

Predicting NOM Removal by Fixed-Bed GAC Adsorbers

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ABSTRACT

Natural Organic Matter (NOM) normally exists in raw surface water as a complex mixture of organic compounds, mainly humic acids and fulvic acids. In water treatment plants, free chlorine reacts with NOM and forms a wide range of substances known as Disinfection Byproducts (DBPs). Granular Activated Carbon (GAC) adsorption is one of the best available technologies employed for the removal of NOM. A mathematical model for the adsorption of NOM onto GAC in a fixed bed column and in a batch reactor was built. The mathematical model was solved numerically using finite element and orthogonal collocation methods.

Experiments were conducted using Rapid Small Scale Column Test (RSSCT) to evaluate the performance of GAC column to remove or reduce the concentration of NOM in raw water. The predicted values from the mathematical model showed very good agreement with the experimental measurements for a range of empty bed contact time, GAC particle size and raw water pH. Most of the mathematical model parameters were determined experimentally in adsorption equilibrium isotherm and batch reactor experiments.

KEYWORDS: Adsorption, GAC, RSSCT, TOC, NOM.

INTRODUCTION

Natural Organic Matter (NOM) is best described as a complex mixture of organic compounds, mainly humic acids and fulvic acids. Most water sources throughout the world contain NOM. These are always site-specific and even season-specific for the same site. Rook (1974) discovered that free chlorine reacts with NOM in raw water and forms a wide range of substances known as Disinfection Byproducts (DBPs). Two main classes of these compounds are Trihalomethanes (THMs) and Haloacetic Acids (HAAs) which have led to concern by regulators such as the United States Environmental Protection Agency (USEPA) following research showing them to cause cancer in laboratory animals (Fearing et al., 2004). Currently, USEPA allows an upper limit of 40 µg/l

for THMs and 30 µg/l for HAAs.

Granular Activated Carbon (GAC) adsorption is one of the best technologies employed for the removal of NOM, and it has already been used as a medium in a filter-adsorber or a postfilter-adsorber in many water treatment plants in the world (Babi et al., 2007). GAC adsorption systems typically use fixed beds with the liquid containing the adsorbate flowing through the adsorbent. To evaluate GAC fixed bed performance, an appreciation of the relevant transport mechanisms is essential in order to incorporate them into a predictive mathematical model.

The objective of this study was to evaluate the performance of GAC fixed bed system for the removal of NOM from raw surface water and compare the experimental results at different operating parameters (Empty Bed Contact Times (EBCT) and GAC particle sizes) with the theoretical values obtained from the solution of the developed mathematical model.

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MATHEMATICAL MODELS FOR GAC ADSORPTION

Fixed bed dynamics are described basically by a set of convection-diffusion equations, coupled with source terms due to adsorption and diffusion inside the adsorbent particles. Solution of these equations gives rise to the prediction of the needed breakthrough curves.

A number of researchers have developed various models to predict one-dimensional transport of adsorbate from the liquid towards the adsorbent particles (Clark, 1987; Crittenden et al., 1986a; Fritz et al., 1981; Rasmuson, 1981; Hand et al., 1984; Crittenden and Weber, 1978). All of these models have the same common assumptions, which include:

1. Constant convection flow, i.e. plug flow.
2. The adsorbate material is non-degradable.
3. The column is saturated.
4. Pellets of adsorbent are aggregates and considered as spherical particles, uniformly distributed.
5. The adsorbent is homogenous.
6. Radial concentration gradient is neglected.
7. Local adsorption equilibrium exists between the adsorbate adsorbed onto the adsorbent particle surface and the solute in the intra-particle stagnant fluid.

The fixed bed column is usually a cylindrical shape with a pack of GAC (stationary phase). The flow of adsorbate (mobile phase) is vertical along the longitudinal axis of the column. The most general form of the mathematical model incorporates axial dispersion, film mass transfer from the mobile to the stationary phase and both surface and pore diffusion as intra-particle phase mass transport mechanisms (Crittenden et al., 1986a). The model adopted in this work is a simplified form of the general fixed bed model by ignoring pore diffusion. Sensitivity analysis for both surface and pore diffusivities in the batch reactor model showed that pore diffusion is not a significant mechanism for the mathematical model applied for NOM adsorption (Al-Naseri, 2006).

