature indicating endothermic nature of adsorption process (Fig. 4). Reverse trend was observed on CGAC at 100 mg/L initial DCM concentration where the adsorption decreases with increase in temperature. This supports the fact that adsorption process is exothermic in nature. Similar trend was observed for the adsorption of phenols on activated carbon [14], activated bentonite [15] and VOCs on AC [16,17]. The maximum adsorption capacity on CGAC was 60.3 mg/g at 300 mg/L initial DCM concentration and 35 °C temperature attaining equilibrium in 150 min (Fig. 4(c)). The adsorption capacity for 300 mg/L initial DCM concentration on LGAC was 52.2 mg/g at 10 °C (Fig. 5(a)) increased to 65.5 mg/g at 35 °C (Fig. 5(c)) reaching to equilibrium in 210 min. The decrease in initial DCM concentration to 200 mg/L leads to decrease in the adsorption capacity (35.0 mg/g) on LGAC at 10 °C with almost negligible increase at 25 and 35 °C (Fig. 5(b) and (c)) attaining equilibrium in 210 min for a given temperature range. At 100 mg/L initial DCM concentration the time required to reach the equilibrium on LGAC was observed at 120 min. The adsorption capacity was 18.2 mg/g at 10 °C. It increases to 20.7 mg/g with increase in temperature to 35 °C. The adsorption on WGAC at 300 mg/L initial DCM concentration increased from 53.7 to 55.7 mg/g as temperature increased from 10 to 35 °C (Fig. 6). The equilibration time decreases from 240 to 150 min with increase in temperature. The adsorption on WGAC at 200 mg/L initial DCM concentration increased from 34.3 to 38.3 mg/g as temperature increased from 10 to 35 °C. The equilibrium attainment time decreased from 240 to 210 min with increase in temperature. The adsorption capacity on WGAC at 100 mg/L initial DCM concentration was 19.6 mg/g with no observable rise in the capacity with temperature attaining equilibrium from 210 to 240 min. The adsorption capacity on BGAC at 300 mg/L initial DCM concentration increases from 33.5 to 47.4 mg/g with increase in temperature from 10 to 35 °C (Fig. 7) attaining equilibrium within 210 min. At 200 mg/L initial DCM concentration the adsorption capacity on BGAC increased from 22.6 to 35.8 mg/g with increase in temperature from 10 to 35 °C. At 100 mg/L initial DCM concentration the adsorption capacity increased from 13.2 to 19.6 mg/g with increase in temperature from 10 to 35 °C. These observations suggest that the adsorption of DCM on LGAC, WGAC and BGAC under specified concentration and temperature range was endothermic in nature. The time required to attain the equilibrium on these adsorbents was in between 120 and 210 min. Maximum adsorption capacity (65.5 mg/g) compared to other adsorbents was observed for LGAC at 300 mg/L initial DCM and at temperature 35 °C. While the minimum equilibrium attainment time (120 min) was observed for LGAC at 100 mg/L initial DCM concentration with no observable change in equilibrium time with increase in temperature.

### 3.5. Effect of adsorbent dosages

The adsorption of DCM on various adsorbents (CGAC, LGAC, WGAC, and BGAC) was studied by changing the amount of adsorbent in the solution making the initial DCM concentration, pH

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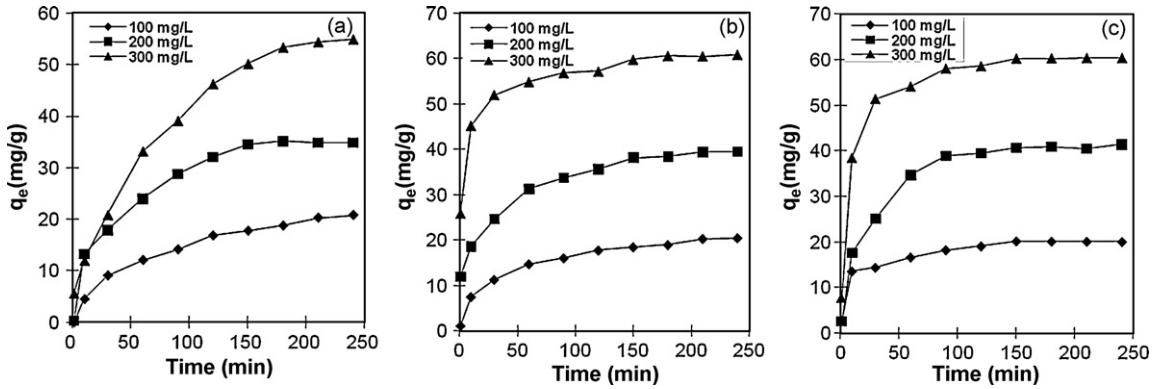


**Fig. 4.** Effect of contact time on the adsorption of different concentrations of DCM on CGAC at different temperatures (a) 10, (b) 25, and (c) 35 °C.

