Full Length Research Paper

Batch and column study of haloacetic acids adsorption onto granular activated carbon

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The granular activated carbon (GAC) was used as an adsorbent for its ability to remove haloacetic acids (HAAs) from drinking water by batch and column experiments. Various thermodynamic parameters such as $\triangle G^{\circ}$, $\triangle H^{\circ}$ and $\triangle S^{\circ}$ have been calculated. The thermodynamics of HAAs onto GAC system indicates spontaneous and exothermic nature of the process. The ability of GAC to adsorb HAAs in a fixed bed column was investigated as well. The effect of operating parameters such as flow rate and inlet HAAs concentration on the sorption characteristics of GAC was investigated. The total adsorbed quantities, equilibrium uptakes and total removal percents of HAAs related to the effluent volumes were determined by evaluating the breakthrough curves obtained at different flow rates and different inlet HAAs concentrations for adsorbent. The data confirmed that the total amount of sorbed HAAs and equilibrium HAAs uptake decreased with increasing flow rate and increased with increasing inlet HAA_5 concentration. The Adams–Bohart model was used to analyze the experimental data and the model parameters were evaluated.

Key words: Adams–Bohart model, adsorption, fixed bed column, granular activated carbon, haloacetic acid removal, breakthrough curve.

INTRODUCTION

Chlorination is the most common disinfection method of drinking water. It is an effective way to kill many kinds of bacteria and other germs that may be harmful to one's Health. Thought unquestionably important to the supply of safe drinking water, it also leads to the formation of undesirable organic-by-product (disinfection-by-product, DBPs). The two main classes of these compounds are trihalomethanes (THMs) and haloacetic acids (HAAs) (Arora, 1997; Singer, 1994). Haloacetic acids are formed during disinfection of water that contains bromide ions and organic matter (Pourmoghaddas, 1993). Haloacetic acids are formed when chlorine reacts with bromide (Br⁻) and natural organic matter (NOM) in source waters (Singer, 1995, 1999; Nikolaou, 2002). Although there are

nine HAA species, only five of them are regulated by the current disinfectants/disinfection by-products (D/DBP) rule due to limited formation and occurrence data for some of the species (contact time of HAAs). The five HAAs are monochloro and monobromoacetic acid, dichloro and trichloroacetic acid, and dibromoacetic acid (ClAA, BrAA, Cl_2AA, Cl_3AA and Br_2AA, respectively). HAAs are colorless, have a low volatility, dissolve easily in water and are fairly stable. When consumed in drinking water, HAAs are rapidly absorbed into the bloodstream and are carried throughout the body. However over long periods of time, exposure to levels of HAAs at or above the maximum contaminant level can cause injury to brain, breast, nerves, liver, kidneys, eyes and reproductive systems (Ronald, 2007). Those HAA_5 of most concern have carcinogenic, reproductive and developmental effects on the basis of current knowledge, a number of CBPs (chlorination-by-products) have been regulated by EPA (1998), WHO (2004) and European Union (2008).

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Table 1. THMs and HAA_5 regulations (maximum allowable DBP levels: $\mu g\ l^{-1}$).

	TCM	BDCM	DBCM	TBM	TTHMs	MCA	DCA	TCA	HAA_5
EEC(2008)	40	15			100				
US.EPA (1998)					80				60
WHO (2004)	200	60	100	100		20	50	200	

Table 2. Characteristics of the GAC.

Parameter	Value
Bulk density ($g\ ml^{-1}$)	0.425
Solid density ($g\ ml^{-1}$)	4.04
Moisture content (%)	0.52
Ash content (%)	6.5
Particle size (mm)	0.6-1.1
Porosity (dimensionless)	0.67
BET surface area ($m^2\ g^{-1}$)	413.3
Surface acidity (meq.v g)	0.02
Surface basicity (meq.v g)	2.34

These standards have been shown in Table 1 (US EPA, 1998).

