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Adsorption of Dichloromethane from Aqueous Phase Using Granular Activated Carbon: Isotherm and Breakthrough Curve Measurements

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Abstract: The adsorption equilibria and column dynamics for the removal of dichloromethane from aqueous phase by a coal-based granular activated carbon (GAC) and the operating factors affecting on their performances were experimentally investigated. The adsorption isotherms of this volatile organic compound on GAC were measured at three different temperatures (i.e. 298, 303 and 313 K). The highest removal of dichloromethane was found with maximum 93% removal at low concentration. The results indicated that the adsorption isotherm dichloromethane on GAC follows Langmuir model and the model parameters were recovered through a nonlinear fit of experimental data to Langmuir equation with a high confidence. The adsorption breakthrough of dichloromethane and the operational parameters such as initial concentration, flow rate, column length and temperature on breakthrough curves were investigated in a packed column. The result also indicated that the breakthrough time decreases by an increase in initial concentration, flow rate and with a decrease in column length and temperature. Thomas, Yan and Yoon-Nelson models were applied to predict the dynamic of column. It was found that Yan model well fitted the breakthrough curves.

Key words: Granular activated carbon · Adsorption · Breakthrough curve · Dichloromethane · Isotherm

INTRODUCTION

Chlorinated volatile organic compounds (CVOCs) are a subgroup of VOCs containing some chlorine compounds. Their sources of origin in environment are wastewaters from industries manufacturing herbicide, pesticide, paint, solvent, pharmaceutical, pulp and paper [1]. A number of VOCs control techniques are presently employed world-wide. These are condensation thermal oxidation, catalytic oxidation, absorption and adsorption. The removal of VOCs by adsorption has not drowned much attention in the past. However, with increasing environmental awareness and stringent regulations of pollutants emission, adsorption offers an effective means to control VOCs emissions in low concentration levels [2]. Granular activated carbon (GAC) is an amorphous solid which is exploited in many industrial and environmental applications due to its large internal surface area [3] and its unique mesoporosity and microporosity. Their systematic use in wastewater treatment is the result of several factors: (a) creation of an efficient technology of carbon activation, (b) decrease in prices of water treatment by reusing carbon after regeneration and (c) the use of carbonaceous wastes material for the manufacture of activated carbon [4].

In the present study, the adsorption equilibrium of dichloromethane, as a major VOCs pollutant of water, from aqueous phase on GAC as well as column dynamics for the removal of dichloromethane were experimentally investigated. Then, the experimental data were correlated with several adsorption isotherm models at three variable temperatures. Different models including Thomas, Yan and Yoon-Nelson was also used to describe the adsorption breakthrough curves of dichloromethane in the column dynamics.

MATERIALS AND METHODS

Adsorbent and Adsorbate: Coal-based granular activated carbon (GAC) with a size range of 1-3 mm was purchased from Appli Chem Co. (Germany). The main characteristics of the granular activated carbon sample were measured and are summarized in Table 1 which shows its high BET surface area in compare with other commercial adsorbents.

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Table 1: Physical properties of GAC

	Unit	GAC
Chemical structure		Coal-based
Particle size	mm	1-3
Micro pore volume	$cm^3.g^{-1}$	0.35
BET surface area	$m^2.g^{-1}$	893
True density	$g.\ cm^{-3}$	0.85
Molecular weight MW	$g.\ mol^{-1}$	12.01
Solubility at 20°C		Insoluble (H_2O)

Table 2: Physical Properties of dichloromethane

Adsorbate	Unit	Dichloromethane
Formula		CH_2Cl_2
Molecular weight MW	$g\ mol^{-1}$	84.93
Normal boiling point T_{eb}	°C	39.8
liquid density at 20°C	$\rho.\ g^{-1}.\ cm^{-3}$	1.318
Solubility in water	Mass %	1.32
Vapor pressure at 293 K	mm Hg	350

The selected VOC for this study, dichloromethane (mass fraction 0.998 purity), were provided from Merck. The properties of dichloromethane are stated in Table 2.