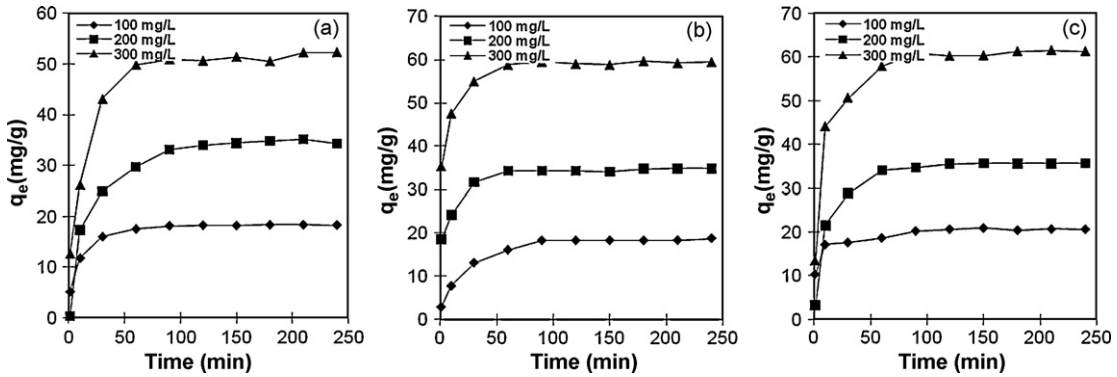


**Fig. 5.** Effect of contact time on the adsorption of different concentrations of DCM on LGAC at different temperatures (a) 10, (b) 25, and (c) 35 °C.

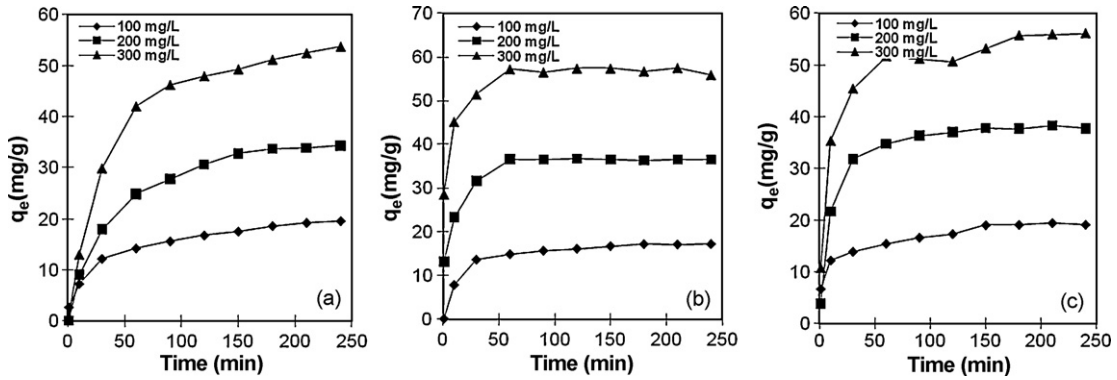


**Fig. 6.** Effect of contact time on the adsorption of different concentrations of DCM on WGAC at different temperatures (a) 10, (b) 25, and (c) 35 °C.