There are various mefthods to remove HAAs including chemical precipitation, membrane process, ion exchange, liquid extraction and electrodialysis. The adsorption technique is one of the preferred methods for removal of HAA_5 because of its efficiency and low cost (Lekkas, 2009). Several treatment alternatives have been proposed for the removal of DBPs. Granular activated carbon (GAC) has been of a special interest due to its ability to remove a wide range of compounds such as odor as color causing compounds, NOMs, THMs, HAAs and other toxic compounds (Lekkas, 2009; Zhou, 2002; Clark, 1991). The objectives of the present study are to adsorb HAA_5 from aqueous solution by GAC using batch and four fixed-bed columns. In batch studies, the dynamic behavior of the adsorption was investigated on the effect of initial HAA_5 concentration, temperature and adsorbent dosage. The thermodynamic parameters were also evaluated from the adsorption measurements. The Langmuir and Freundlich were used to fit the equilibrium isotherm. The important design parameters such as flow rate of fluid and initial concentration of HAA_5 solution have been investigated. The breakthrough curves for the adsorption of HAA_5 were analyzed using Adams–Bohart model.

MATERIALS AND METHODS

The stock solutions of HAA_5 for these studies were obtained from Merck, Germany. All working solutions were prepared by diluting the stock solution with deionized water. Analytical reagents used for determination of HAA_5 concentrations were purchased from Merck, Germany. GAC was prepared from a local municipal water treatment plant. It was sieved to obtain the desired size fractions, washed thoroughly with hot distilled water several times and then dried in hot air oven (Shinsaeng Fine Tech., SFCN-301, China) for 9 h at 100 ± 5°C. Some physicochemical characteristics of the adsorbent existing in this plant are summarized in Table 2.

Analytical method

The amount of haloacetic acids was determined by EPA Method 552.2. This method involves a liquid–liquid extraction procedure after which the acetic acids are converted to methyl esters. This method uses gas chromatography and electron capture detection (Agilent, 6890N, USA) (Munch, 1995).

Batch studies

The stock solutions of HAA_5 for these studies were obtained from Merck, Germany. All working solutions were prepared by diluting the stock solution with deionized water. Experiments were conducted in 500 ml Erlenmeyer flasks containing 200 ml of known HAA_5 synthetic solutions. Experiments were done with variable initial HAA_5 concentration (100, 200, 300, 400 $\mu g\ l^{-1}$), constant temperature (15, 25°C) and 8 g of adsorbent dose (40 $g\ l^{-1}$). Flasks were agitated on a shaker at constant shaking rate (200 rpm) for 80 h to ensure equilibrium was reached.

Column studies

Four fixed-bed columns were made up of glass with 4.0 cm internal diameter and 90 cm in height. The bed length of each column used in the experiments was 75 cm. In typical experiments, the known concentration of HAA_5 was pumped (Piston pump, Diamond OS-30A, China) at a fixed flow rate to the filled bed of adsorbent. The particle size of adsorbent used in the experiment was 0.7 to 1.2 mm. The temperature of stream feeding solution was controlled at 25°C through a thermostatic bath and also, the temperature of columns was controlled at 25°C with a thermal jacket. The bed porosity calculated by Equation 1 was equal to 0.22 (Pushnov, 2006).

$$\varepsilon = 1 - \frac{m_p}{(\rho_p A_T H)} \tag{1}$$

Where ε, H and A are the porosity, height (cm) and cross surface area (cm^2) of the bed in column, respectively. m_p and ρ_p are the mass (g) and bulk density ($g\ ml^{-1}$) of GAC in column, respectively.

Table 3. The equilibrium uptake capacities and adsorption yields obtained at different initial concentrations and temperatures.

C_0 µg l^{-1}	15°C		25°C	
	q_e (µg mg^{-1})	Adsorption (%)	q_e (µg mg^{-1})	Adsorption (%)
100	0.002285	91.4	0.002253	90.1
200	0.004490	89.8	0.004415	88.3
300	0.006448	86.0	0.006343	84.5
400	0.007933	79.3	0.007755	77.5

RESULTS AND DISCUSSIONS

Batch studies

Effect of adsorbent dosage

The removal of HAA$_5$ by GAC at different adsorbent dosages (2 to 8 g l^{-1}), 25°C, 80 h and 200 rpm for the HAA$_5$ concentration 100 µg l^{-1} is investigated. The results are shown that the percent removal of HAA$_5$ increases with increase in the dose of GAC due to the greater availability of the adsorbent (Mohan, 2006). The increase in adsorbent dosage from 2 to 8 g l^{-1} resulted in an increase from 46.1 to 90.1% in adsorption of HAA$_5$. However, uptake of HAA$_5$ showed a reverse trend to the removal percentage adsorptions, with increasing adsorbent dosage from 2 to 8 g l^{-1}, the adsorption of HAA$_5$ per unit weight of adsorbent decreased from 23.05 to 11.26 µg g^{-1}. The HAA$_5$ removal (%) at any instant of time was determined by Equation 2.