Methods: Prior to start any experiment, the granular activated carbon (GAC) was dried for 48 hours in oven at 115°C to remove all adsorbed gases and moisture content. The equilibrium experiments were achieved by contacting a given amount of adsorbent (3g) (weighted by a balance Sartorius Model GE 412, Germany with an accuracy of 0.01 g) with defined initial concentration of dichloromethane solutions in an incubator shaker at constant temperature. For each experimental run, 100 ml of dichloromethane solution of known initial concentration (C_0) and adsorbent dose (m= 3g) taken in a 250 ml conical flask with a stopper, was agitated in a temperature-controlled shaker at a constant speed of 190 rpm. Samples were periodically collected for each 0.5 hour and their concentrations were determined by a spectrophotometer until the equilibrium was reached (normally after 2 hours). Effect of temperature on dichloromethane adsorption was studied at three different temperatures.

The adsorption capacity of the granular activated carbon was calculated as:

$$q = \frac{V(C_0 - C_e)}{m} \qquad (1)$$

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

Table 3: Experimental conditions for different test runs

Experiment	C_0 (mg. l^{-1})	Q (ml. min^{-1})	L (m)	T (K)
Run 1	12380	20	0.1	303
Run 2	7370	20	0.1	303
Run 3	4110	20	0.1	303
Run 4	12380	15	0.1	303
Run 5	12380	10	0.1	303
Run 6	12380	20	0.15	303
Run 7	12380	20	0.1	313
Run 8	12380	20	0.1	303

For dynamic study, a fixed-bed glass column with inside diameter of 0.012 m and total length of 0.25 m was used. Figure 1 shows schematic diagram of experimental fixed-bed set up. For each set of experiment, a known dried weight of activated carbon was packed into the column and two layers of glass beads with length of 0.025m were packed in the top and the bottom of the column. The role of the glass beads were to moderate the oscillating flow that induced by pump and distribute properly across the column. Before the start of experimental run, deionized water was used for two hours to wash out the carbons and remove bubbles in the column. The feed (dichloromethane) with known concentration was pumped into the bottom of the column. A water bath was used to keep the feed in a desired constant temperature. The effluent was collected at time intervals and its concentration was determined. The experimental conditions for each test run were summarized in Table 3.

RESULTS AND DISCUSSION

Adsorption Equilibrium Study: Adsorption equilibrium is the most significant and helpful data on an adsorption system. It is also helpful in model prediction for analysis and design of an adsorption process. Several equilibrium isotherm equations, namely, Langmuir, Freundlich, Redlich-Peterson have been evaluated to represent the experimental sorption isotherm data. Langmuir model described by the following equation:

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

Were C_e is the equilibrium concentration of the adsorbate (mol.m^{-3}) and q_e is the amount of adsorbate adsorbed per unit weight of the adsorbent (mol.kg^{-1}), q_m and b are the Langmuir isotherm constants related to maximum adsorption capacity and energy of adsorption, respectively [5].