The partial differential equation describing mobile phase dynamics in a fixed bed is:

$$\frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial z^2} - V_i \frac{\partial C}{\partial Z} - \frac{3k_f(1-\varepsilon)}{R\Psi\varepsilon} [C - C_p(r=R)] \quad (1)$$

Initial and boundary conditions are:

$$C(z,t) = 0 \quad \text{at} \quad 0 \leq z \leq L, t = 0 \quad (2)$$

$$C(z,t) = C_0 \quad \text{at} \quad z = 0, t > 0 \quad (3)$$

$$\frac{\partial C(z,t)}{\partial z} = 0 \quad \text{at} \quad z = L, t > 0 \quad (4)$$

The partial differential equation describing stationary phase dynamics is:

$$\frac{\partial q(r,t)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D_s \frac{\partial q(r,t)}{\partial r} \right] \quad (5)$$

Initial and boundary conditions are:

$$q = 0 \quad \text{at} \quad 0 \leq r \leq R, t = 0 \quad (6)$$

$$\frac{\partial q}{\partial r} = 0 \quad \text{at} \quad r = 0 \quad (7)$$

$$D_s \rho_a \frac{\partial q}{\partial r} = k_f [C(t) - C_p(r=R)] \quad \text{at} \quad r = R \quad (8)$$

The coupling equation is the Adsorption Equilibrium Isotherm (AEI). The Freundlich adsorption model is perhaps the most widely used mathematical description of adsorption equilibrium in aqueous systems (Chen et al., 1996):

$$q = K \cdot C_p^{1/n} \quad (9)$$

When these coupled equations (1, 5 and 9) are solved, they provide effluent history (concentration vs. time). In addition, the solution provides transient concentration profiles anywhere inside the column. However, only effluent history is used to study GAC column performance. Equations (1 and 5) represent a set of simultaneous, non-linear, partial differential equations that can be solved numerically. They were discretized with respect to space coordinate (Z) using finite elements and with respect to space coordinate (r) using orthogonal

collocation method (Finlayson, 1980). The discretization converted the partial differential equations to a set of Ordinary Differential Equations (ODEs). The resulting ODEs were solved using an existing ODE solver provided by MATLAB (Lazo, 1999).

Another useful model, needed to find surface diffusion coefficient, is the batch reactor model. Equation

(5) with its boundary and initial conditions is still valid for this case. However, the mobile phase equation should be modified to describe the adsorbate concentration in a batch reactor. The following equation was used (Ljiljana, 2006):

$$V(C_o - C) = M \frac{3}{R^3} \int_0^R qr^2 dr \quad (10)$$

Table (1): Characteristics of activated carbon utilized in experimental columns.

Item Name		Granulated activated carbon			
Base		Coconut shell			
Origin		Italy			
Size		12 x 40 U.S. standard mesh size			
Apparent density (kg/m ³)		480-490			
Particle porosity		0.5			
Ash content (%)		5 Max.			
Iodine number (mg/g)*		1100-1130			
Particle size distribution as mass (%)					
+12	12-16	16-20	20-30	30-40	-40
0.2	20.66	25.05	34.18	18.83	1.08

* Iodine number refers to the milligrams of a 0.02 normal iodine solution adsorbed per gram of GAC during a standard test (ASTM D4607).

Table (2): Tigris River raw water quality parameter average values during the period from August 2004 to July 2005.