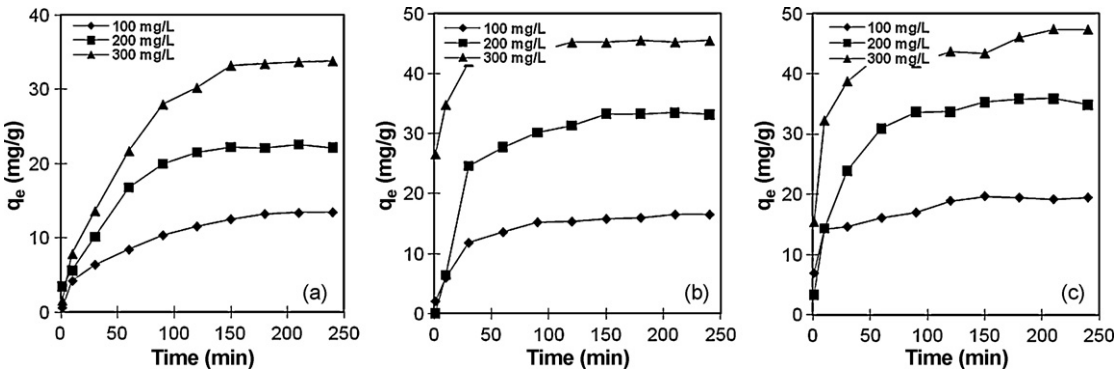


**Fig. 7.** Effect of contact time on the adsorption of different concentrations of DCM on BGAC at different temperatures (a) 10, (b) 25, and (c) 35 °C.

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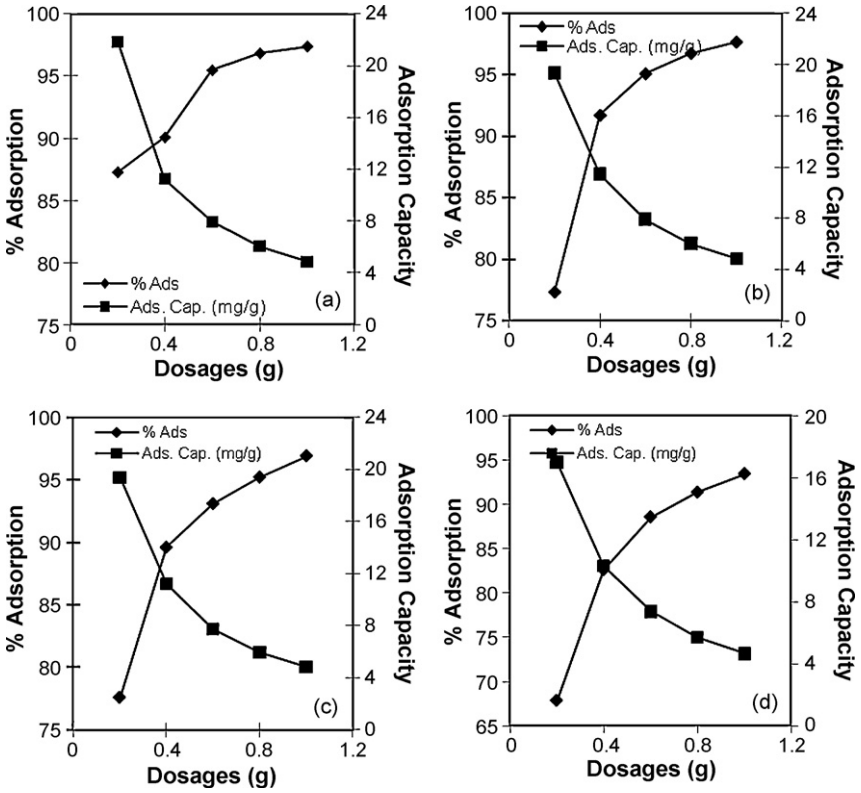


**Fig. 8.** Effect of adsorbent dosages on the adsorption of DCM (a) CGAC, (b) LGAC, (c) WGAC, and (d) BGAC.

and contact time constant. The effect of adsorbent dosage on the amount of DCM adsorbed at equilibrium on different adsorbents is shown in Fig. 8. In general, the amount of DCM adsorbed (adsorption capacity) decreases with an increase of adsorbent dose for all the adsorbents studied. This may be due to the fact that an increase in the adsorbent dosages at constant DCM concentration and volume leads to unsaturation of adsorbent sites and hence a fixed mass of adsorbent can adsorb only a certain amount of DCM. Therefore higher adsorbent dosages can purify large volume of effluent containing DCM. The increase in the adsorption percentage with increase in the adsorbent dosages may be attributed to increased surface area and the availability of more adsorption sites [18].

### 3.6. Adsorption isotherms

Adsorption isotherms are prerequisites to understand the nature of the interaction between adsorbate and the adsorbent used for the removal of organic pollutants [19]. Experimental data in this study have been analyzed by Langmuir and Freundlich isotherm models.