$$HAA_5\ Removal\ (\%) = \frac{C_0 - C_t}{C_0} 100 \qquad (2)$$

The HAA$_5$ concentration retained in the adsorbent phase was calculated by using Equation 3:

$$q_e = \frac{(C_0 - C_t)V}{W} \qquad (3)$$

Where q_e is the adsorption capacity at equilibrium (µg g^{-1}), C_0, C_t and C_e are the initial, any instant of time and equilibrium concentrations of HAA$_5$ in solution (µg l^{-1}), respectively. V is the solution volume (lit) and W is the adsorbent weight (g).

Effect of initial HAA$_5$ concentration on temperature dependent adsorption

In Table 3, at 25°C when the initial HAA$_5$ concentration increased from 100 to 400 µg l^{-1}, HAA$_5$ adsorption removal decreased from 90.1 to 77.5% and the uptake

capacity of GAC increased from 11.26 to 38.75 µg g^{-1}. At 25°C for a HAA$_5$ concentration of 100 µg l^{-1} after an 80 h of sorption time, while HAA$_5$ concentration was measured as 9.9 µg l^{-1}, for 15°C HAA$_5$ concentrations was measured as 8.6 µg l^{-1}. Table 3 shows that the equilibrium uptake capacity of GAC increased with increasing initial HAA$_5$ concentration up to 400 µg l^{-1} because the initial HAA$_5$ concentration provided an important driving force to overcome all mass transfer resistance. The increases of loading capacity of GAC with increasing initial HAA$_5$ concentration may also be due to higher interaction between HAA$_5$ and adsorbent. As GAC offered a finite number of surface binding sites, HAA$_5$ adsorption showed a saturation trend at higher initial HAA$_5$ concentration. The Langmuir and Freundlich equations were used in the analysis of the adsorption results and the data for adsorption of HAA$_5$ on activated carbon are fitted to these Isotherm models (Dursun, 2005). The linear forms of Freundlich and Langmuir models are represented by Equations 4 and 5:

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

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_0 K_L}\right) + \left(\frac{1}{Q_0}\right) C_e \qquad (5)$$

Where K_F, $1/n$ and K_L are characteristic constants, C_e is the equilibrium concentration or concentration in bulk fluid phase (µg l^{-1}) and Q_0 is the solid phase concentration corresponding to complete coverage of available adsorption sites. The value of K_F has been used as a relative measure of adsorption capacity. Q_0, K_L, K_F and $1/n$ of Langmuir and Freundlich model constants were determined and presented in Table 4. The value of correlation coefficient ($R^2 > 0.997$) indicates that there is a strong positive relationship for the data and that sorption data of the HAA$_5$ onto GAC follows the Langmuir isotherm. The Q_0 for HAA$_5$ on GAC was increased from 0.01096×10^{-3} to 0.01097×10^{-3} µg mg^{-1} with the increase in temperature from 15 to 25°C (Table 4). All these results showed that Langmuir isotherm model fitted the results quite well suggesting that the surface of the

Table 4. Freundlich and Langmuir isotherms constants of HAA$_5$ adsorption on GAC at different temperature.

T°C	Langmuir constants			Freundlich constants		
	$Q_o \times 10^3$ (μg mg^{-1})	K_L (l μg^{-1})	R^2	$K_F \times 10^3$	1/n	R^2
15	0.01096	32.448	0.997	0.7638	0.551	0.962
25	0.01097	27.739	0.996	0.6729	0.564	0.963

Table 5. Thermodynamic parameters for the uptake of HAA$_5$ on activated carbon calculated under standard conditions.