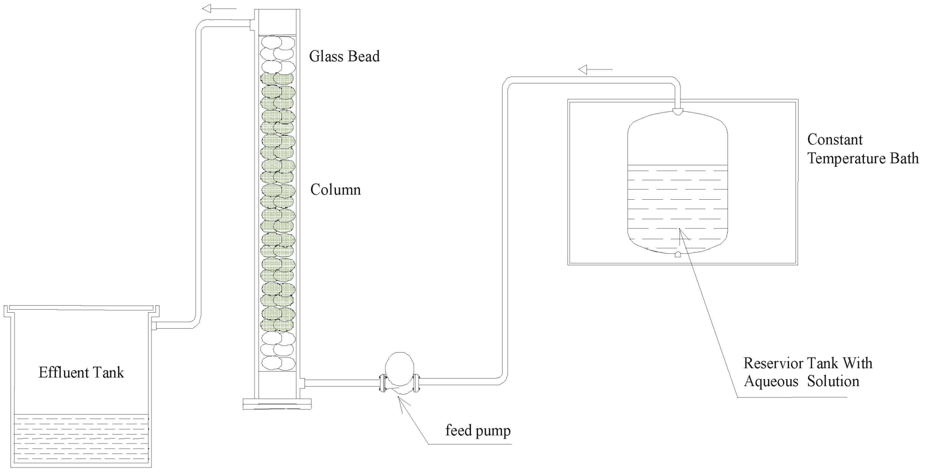

Fig. 1: Schematic diagram of experimental set up used for the column studies

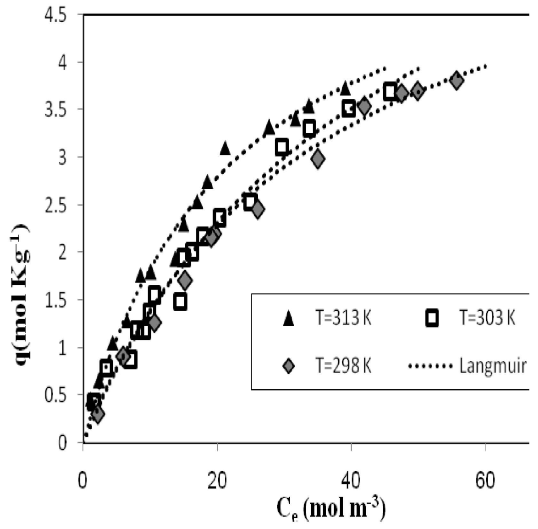

Fig. 2: Adsorption isotherms of dichloromethane on GAC at 298, 303 and 313 K, symbols: experimental data, line: model

The Freundlich model is described by the following equation:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{3}$$

Where, the parameters K_F and n are Freundlich constants. The K_F is a measurement of the adsorption capacity and n is a measure of the adsorption intensity and C_e and q_e have the same definition as stated in equation 2 [5].

Redlich-Peterson model describes a three-parameter isotherm, which combines elements of the Langmuir and Freundlich isotherms in a single equation given below:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{4}$$

Where K_R and a_R are the Redlich-Peterson isotherm constants and β the Redlich-Peterson isotherm exponent, which lies between 0 and 1. The C_e and q_e have the same definition as described in equation equation 2 [6].

Adsorption Isotherms: Figure 2 depicts the adsorption isotherms of dichloromethane on GAC at the temperatures of 298, 303 and 313 K. As it is observed from this figure; the adsorption capacity of adsorbate increased by an increase in temperature. The rate of adsorption is a good indicator for determining type of adsorption whether it is a physical adsorption or chemisorption. By investigation the effect of contact time, it is found that the adsorption of dichloromethane is fast in the first 30 min, thereafter, the dichloromethane uptake by GAC becomes very slow.

Matlab software, version 7.5 (2007) has been used to recover isotherm equation parameters through a nonlinear fit to the experimental data. By comparing the experimental results with equilibrium isotherm equations, it was found that Langmuir, Freundlich and Redlich-Peeterson all well fitted with the experimental isotherms. However, the best fit was achieved by the Langmuir. The fitting results also are shown for comparison in Figure 2. The model parameters of isotherm for adsorption of dichloromethane on granular activated carbon at three different temperatures are listed in Table 4.

Effect of Temperature and Initial Concentration: The effect of temperature and initial concentration (C_0) on the

Table 4: The fitting parameters of Langmuir equation for dichloromethane at three temperatures

		Temperature (K)		
Isotherms	Constants	298	303	313
Langmuir	b	7.12	7.3382	5.8510
	q_m	0.02166	0.0230	0.04565
	R^2	0.9959	0.9849	0.9881
Freundlich	K_F	0.2852	0.2981	0.4847
	n	1.508	1.487	1.752
	R^2	0.9942	0.9839	0.9832
Redlich-Peterson	K_R	0.1841	0.2633	0.3146
	a_R	0.08087	0.2295	0.102
	$\hat{a}$	0.7344	0.5836	0.3146
	R_2	0.9963	0.9837	0.9875