Langmuir model may be described as:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{1}{q_m}C_e \quad (2)$$

where $C_e$ is the equilibrium concentration of adsorbent (mg/L), $q_e$ is the adsorption capacity (mg/g), $b$ (L/mg) and $q_m$ (mg/g) are Langmuir constants. Langmuir constant $b$ is related to the binding energy with a pH-dependent equilibrium constant and $q_m$ is the maximum adsorption capacity determined by the number of reactive surface sites in an ideal monolayer system.

The values of Langmuir constants $b$ and $q_m$ were calculated from the slope and intercept of the linear plot of $C_e/q_e$ vs. $C_e$ (figures not shown). Higher value of $b$ (80.17 L/mg) for WGAC shows strong affinity to adsorb DCM in comparison to other adsorbents [20] (Table 1). The monolayer adsorption capacity value $q_m$ was highest for CGAC (2.364 mg/g) (Table 1). Regression coefficient ($R^2$) (0.991) value for the adsorption of DCM on LGAC suggest that Langmuir model fits well on LGAC in comparison to other adsorbents supporting monolayer coverage of the DCM on the surface of LGAC.

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:

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

The values of $R_L$ for all the adsorbents lie in between 0 and 1 indicating the favorable adsorption (Table 1) [21].

Freundlich model may be described by equation.

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

where $C_e$ is the equilibrium concentration (mg/L), $q_e$ the amount of DCM adsorbed per unit weight of adsorbent (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. 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 values of $n$ are 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 $n$ were found to be $n > 1$ for the adsorption of DCM on various adsorbents indicating favorable adsorption [22]. The value of $K_f$ was highest for BGAC (4.150) indicating higher adsorption efficiency of DCM on BGAC compared with other adsorbents [20]. The regression coefficient ($R^2$) values show better applicability of Freundlich model on CGAC, WGAC and BGAC. These results were in agreement for the adsorption of DCM on defatted seeds [23].

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

| Adsorbents | Langmuir constants | | | | Freundlich constants | | |
|---|---|---|---|---|---|---|---|
| | $q_m$ (mg/g) | $b$ (L/mg) | $R^2$ | $R_L$ | $K_f$ (mg/g) (L/mg)$^{1/n}$ | $n$ | $R^2$ |
| CGAC | 2.364 | 47 | 0.853 | 0–0.680 | 2.339 | 1.259 | 0.924 |
| LGAC | 2.188 | 22.85 | 0.991 | 0–0.814 | 1.832 | 1.536 | 0.896 |
| WGAC | 2.079 | 80.17 | 0.683 | 0–0.550 | 2.188 | 1.185 | 0.944 |
| BGAC | 1.602 | 78 | 0.707 | 0–0.562 | 4.150 | 1.715 | 0.974 |

### 3.7. Adsorption kinetics

The rate constants were calculated by using pseudo-first-order and pseudo-second-order kinetics models.

The pseudo-first-order kinetics expression is given as [24]

$$\log(q_e - q_t) = \log\ q_e - \frac{K_1}{2.303}t \tag{5}$$

where $q_e$ is the amount of DCM adsorbed per unit weight of adsorbent at equilibrium or adsorption capacity (mg/g), $q_t$ the amount of DCM adsorbed per unit weight of adsorbent at any given time $t$. $K_1$ is the rate constant for pseudo-first-order model.

The values of $K_1$ and $q_{e(theo)}$ were calculated from slope of the linear plot of $\log(q_e - q_t)$ vs. $t$ (figure not shown). The values of regression coefficient ($R^2$) and rate constants for different adsorbents at various initial concentrations and temperatures are reported in Tables 2a–2c.

The pseudo-second-order kinetic rate equation is given as [25]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{1}{q_e}t \tag{6}$$

where $K_2$ is the pseudo-second order rate constant (g/mg min). The values of $K_2$ and $q_{e(theo)}$ calculated from the slope and intercept of the linear plots of $t/q_t$ vs. $t$ (figure not shown) at various initial concentrations and temperature (Tables 2a–2c).