Temperature (°C)	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (J mol^{-1} K^{-1})
15	-8.334	-11.188	-9.909
25	-8.232	---	---

sorbent is homogenous. Each binding site accepts only one of the HAA$_5$ molecules that sorbed molecules are organized as a monolayer and all sites are energetically equivalent and there is no interaction between sorbed molecules (Tewari, 2005). Thermodynamic parameters such as change in free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) were determined using the following equations:

$$\Delta G^o = -RT\ln K \tag{6}$$

$$\Delta H^o = -R(\frac{T_2 - T_1}{T_2 - T_1})\ln\frac{K_2}{K_1} \tag{7}$$

$$\Delta S^o = \frac{\Delta H^0 - \Delta G^0}{T} \tag{8}$$

Where K, K$_1$ and K$_2$ are the Langmuir constants. K$_1$ and K$_2$ are corresponding to temperatures of T$_1$ and T$_2$. Also, R is the universal gas constant (J mol^{-1} K^{-1}). A negative $\Delta G°$ value confirms the feasibility of the process and spontaneous nature of adsorption. Negative values of $\Delta H°$ indicate the exothermic nature of the process while the negative $\Delta S°$ corresponds to a decrease in the degree of freedom of the adsorbed species (Meena, 2008). Thermodynamic parameters, namely: free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) changes are given in Table 5.

Column studies

Column data analysis

The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of an adsorption column. The breakthrough curves show the loading behavior of adsorbate to be removed from solution in a fixed bed and is usually expressed in terms of adsorbed adsorbate concentration (C_{ad}) or normalized concentration defined as the ratio of effluent adsorbate concentration to inlet adsorbate concentration (C_t/C_o) as a function of time or volume of effluent for a given bed height (Aksu, 2004).

C_{ad} = C_o (inlet adsorbate concentration) – C_t (outlet adsorbate concentration) (9)

Effluent volume (V_{eff}) can be calculated from the following equation:

$$V_{eff} = Q^* t \tag{10}$$

Where t and Q are the total flow time (min) and volumetric flow rate (ml min^{-1}), respectively. The area under the breakthrough curve (A) obtained by integrating the adsorbed concentration (C_{ad}; μg l^{-1}) versus time (t; min) plot can be used to find the total adsorbed adsorbate quantity (maximum column capacity). Total adsorbed adsorbate quantity (q_{total}; μg) in the column for a given feed concentration and flow rate is calculated from the following equation:

$$q_{total} = \frac{(Q*A)}{1000}\int_t^{t_{total}} C_{ad} dt \tag{11}$$

Total amount of HAA$_5$ sent to column (m_{total}) is calculated from the following equation (Padmesh, 2005):

$$m_{total} = \frac{C_o * Q * t_{total}}{1000} \tag{12}$$

Total removal is calculated from the following equation (Aksu, 2004):

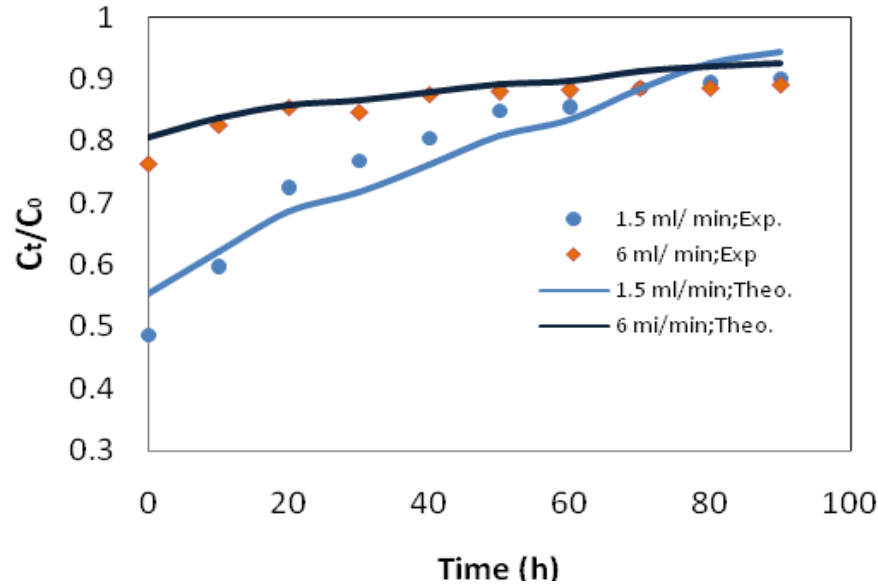$$Total\ Removal\ (\%) = \frac{q_{total}}{m_{total}} * 100 \tag{13}$$

Figure 1. Comparison of the experimental and predicted breakthrough curves obtained at different flow rates according to the Adams-Bohart model (C_o = 400 µg l^{-1}, particle size = 0.7 to 1.2 mm, total bed height = 300 cm).