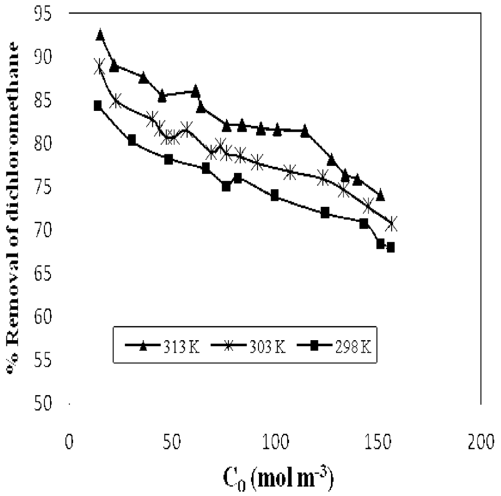

Fig. 3: Effect of initial concentration and temperature on removal of dichloromethane (m = 3g, t = 120 min)

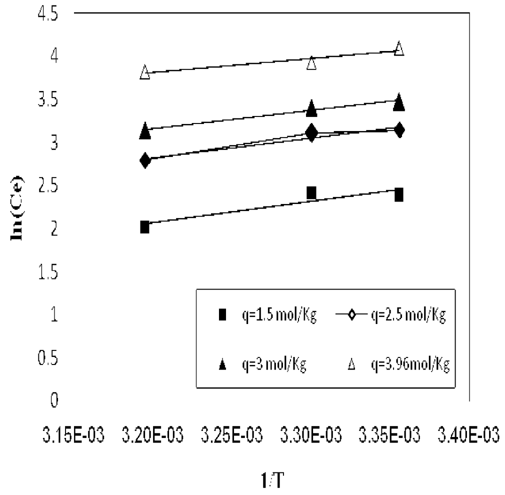

Fig. 4: Adsorption isotherm for determining heat of adsorption for dichloromethane on GAC

equilibrium adsorption of dichloromethane by GAC is shown in Figure 3. It is clear from this figure that the removal of dichloromethane increased by increasing the temperature and decreasing the initial concentration. At the concentration of 14 mol. m^{-3} (minimum concentration used) and at the temperature of 313, 303 and 298 K, the highest removals were 96.62, 88.80 and 84.42%, respectively. In addition, with the same dosage of GAC (3g), at the concentration of 156 mol. m^{-3} (minimum concentration used) and at the temperature of 313, 303 and 298 K, the lowest removals were 74.11, 70.78 and 68.06%, respectively. An increase in amount of adsorption with temperature indicates that the adsorption phenomenon is dominated by the chemisorption. Increasing trend in adsorption uptake with a decrease in initial concentration can be justified by the fact that as the initial concentration decreases, most active sites becomes available for the adsorbate.

Estimation of Adsorption Heat: The isosteric heat of adsorption ($\Delta H_{st,a}$) at different constant equilibrium uptake (q_e =1.5 mol. kg^{-1}, 2.5 mol. kg^{-1}, 3 mol. kg^{-1} and 3.95 mol. kg^{-1}) was calculated using the Clausius-Clapeyron equation:

$$\frac{d\ln C_e}{dT} = \frac{-\Delta H_{st,a}}{RT^2} \qquad (5)$$

$$\Delta H_{st,a} = \frac{d\ln C_e}{d(1/T)\big|_{q_e}}$$

For this purpose, C_e at constant q_e was obtained from the Langmuir adsorption isotherm equation at different temperatures. Also, $\Delta H_{st,a}$ was calculated from the slope of a linear plot of In(C_e) versus ($1/T$) according to equation 6. The results of fitting were shown in Figure 4. Table 5 shows that $\Delta H_{st,a}$ decreased as the equilibrium uptake increased. The positive value for heat of adsorption (positive slope) shows that the sorption of dichloromethane on GAC is an endothermic process. The calculated heat of adsorption at different constant equilibrium uptakes have been shown in Table 5.