The data showed that the adsorption of DCM at various initial concentrations on CGAC and BGAC at 10 °C follows pseudo-first-order kinetics model (Table 2a) as evident from $q_{e(exp)}$ and $q_{e(theo)}$ values which are very close. The regression coefficient ($R^2$) values are higher for pseudo-first-order model as compared to pseudo-second-order model. The adsorption of DCM on LGAC and WGAC at 100 and 300 mg/L initial concentrations at 10 °C follows pseudo-second-order kinetics model (Table 2a), while for 200 mg/L initial concentration it follows pseudo-first-order kinetics model for both the adsorbents. The adsorption of DCM at various initial concentrations onto different adsorbents at 25 and 35 °C follows pseudo-second-order kinetics model as evident from higher regression coefficient ($R^2$) values. The values of $q_{e(exp)}$ and $q_{e(theo)}$ were almost very similar (Tables 2b and 2c).

### 3.8. Adsorption thermodynamics

The thermodynamics studies were performed at temperature ranging from 10 to 35 °C for different DCM concentration (100–300 mg/L). Thermodynamic parameters such as standard free energy change ($\Delta G^\circ$), standard enthalpy change ($\Delta H^\circ$) and standard entropy change ($\Delta S^\circ$) were calculated from Eqs. (7)–(9) [20].

$$K_c = \frac{C_{Ac}}{C_e} \tag{7}$$

where $K_c$ is the adsorption equilibrium constant, $C_{Ac}$ and $C_e$ are equilibrium concentrations of DCM on the adsorbent and in the solution, respectively.

$$\Delta G^\circ = -RT\ \ln K_c \tag{8}$$

where $T$ is the absolute temperature in Kelvin and $R$ is the gas constant.

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \tag{9}$$

$\Delta H^\circ$ and $\Delta S^\circ$ were calculated from the slope and intercept of Von't Hoff plot of $\log K_c$ vs. $1/T$. Tables 3a–3d show the values of $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$. The values of $\Delta H^\circ$ for various adsorbents were found to be positive indicating endothermic nature of the adsorption process. Reverse trend was observed in case of CGAC at 100 mg/L initial concentration where $\Delta H^\circ$ is negative showing exothermic process (Table 3a). $\Delta G^\circ$ is negative and decreases further with increase in temperature indicating spontaneous adsorption process and spontaneity increases with increase in temperature (Tables 3a–3d). Positive value of $\Delta S^\circ$ suggests randomness at the solid–solution interface during adsorption [26]. But in case of CGAC at 100 mg/L $\Delta S^\circ$ was found to be negative indicating an increase in the state of orderness during the adsorption process at solid–solution interface [27]. Generally, the change in adsorption enthalpy ($\Delta H^\circ$) for physisorption is in the range of −20 to 40 kJ/mol, but for chemisorption it is between −400 and −80 kJ/mol [28]. The values of $\Delta H^\circ$ for DCM adsorption of on various adsorbents lie in the range of physisorption process.

The nature of adsorption was also analyzed by Dubinin–Redushkevich (D–R) isotherm based on the heterogeneous nature of the adsorbent surface. The linear form of (D–R) isotherm equation is [29].

$$\ln\ q_e = \ln\ \ q_m - \beta\varepsilon^2 \tag{10}$$

where $\beta$ is the activity coefficient constant (mol$^2$/J$^2$), $q_m$ is the maximum adsorption capacity (mol/g), $q_e$ is the adsorption capacity (mol/g), and $\varepsilon$ is the Polanyi potential.

The value of $\varepsilon$ can be calculated from the relation.

$$\varepsilon = RT\ \ln\left(1 + \frac{1}{C_e}\right) \tag{11}$$

where $T$ is the absolute temperature (K), $R$ is the gas constant (J/mol K) and $C_e$ is the concentration at equilibrium (mol/L). Hence, by plotting $\ln q_e$ vs. $\varepsilon^2$, the values of $q_m$ from the intercept and $\beta$ from the slope were generated.

The constant $\beta$ gives an idea about the mean free energy ($E$) (kJ/mol) of the adsorption per molecule of the adsorbent when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship [29].

$$E = \frac{1}{(-2\beta)^{1/2}} \tag{12}$$

The magnitude of E for the adsorption of DCM on CGAC, LGAC, WGAC and BGAC at different concentration was found to be in between 0 to 8 kJ/mol (Tables 3a–3d), indicating physical nature of adsorption process, similar nature for the adsorption of DCM was reported elsewhere [1].