Equilibrium HAA$_5$ uptake (q_{eq}) (or maximum capacity of the column) in the column is defined by Equation 14 as the total amount of HAA$_5$ sorbed (q_{total}) per gram of sorbent (X) at the end of total flow time (Aksu, 2004):

$$q_{eq} = \frac{q_{total}}{X} \tag{14}$$

The breakthrough is usually defined as the phenomenon when the effluent concentration from the column is about 3 to 5% of the influent concentration (Chen, 2005, 2003). The number of bed volumes (BV) is defined by Equation 15.

$$Number\ of\ bed\ volumes = \frac{Volume\ of\ solution\ treated}{Volume\ of\ adsorption\ bed} = \frac{Operating\ time}{EBRT} \tag{15}$$

The empty bed residence time EBRT is the time required for the liquid to fill the empty column (Ko, 2000):

$$EBRT = \frac{Bed\ volume}{Volumetric\ flow\ rate\ of\ liquid} \tag{16}$$

The adsorbent exhaustion rate is the mass of adsorbent used per volume of liquid treated at breakthrough (Ko, 2000).

$$Adsorbent\ exhaustion\ rate = \frac{Mass\ of\ adsorbent\ in\ column}{Volume\ treated\ breakthrough} \tag{17}$$

Effect of flow rate

The solution was passed through the four GAC columns-in-series at 1.5 ml min^{-1} for a 90 h test period and total amount of GAC used in columns was 640 g. The influent HAA$_5$ concentration was 400 µg l^{-1}. The HAA$_5$ concentration in the effluent decreased after each GAC column. The breakthrough curves of HAA$_5$ adsorption by GAC at 1.5 ml min^{-1} flow rate and at fixed bed height of 75 cm are shown in Figure 1. An earlier breakthrough and exhaustion time were observed in the profile, when the flow rate was increased to 6 ml min^{-1}. The flow rate also strongly influenced the HAA$_5$ uptake capacity of 1.087 and 0.4646 µg g^{-1} which were recorded at 1.5 and 6 ml min^{-1}, respectively. The breakthrough curves indicate that the break point time and adsorbed HAA$_5$ concentration decrease when the flow rate is increased. The probable reason behind this is that when the residence time of the solute in the column is not long enough for adsorption equilibrium to be reached at that flow rate, the HAA$_5$ solution leaves the column before equilibrium occurs (Ghorai, 2005). Thus, the contact time of HAA$_5$ with GAC is very short at higher flow rate, causing a reduction in removal efficiency. Accordingly, the breakthrough takes place at 2.15 and 8.6 BV for flow rates 1.5 and 6 ml min^{-1}, respectively. The empty bed residence time is 2512 min for four column which its value for each column is 628 min. Comparison of these values indicates that the treated bed volume (BV) increases with a higher EBRT. In other words, with a higher EBRT, HAA$_5$ had more time to contact with GAC,

Table 6. The effect of flow rate and initial HAA5 concentration on the total adsorbed quantity of HAA5 (q_{total}), equilibrium HAA5 uptake (q_{eq}) and total removal percentage of HAA5 for adsorption to HAA5 onto GAC.