Season	Turbidity (NTU)	pH	Alkalinity (mg/l) as CaCO ₃	TDS (mg/l)	TOC (mg/l)
Summer	11	7.9	142	355	2.338
Autumn	10	7.9	138	330	1.766
Winter	9	7.8	138	330	1.415
Spring	12	7.8	142	332	1.935

EXPERIMENTAL ARRANGEMENT AND PROCEDURES

The GAC used in the experiments was a coconut-shell-based supplied by Unicarbon, an Italian firm. Its physical properties are listed in Table (1). The required sizes of GAC (0.105, 0.162, 0.230 and 0.353 mm) were obtained by crushing and sieving a sample of GAC of the large-scale column (12x40 U.S. standard mesh; geometrical mean particle diameter 1.1 mm). The crushed GAC was boiled, washed more than thirty times in distilled water and dried at 105°C for 24 hours before being used as an adsorbent. The raw water was taken from Tigris River, Baghdad, Iraq. Table (2) shows the raw water quality data during the testing period (August 2004 - July 2005).

Table (3): Experimental values of Freundlich equilibrium isotherm parameters for different raw water pH.

Sample pH	<i>K</i>	<i>1/n</i>
7.9 (Natural)	8.32	1.34
7.5	9.67	1.31
7.0	10.01	1.26
6.5	11.39	1.22

Rapid Small-Scale Column Tests

The RSSCT process was developed for evaluating adsorption of organic matter onto GAC by (Crittenden et al., 1986b). Extensive description of the method with operating parameters can be found in USEPA literature (USEPA, 1996). In this work, RSSCT experiments were performed using 8 mm I.D. glass columns packed with 1.5 to 9 g of the prepared GAC. The GAC bed was 6 to 36 mm long (corresponding EBCT of 0.5 to 3 min. for small scale columns). The GAC bed was supported by a 200 mesh stainless-steel screen, a layer of glass beads (250 µm – 500 µm) and another 200 mesh stainless-steel screen. Glass wool was placed above the GAC to aid in producing plug flow through the GAC bed. Water samples were slowly pumped from a 300 l plastic tank

using a stainless steel piston pump at a flow rate of 6 ml/min. Influent and effluent samples were periodically collected for analysis.

Batch Experiments

These were performed to estimate the surface diffusion coefficient D_s . This was done by adjusting the predicted batch concentration curves, obtained from the solution of the batch reactor model, to best-fit the experimental results. A 2-liter flask was filled with 1.75 liter raw water, then 0.7 g of activated carbon was added to the flask, and agitation was started. The quantity of activated carbon was calculated using the following mass balance equation:

$$M = \frac{C_o - C_e}{K \cdot C_e^{1/n}} \cdot V \quad (11)$$

Samples were taken for analysis at least every 30 minutes during the first 4 hours and one sample per hour after that. Samples of the raw water were analyzed before the experiments were started. A mixing speed of 800 rpm was found appropriate and consequently adopted for all batch experiments. Other researchers used the same speed for particle size range from 12 to 20 standard mesh size while 700 rpm was used for smaller sizes (Mathews and Inna, 1989).

Adsorption Equilibrium Isotherm Experiments

AEI experiments were conducted using six 250 ml volume bottles. The GAC used in these experiments was the same pulverized GAC prepared for RSSCT. Amounts of GAC weighing from 0.1 to 1.0 mg were added to the bottles, which were then filled with 200 ml raw water to make the GAC dosage from 0.5 to 5.0 g/lit. The bottles were kept shaken continuously for 3 days to keep the activated carbon mixed with the raw water (Hand et al., 1983). Liquid phase concentrations in terms of TOC were obtained for each sample and the reference sample.

ANALYTICAL INSTRUMENTS AND ANALYSIS

TOC measurements were conducted to reflect the natural organic matter content of the raw water using

Dohrmann DC-180 Total Organic Carbon Analyzer (USA). The TOC determination procedure followed that

outlined in Standard Method No. 5310C in (APHA, 1998).