### 3.9. Competitive adsorption studies

The effectiveness of the various adsorbents for the removal of DCM in presence of various ionic salt solutions was studied since

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**Table 2a**
Pseudo-first-order and pseudo-second-order kinetics constants at 10 °C for the adsorption of DCM on GACs at different concentrations.

| Adsorbents | Concentration (mg/L) | $q_{e(exp)}$ | Pseudo-first-order kinetics | | | Pseudo-second-order kinetics | | |
|---|---|---|---|---|---|---|---|---|
| | | | $q_{e(theo)}$ | $K_1$ | $R^2$ | $q_{e(theo)}$ | $K_2$ | $R^2$ |
| CGAC | 100 | 20.2 | 18.75 | 0.014 | 0.993 | 25 | 0.0007 | 0.988 |
| | 200 | 35 | 31.40 | 0.018 | 0.980 | 41.67 | 0.0007 | 0.978 |
| | 300 | 54.9 | 60.81 | 0.018 | 0.943 | 62.50 | 0.0004 | 0.946 |
| LGAC | 100 | 18.3 | 11.38 | 0.048 | 0.982 | 19.23 | 0.0111 | 0.998 |
| | 200 | 35.2 | 35.16 | 0.037 | 0.971 | 38.46 | 0.0018 | 0.998 |
| | 300 | 52.2 | 24.15 | 0.023 | 0.879 | 55.55 | 0.0030 | 0.998 |
| WGAC | 100 | 19.6 | 14.39 | 0.014 | 0.968 | 20.41 | 0.0026 | 0.991 |
| | 200 | 34 | 33.96 | 0.018 | 0.985 | 40 | 0.0007 | 0.999 |
| | 300 | 53.7 | 42.27 | 0.016 | 0.976 | 62.50 | 0.0005 | 0.998 |
| BGAC | 100 | 13.5 | 12.42 | 0.016 | 0.981 | 15.87 | 0.0015 | 0.983 |
| | 200 | 22.9 | 23.12 | 0.025 | 0.981 | 26.31 | 0.0013 | 0.980 |
| | 300 | 33.8 | 33.19 | 0.018 | 0.992 | 41.67 | 0.0005 | 0.960 |

**Table 2b**
Pseudo-first-order and pseudo-second-order kinetics constants at 25 °C for the adsorption of DCM on GACs at different concentrations.

| Adsorbents | Concentration (mg/L) | $q_{e(exp)}$ | Pseudo-first-order kinetics | | | Pseudo-second-order kinetics | | |
|---|---|---|---|---|---|---|---|---|
| | | | $q_{e(theo)}$ | $K_1$ | $R^2$ | $q_{e(theo)}$ | $K_2$ | $R^2$ |
| 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 |
| LGAC | 100 | 18.3 | 14.86 | 0.032 | 0.994 | 20.41 | 0.0040 | 0.984 |
| | 200 | 34.8 | 17.62 | 0.062 | 0.994 | 35.71 | 0.0098 | 0.996 |
| | 300 | 59.3 | 24.38 | 0.057 | 0.996 | 62.50 | 0.0077 | 0.999 |
| 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 | 0.0052 | 0.991 |
| | 300 | 57.5 | 19.19 | 0.046 | 0.687 | 58.82 | 0.0072 | 0.999 |
| BGAC | 100 | 16.9 | 12.16 | 0.028 | 0.978 | 17.24 | 0.0043 | 0.997 |
| | 200 | 33.5 | 27.29 | 0.023 | 0.944 | 37.04 | 0.0574 | 0.997 |
| | 300 | 45.6 | 12.91 | 0.025 | 0.862 | 45.45 | 0.0093 | 0.999 |

**Table 2c**
Pseudo-first-order and pseudo-second-order kinetics constants at 35 °C for the adsorption of DCM on GACs at different concentrations.