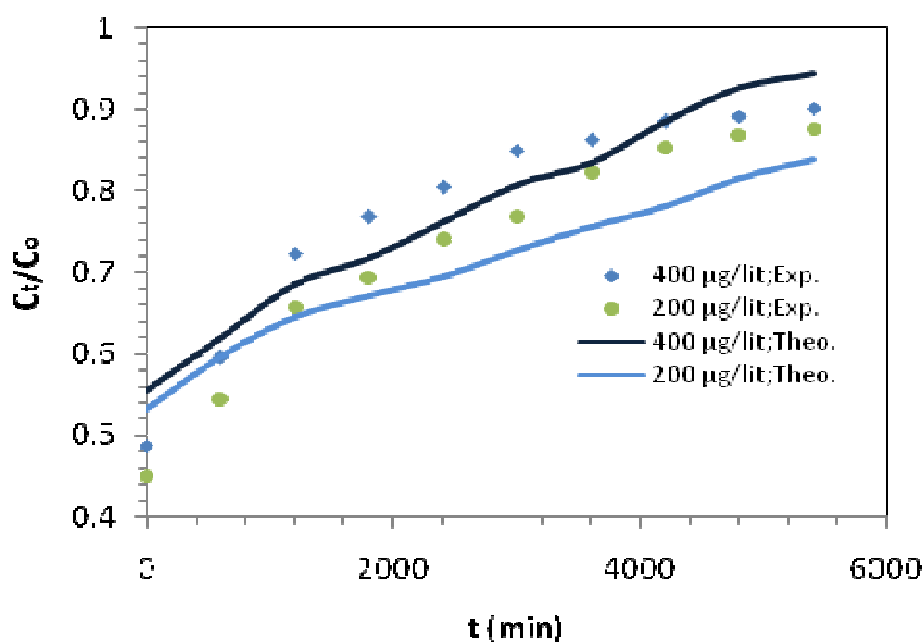| Q (ml min^{-1})	C_0 (µg l^{-1})	m total (µg)	q total (µg)	q_{eq} (µg g^{-1})	Total HAA5 removal (%)
1.5	400	3240	696.24	1.087	21.48
1.5	200	1620	258.58	0.404	15.96
6	400	12960	1784.16	2.787	13.76

Figure 2. Comparison of the experimental and predicted breakthrough curves obtained at different inlet HAA5 concentration according to the Adams–Bohart model (Q = 1.5 ml min^{-1}, particle size = 0.7 to 1.2 mm, total bed height = 300 cm).

which resulted in higher removal of HAA5 in fixed-bed columns. While adsorbent exhaustion rate was 85.92 µg l^{-1} at 1.5 ml min^{-1} flow rate, adsorbent exhaustion rate obtained at 6 ml min^{-1} flow rate was increased at 14.4 µg l^{-1}. The sorption data were evaluated and the total sorbed quantities, maximum HAA5 uptakes and removal percents with respect to flow rate are presented in Table 6. As seen in Table 6, in general HAA5 removal percentage values decreased with increasing flow rate. Furthermore, maximum values of total sorbed HAA5 quantity, maximum HAA5 uptake and HAA5 removal percentage were obtained as 696.24 µg, 1.087 µg g^{-1} and 21.48%, respectively, at 1.5 ml min^{-1} flow rate.

Adams–Bohart model based on the surface reaction theory and it assumes that equilibrium is not instantaneous; therefore, the rate of the sorption is proportional to the fraction of sorption capacity still remains on the sorbent (Goel, 2005). The Adams–Bohart model is used for the description of the initial part of the breakthrough curve (Aksu, 2004):

$$\ln \frac{C_t}{C_o} = k_{AB}C_o t - \frac{k_{AB}N_o Z}{U_o} \qquad (18)$$

Where C_o and C_t are the inlet and effluent HAA5 concentrations (µg l^{-1}), respectively. Z is the height of the column (cm), U_o is the linear flow rate (cm min^{-1}) obtained by dividing the flow rate by the column section area, N_o is saturation concentration in the Adams–Bohart model (µg l^{-1}) and k_{AB} is the mass-transfer coefficient (l µg^{-1} min^{-1}). The range of time should be considered from the beginning to the end of breakthrough. A straight line was attained for this system by plotting ln (C_t/C_o) against t, which gives the value of k_{AB} from the slope of the line. The breakthrough curves showed that the superposition of experimental results (points) and the theoretical calculated points (lines) (Figures 1 and 2). According to Adams–Bohart model, average percentage errors (ε %) calculated (Loukidou, 2004) according to Equation 13 which indicated the fit between the experimental and

Table 7. Parameters predicted from the Adams–Bohart models for HAA$_5$ adsorption onto GAC at different inlet HAA$_5$ concentrations and flow rate.

C_o (µg l^{-1})	Q (ml min^{-1})	Adams-Bohart		R^2	ε (%)
		K_{AB} *10^7(l µg^{-1} min^{-1})	N_o (µg l^{-1})		
400	1.5	2.475	870.18	0.79	7.50
200	1.5	3.345	443.78	0.79	4.91
400	6	0.562	1537.14	0.74	1.99

predicted values of C_t /C_o used for plotting breakthrough curves.

$$\varepsilon = \frac{\sum_{i=1}^{N}[|\frac{(C_t/C_o)exp-(C_t/C_o)_{theo}}{(C_t/C_o)_{theo}}|]}{N} \times 100 \qquad (19)$$

N is the number of measurements. Respective values of N_o and k_{AB} were calculated from the ln (C_t/C_o) versus t plots at all flow rates and inlet HAA$_5$ concentrations studied are presented in Table 7 together with the correlation coefficients and average percentage error.