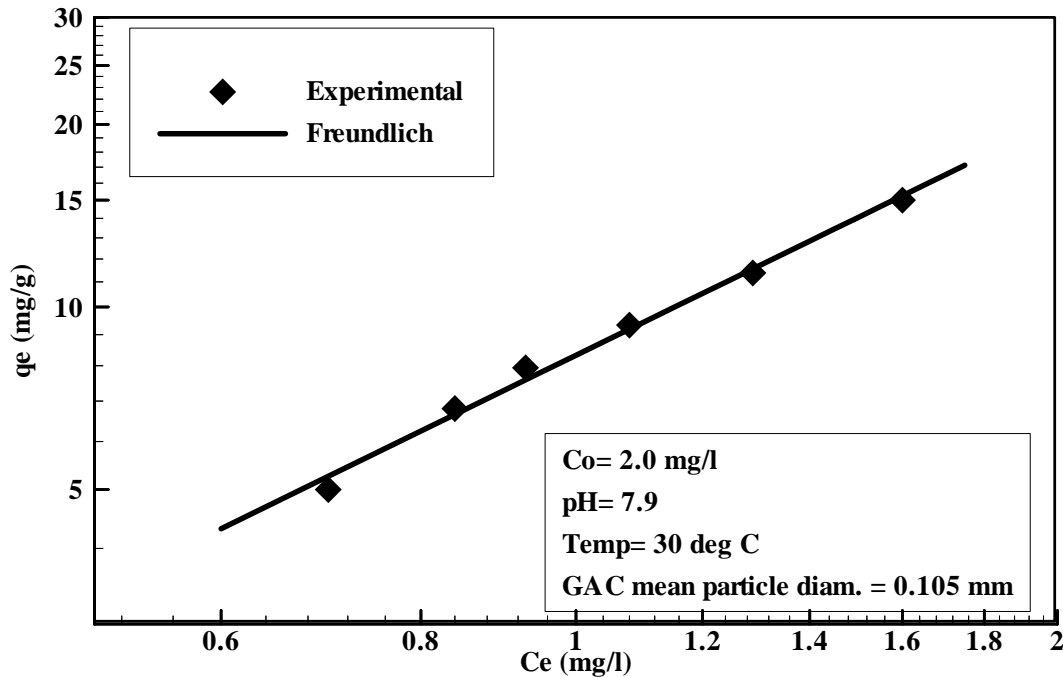


Figure (1): Raw water NOM adsorption equilibrium isotherm.

RESULTS AND DISCUSSION

Determination of AEI Parameters

Freundlich adsorption equilibrium isotherm model was used and its two parameters, K and $(1/n)$, were determined. Figure (1) shows the fitting of the Freundlich isotherm model to the equilibrium data. It is clear that the model fits the experimental data reasonably well. An additional advantage of the Freundlich model is its relative simplicity in kinetics-of-adsorption applications.

By fitting the experimental isotherms with the Freundlich equation, the parameter values K and $(1/n)$ were found as follows:

$$K = 8.325 \quad (\text{mg/g})(\text{mg/l})^{-1/n}$$

$$1/n = 1.345$$

Liquid Film Mass Transfer Coefficient Calculation

This parameter was calculated using the following correlation (Crittenden et al., 1987):

$$k_f = 2.4V_s / (Sc^{0.58} Re^{0.66}) \quad [\text{m/s}] \quad (12)$$

in which the Reynolds (Re) and Schmidt (Sc) numbers were calculated as follows:

$$Re = \frac{V_s d}{\nu \epsilon} \quad Sc = \frac{\nu}{D_l} \quad (13)$$

Typically, for a kinematic viscosity (ν) of $1.0 \times 10^{-6} \text{ m}^2/\text{s}$, a superficial velocity (V_s) of 0.002 m/s , a particle size (d) of $0.105 \times 10^{-3} \text{ m}$ and a porosity (ϵ) of 0.4 , the value of Re is 0.53 . The value of liquid diffusivity coefficient (D_l) was calculated using the following formula (Hand et al., 1983):