| Adsorbents | Concentration (mg/L) | $q_{e(exp)}$ | Pseudo-first-order kinetics | | | Pseudo-second-order kinetics | | |
|---|---|---|---|---|---|---|---|---|
| | | | $q_{e(theo)}$ | $K_1$ | $R^2$ | $q_{e(theo)}$ | $K_2$ | $R^2$ |
| CGAC | 100 | 20.1 | 11.75 | 0.018 | 0.933 | 20.83 | 0.0050 | 0.994 |
| | 200 | 41.4 | 35.40 | 0.030 | 0.984 | 47.62 | 0.0210 | 0.997 |
| | 300 | 60.3 | 31.84 | 0.025 | 0.925 | 62.50 | 0.0020 | 0.999 |
| LGAC | 100 | 20.9 | 6.40 | 0.025 | 0.743 | 20.83 | 0.0200 | 0.998 |
| | 200 | 35.6 | 24.15 | 0.039 | 0.952 | 38.46 | 0.0030 | 0.999 |
| | 300 | 61.5 | 23.17 | 0.025 | 0.791 | 66.67 | 0.0029 | 0.999 |
| WGAC | 100 | 19.5 | 9.33 | 0.014 | 0.941 | 19.23 | 0.0064 | 0.990 |
| | 200 | 38.3 | 22.28 | 0.028 | 0.954 | 40 | 0.0029 | 0.999 |
| | 300 | 55.7 | 23.01 | 0.014 | 0.775 | 58.82 | 0.0025 | 0.997 |
| BGAC | 100 | 19.4 | 9.79 | 0.018 | 0.881 | 20 | 0.0064 | 0.989 |
| | 200 | 35.9 | 26.61 | 0.025 | 0.951 | 38.46 | 0.0019 | 0.997 |
| | 300 | 47.4 | 17.66 | 0.011 | 0.815 | 47.62 | 0.0044 | 0.997 |

**Table 3a**
Effect of concentration on the thermodynamics parameters for the adsorption of DCM at different temperature on CGAC.

| Concentration (mg/L) | Temperature (°C) | $\Delta S^\circ$ (J/K mol) | $\Delta H^\circ$ (kJ/mol) | $\Delta G^\circ$ (kJ/mol) | $E_a$ (kJ/mol) |
|---|---|---|---|---|---|
| 100 | 10 | | | −3.746 | 1.587 |
| | 25 | −4.327 | −5.045 | −3.749 | 2.236 |
| | 35 | | | −3.582 | 4.082 |
| 200 | 10 | | | −1.955 | 0.707 |
| | 25 | 78.159 | 20.353 | −3.252 | 1.581 |
| | 35 | | | −4.015 | 2.357 |
| 300 | 10 | | | −6.416 | 0.913 |
| | 25 | 311.907 | 82.218 | −13.617 | 2.236 |
| | 35 | | | −14.058 | 2.236 |

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**Table 3b**
Effect of concentration on the thermodynamics parameters for the adsorption of DCM at different temperature on LGAC.

| Concentration (mg/L) | Temperature (°C) | $\Delta S^\circ$ (J/K mol) | $\Delta H^\circ$ (kJ/mol) | $\Delta G^\circ$ (kJ/mol) | $E_a$ (kJ/mol) |
|---|---|---|---|---|---|
| 100 | 10 | | | −2.369 | 1.581 |
| | 25 | 65.08 | 16.122 | −3.749 | 2.236 |
| | 35 | | | −3.992 | 4.082 |
| 200 | 10 | | | −2.033 | 1.581 |
| | 25 | 9.78 | 0.779 | −2.054 | 2.236 |
| | 35 | | | −2.317 | 2.236 |
| 300 | 10 | | | −1.962 | 0.707 |
| | 25 | 90.85 | 24.010 | −3.345 | 2.236 |
| | 35 | | | −4.392 | 2.673 |

**Table 3c**
Effect of concentration on the thermodynamics parameters for the adsorption of DCM at different temperature on WGAC.

| Concentration (mg/L) | Temperature (°C) | $\Delta S^\circ$ (J/K mol) | $\Delta H^\circ$ (kJ/mol) | $\Delta G^\circ$ (kJ/mol) | $E_a$ (kJ/mol) |
|---|---|---|---|---|---|
| 100 | 10 | | | −2.369 | 2.673 |
| | 25 | 65.08 | 16.122 | −3.749 | 2.236 |
| | 35 | | | −3.992 | 3.535 |
| 200 | 10 | | | −2.033 | 1.290 |
| | 25 | 9.78 | 0.779 | −2.054 | 2.236 |
| | 35 | | | −2.317 | 2.236 |
| 300 | 10 | | | −1.962 | 1.290 |
| | 25 | 90.85 | 24.010 | −3.345 | 2.236 |
| | 35 | | | −4.392 | 2.236 |