Effect of feed HAA$_5$ concentration

In the sorption of HAA$_5$ to GAC, a change in inlet HAA$_5$ concentration affected the operating characteristics of the fixed bed column. The sorption breakthrough curves obtained by changing inlet HAA$_5$ concentration from 200 to 400 µg l^{-1} at 1.5 ml min^{-1} flow rate and 300 cm total bed height of four columns-in-series are given in Figure 2. Decreased inlet HAA$_5$ concentrations gave delayed breakthrough curves and the treated volume was also higher, since the lower concentration gradient caused slower transport due to decreased diffusion coefficient (Padmesh, 2005). At the highest HAA$_5$ concentration (400 µg l^{-1}) the GAC bed saturated quickly leading to earlier breakthrough and exhaustion time. Table 6 shows that highest uptake is obtained at the highest HAA$_5$ concentration. It was seen from Table 6, for tested different initial HAA$_5$ concentrations, maximum bed capacities at 200 and 400 µg l^{-1} HAA$_5$ concentration were 0.404 and 1.087 µg g^{-1}, respectively. The driving force for adsorption is the concentration difference between the HAA$_5$ on the adsorbent and the HAA$_5$ in the solution (Aksu, 2004). Thus the high driving force due to the high HAA$_5$ concentration resulted in better column performance. During the feed solution was sent to the column, upwards of 40% of the inlet HAA$_5$ concentration was exhausted in the initial times (Figure 2). The 200 µg l^{-1} of HAA$_5$ solutions was exhausted within 4600 min and 400 µg l^{-1} of HAA$_5$ solutions was exhausted within 4000 min respectively. The more HAA$_5$ concentration was higher, the more adsorbent usage rate was increased

and the adsorbent exhaustion rate was higher value. While adsorbent exhaustion rate was 85.93 at 400 µg l^{-1} HAA$_5$ concentration, adsorbent exhaustion rate obtained at 31.92 at 200 µg l^{-1} HAA$_5$ concentration. As expected, maximum adsorption capacity (N_o) increased with increasing inlet HAA$_5$ concentration.

Predicted and experimental breakthrough curves with respect to flow rate and inlet HAA$_5$ concentration are shown in Figures 1 and 2. It is clear from Figures 1 and 2 that there was a good agreement between the experimental and predicted normalized concentration values at all HAA$_5$ inlet concentrations and flow rates. Thus, developed model and the constants evaluated can be employed for the design of adsorption columns over a range of feasible flow rates and concentrations.

Conclusion

The objective of this work was to study the dependence of adsorption on adsorbent and adsorbate (HAA$_5$) characteristics by means of both batch and column studies. The removal efficiency of HAA$_5$ on GAC in batch studies was studied in different adsorbent dose, initial concentrations and temperatures and also its removal in column studies were conducted in different flow rates and initial concentrations in optimum constant temperature. Conclusions from the present study are as follows:

i) The removal of HAA$_5$ from aqueous solutions strongly depends on the adsorbent dose, initial HAA$_5$ concentration and temperature. Equilibrium conditions are attained after nearly 80 h.
ii) Increase in the mass of the adsorbent leads to increase in HAA$_5$ adsorption owing to corresponding increase in the number of adsorption sites.
iii) Both the Freundlich and Langmuir models could be used to fit the data and estimate the models parameters. The fit is slightly better for the Langmuir model. The monolayer adsorption capacity (Q_o) was obtained as 0.01096 × 10^{-3} µg mg^{-1} (at temperature 15°C, 8 g l^{-1} adsorbent mass and 90 h contact time).
iv) The thermodynamic parameters values of ΔH°, ΔS°, ΔG° proved that the adsorption of HAA$_5$ on GAC is an exothermic and spontaneous process.

v) Column studies showed that the adsorption of HAA_5 onto GAC depends on flow rate and inlet feed HAA_5 concentration and the data is well fitted by Admas–Bohart model. Comparing the batch and column experiments, batch mode effectively exploited the adsorbent HAA_5 binding capacity rather than fixed bed column.

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