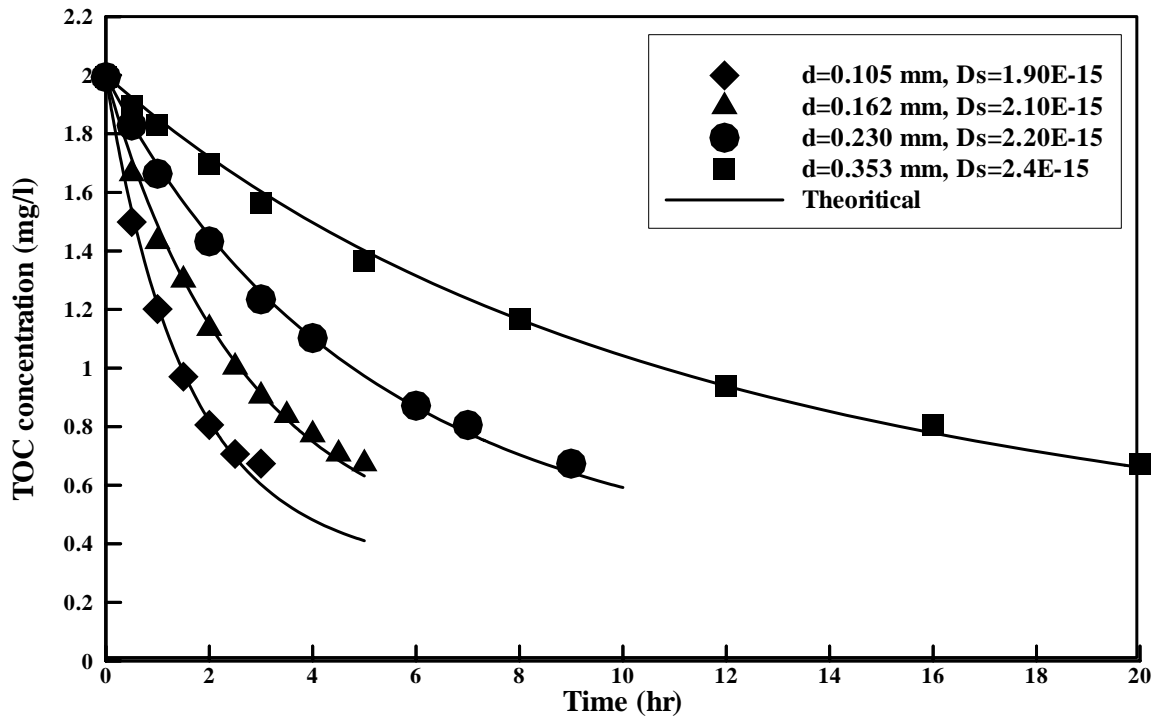


Figure (2): Batch reactor NOM adsorption onto GAC for various GAC particle sizes.

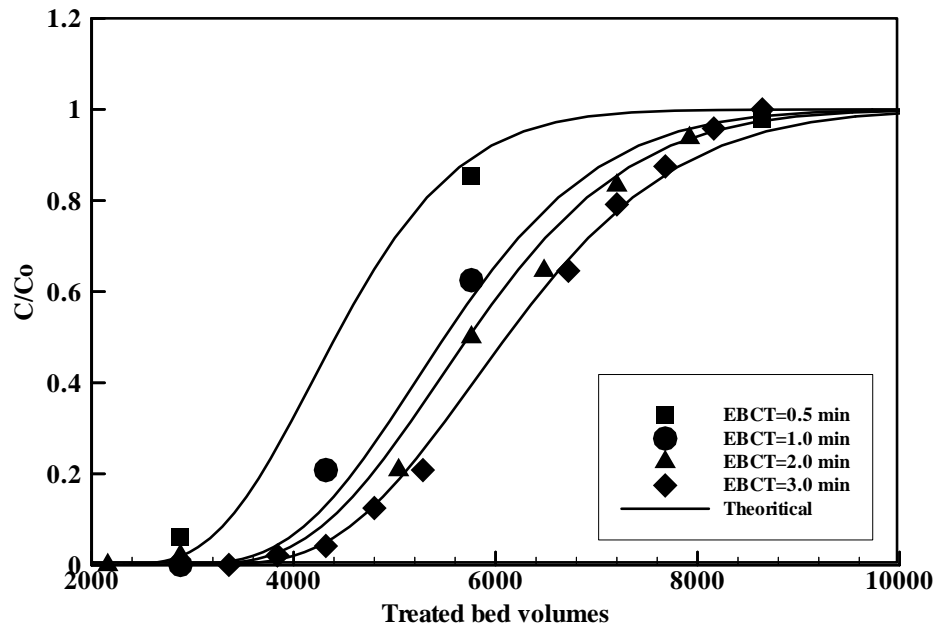


Figure (3): RSSCT experimental results and predictive fixed bed mathematical model results for different EBCTs.