Column Study: The breakthrough curve (concentration versus time profile) for the effluent describes the performance of packed beds. To avoid complexity of the simplified model under certain simplifying assumptions are widely employed. These models are briefly discussed here.

Table 5: $\Delta H_{st,a}$ that calculated from the slope of the $ln(C_e)$ versus $(1/T)$ and the values of C_e at different temperatures for dichloromethane

q_e(mol/Kg)	C_e (molm^{-3}), at T=298 K	C_e (molm^{-3}), at T=303 K	C_e (molm^{-3}), at T=313 K	$\Delta H_{st,a,}$ (J/mol)
1.5	10.97	11.16	7.55	2505
2.5	23.16	22.44	16.34	2279
3	32.07	30.02	23.05	2113
3.95	60.04	50.90	45.87	1583

Table 6: Predicted parameters of Yan model for dichloromethane adsorption on GAC

Experiments	K_Y(ml. mg^{-1}. min^{-1})	q_Y(mg. g^{-1})	R^2
Run 1	4892	508.381	0.9982
Run 2	6137	545.380	0.9988
Run 3	11220	510.517	0.9891
Run 4	2442	761.261	0.9871
Run 5	1493	957.133	0.9913
Run 6	2910	982.130	0.987
Run 7	3388	1037.485	0.9992

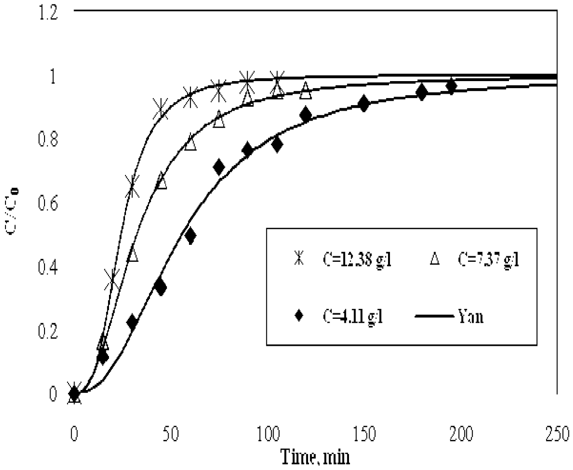

Fig. 5: Effect of initial concentration on breakthrough curves of dichloromethane at constant Q= 0.02 l. min^{-1}, L=10 cm and T=303 K and prediction of Yan model.

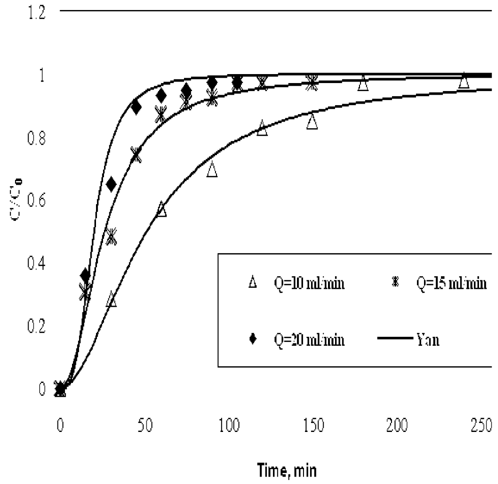

Fig. 6: Effect of flow rate on breakthrough curves of dichloromethane at constant C_0= 12.38 g. l^{-1}, L=10 cm and T=303 and prediction of Yan model.

The Thomas solution is one of the most general and widely used methods in column performance theory. The model is described by the following equation:

$$\frac{C}{C_0} = \frac{1}{1+\exp\left(\frac{k_{Th}}{Q}\left(q_T X - C_0 V_{eff}\right)\right)} \tag{6}$$

Where k_{Th} is the Thomas rate constant (ml. min^{-1}. mg^{-1}) and q_T is the maximum solid-phase concentration of the solute (mg. g^{-1}) [7, 8].