**Table 3d**
Effect of concentration on the thermodynamics parameters for the adsorption of DCM at different temperature on BGAC.

| Concentration (mg/L) | Temperature (°C) | $\Delta S^\circ$ (J/K mol) | $\Delta H^\circ$ (kJ/mol) | $\Delta G^\circ$ (kJ/mol) | $E_a$ (kJ/mol) |
|---|---|---|---|---|---|
| 100 | 10 | | | −0.369 | 1.291 |
| | 25 | 106.74 | 30.252 | −1.667 | 2.236 |
| | 35 | | | −3.331 | 4.082 |
| 200 | 10 | | | 0.456 | 0.745 |
| | 25 | 111.19 | 32.148 | −1.752 | 2.236 |
| | 35 | | | −2.391 | 2.236 |
| 300 | 10 | | | 0.461 | 0.707 |
| | 25 | 73.05 | 21.253 | −1.083 | 1.000 |
| | 35 | | | −1.385 | 1.290 |

wastewater contains these salts in ionic forms. Various salt solutions (NaCl, KCl, $MgCl_2$ and $CaCl_2$) of different concentrations (0.1 and 0.5 M) 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, LGAC, WGAC and BGAC remain almost unchanged in the presence 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 and LGAC in presence of ionic salts with increase in DCM concentration to 200 mg/L.

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

| Adsorbents | Concentration of DCM (mg/L) | Adsorption capacity ($q_e$) (mg/g) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | D.I. | NaCl | | KCl | | $CaCl_2$ | | $MgCl_2$ | |
| | | | 0.1 M | 0.5 M | 0.1 M | 0.5 M | 0.1 M | 0.5 M | 0.1 M | 0.5 M |
| 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 |
| LGAC | 50 | 12.32 | 10.65 | 11.80 | 11.00 | 11.70 | 11.55 | 11.55 | 11.37 | 11.70 |
| | 100 | 23.85 | 21.32 | 23.40 | 22.70 | 22.42 | 23.30 | 21.72 | 21.07 | 22.45 |
| | 200 | 36.69 | 42.21 | 44.57 | 43.26 | 43.87 | 43.37 | 46.66 | 43.30 | 43.78 |
| 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 |
| BGAC | 50 | 9.21 | 9.38 | 10.95 | 10.97 | 11.03 | 11.29 | 9.67 | 10.50 | 10.36 |
| | 100 | 20.28 | 19.12 | 22.30 | 22.90 | 22.90 | 23.30 | 20.23 | 21.85 | 20.10 |
| | 200 | 40.14 | 33.28 | 42.44 | 42.37 | 45.71 | 39.33 | 38.92 | 36.42 | 36.52 |

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This is because the presence of ionic salts nullifies the repulsive forces leading to an increase in the adsorption. Similar results were observed by Halhouli et al. [14] for the adsorption of phenol on activated charcoal in presence of NaCl and by Cooney and Wijaya [30] for the adsorption of benzoic acid on activated carbon in presence of NaCl. This shows the feasibility of CGAC and LGAC to be used as an adsorbent for the removal of DCM from wastewater even at higher concentrations**.** The adsorption capacities on BGAC decreased with increase in DCM concentration to 200 mg/L in presence of ionic salts. The adsorption capacities on WGAC remained unaltered in presence of ionic salts even at 200 mg/L DCM concentration.

## 4. Conclusions

Studies showed that the adsorption process of DCM on various GACs was influenced by temperature, concentration, contact time, dosages and pH. The adsorption was found to be maximum (45.4 mg/g for CGAC) at pH range 6.0–8.0. Adsorption increases with increase in contact time and temperature. Reverse trend was observed on CGAC at 100 mg/L initial DCM concentration where the adsorption decreases with increase in temperature showing exothermic nature of adsorption process. Langmuir model fits well on LGAC supporting monolayer coverage of the DCM on the surface of LGAC. While the adsorption of DCM on CGAC, WGAC and BGAC follows Freundlich model. Pseudo-first-order kinetics model was better obeyed on CGAC and BGAC at 10 °C. At 25 and 35 °C pseudo-second-order kinetics model was better obeyed by the adsorbents. The adsorption of DCM on GACs was physical adsorption. The adsorption capacities remain unaltered even in presence of ionic salts for lower DCM concentration. For higher DCM concentration in ionic salt solutions CGAC and LGAC showed favorable results.

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