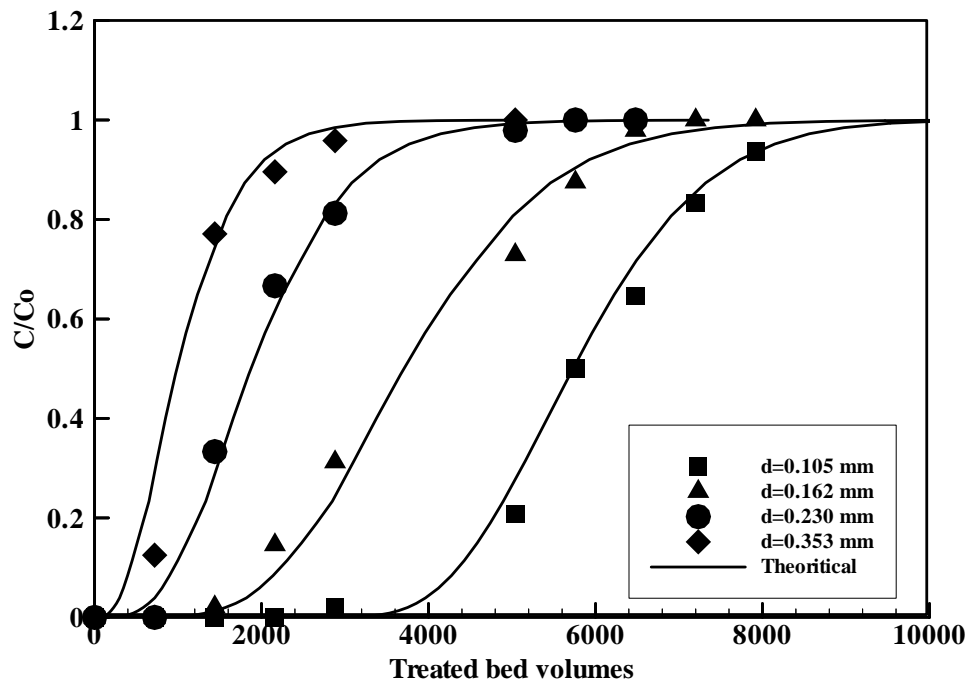


Figure (4): RSSCT experimental results and predictive fixed bed mathematical model results for different GAC mean particle sizes.