Yan *et al.* [9] proposed an empirical equation which could overcome the draw-back in Thomas Model especially its serious deficiency in predicting the effluent concentration with respect to time zero. The empirical equation proposed by Yan *et al.* [9] was found a better description of the breakthrough curves in a fixed bed column. This equation is expressed as follows:

$$\frac{C}{C_0} = 1 - \frac{1}{1+\left(\frac{Q^2 t}{k_Y q_Y m}\right)^{(k_Y C_0 / Q)}} \tag{7}$$

Where k_Y is kinetic rate constant for Yan Model (L. min^{-1}. mg^{-1}); q_Y is maximum adsorption capacity (mg.g^{-1}) of adsorbent estimated by Yan Model.

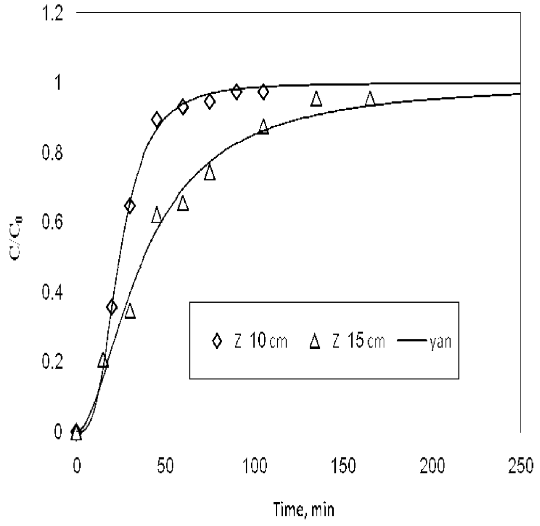

Fig. 7: Effect of column length on breakthrough curves of dichloromethane at constant C_0= 12.38 g. l^{-1}, Q=0.02 l. min^{-1} and T=303K and prediction of Yan model.

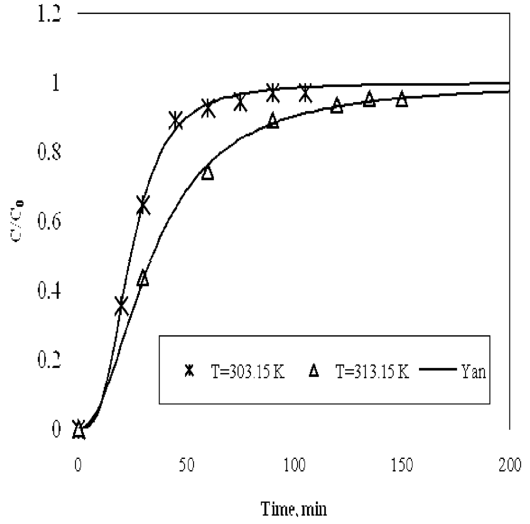

Fig. 8: Effect of temperature on breakthrough curves of dichloromethane at constant C_0= 12.38 g. l^{-1}, Q=0.02 l.min^{-1} and L=10 cm and prediction of Yan model.

Yoon and Nelson [10] have developed a relatively simple model. This model is not only less complicated than other models, but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent and the physical properties of the adsorption bed. The Yoon and Nelson equation for a single component system is expressed as follows:

$$\ln\frac{C}{C_0 - C} = k_{YN}t - \tau k_{YN} \tag{8}$$

Where k_{YN} is the rate constant (min^{-1}); τ, the time required for 50% adsorbate breakthrough (min) and t is the breakthrough (sampling) time (min). The calculation of theoretical breakthrough curves for a single-component system requires the determination of the parameters k_{YN} and τ for the adsorbate of interest. These values may be determined from available experimental data [10-11].

Adsorption Dynamics: The operational parameters such as initial concentration (C_0), flow rate (Q), column length (L) and temperature (T) have great influence on breakthrough and dynamic of column. In this study, the effect of these parameters on dichloromethane breakthrough time was investigated. Figure 5 illustrates the effect of initial concentrations on breakthrough time for dichloromethane at 12.38, 7.37 and 4.11 g. l^{-1}. It is observed that at high concentration of C_0 the breakthrough occurred faster than the low concentration of C_0 and the slope of the breakthrough curves is steeper than the others. This can be explained by the fact that more adsorption sites are being covered with increase in C_0 concentration. These results demonstrate that the change in concentration gradient affected the saturation rate and breakthrough time. As the C_0 increases, dichloromethane loading rate increase, so decrease in driving force or mass transfer which resulted in a decrease in adsorption zone length.

With the purpose of investigating the effect of flow rate on dichloromethane, three different flow rates 20, 15 and 10 ml. min^{-1} were examined. The results of these experiments are depicted in Figure 6. The breakthrough time for a higher flow rates was earlier than for the lower flow rates. At high value of Q, the rate of mass transfer tends to increase, resulted that the amount of adsorbed materials onto GAC per unit bed height (mass transfer zone) increased with an increase in Q leading to a faster saturation at a high value of Q.

The effect of column length was the third parameter that was evaluated. Figure 7 represents that by increasing the column length from 10 to 15 cm the breakthrough time increases. This was due to increase in number of binding sites owing to increase in adsorption surface area of the adsorbent. By increasing the column length, the adsorbate molecules had enough time to diffuse through the activated carbons. This phenomenon has increased the breakthrough time.

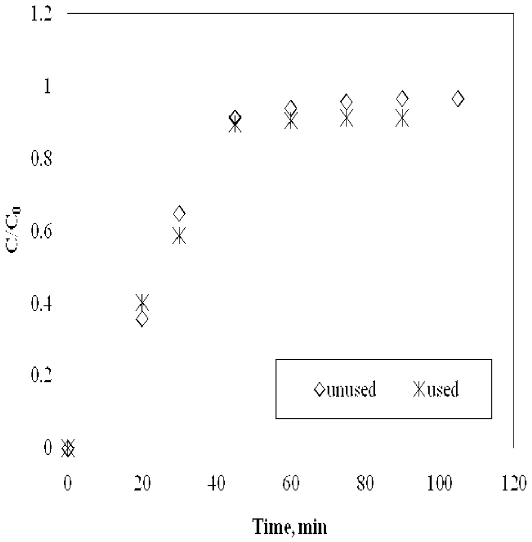

Fig. 9: Comparison of breakthrough curves of dichloromethane on used and unused GAC at constant C_0 =12.38 g. l^{-1}, Q=0.021 l. min^{-1}, L=10 cm and T=303 K.

Temperature was the last parameter that was investigated in this study. The breakthrough curves were examined at two different temperatures (303 and 313 K), while other factors were kept constant. Figure 8 shows that at high temperature, the breakthrough curve occurred slower than at low temperature.

In addition, to investigate the desorption ability of adsorbents, the used GACs were wash out by distilled water at 150°C for 2 h and the regenerated GACs were dried in oven at 115°C for 48 h. The first experiment (Run 1) was repeated by the regenerated GACs (Run 8). The results are shown in Figure 9 confirmed that GACs were completely desorbed from the adsorbed materials through regeneration process.

To predict the acquired breakthrough curves three model, namely Thomas, Yan and Yoon-Nelson have been used. Yan's model proved that to represent the best prediction for dichloromethane breakthrough. The model recovered parameters are listed in Table 6.

CONCLUSION

In this study, equilibrium and dynamic adsorption of dichloromethane from its dilute solution on a commercial coal-based granular activated carbon were investigated. The result of equilibrium study has shown that the uptake of dichloromethane increases with an increase in temperature, which indicated the chemisorption dominates the adsorption process. The positive values of isosteric heat of adsorption revealed that the sorption of dichloromethane is an endothermic process. Adsorption equilibrium data of dichloromethane on GAC were well fitted with Langmuir isotherm. The effect of different operational factors such as initial concentration, temperature, flow rate and column length on breakthrough curve of dichloromethane were examined in a packed column. The result revealed that by increasing the initial concentration, flow rate, decreasing the column length, temperature and the breakthrough time decreased. The breakthrough curves for dichloromethane are well predicted by Yan's model.

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