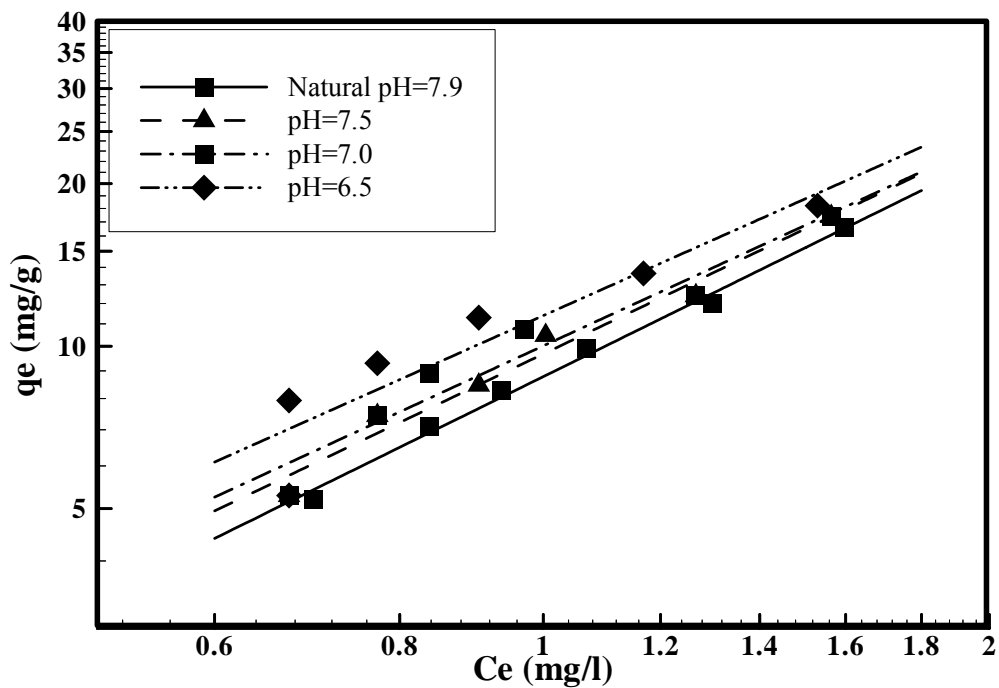


Figure (5): Effect of raw water pH on the adsorption equilibrium isotherm.

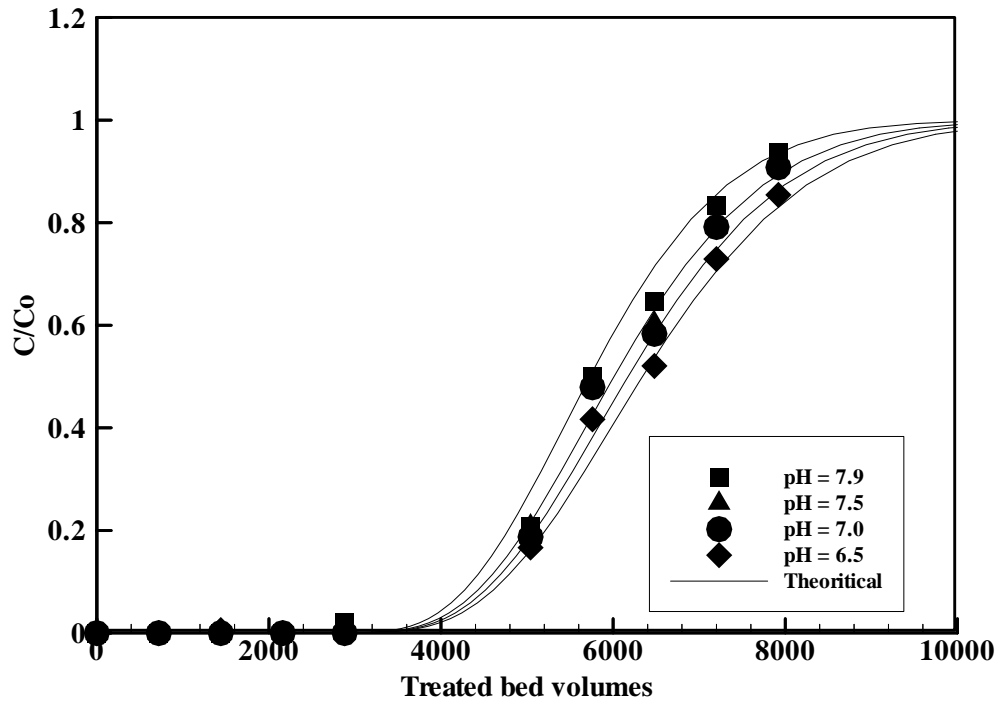


Figure (6): Effect of raw water pH on the behavior of RSSCT breakthrough curves.

$$D_l = 2.74 \times 10^{-9} (MW)^{-1/3} \quad [m^2/s] \quad (14)$$

where *MW* is the molecular mass of adsorbate. Humic/fulvic substances are heterogeneous in nature and values of molecular mass range from less than 500 Dalton up to greater than 30,000 Dalton (Check, 2005; Summers and Roberts, 1984). However, the majority of these substances fall within the range of 10,000 to 30,000 Dalton (Check, 2005). Therefore, a typical *MW* of 20,000 Dalton was used in the calculation. Accordingly, the value of *Sc* became 9900 and *k_f* was equal to 3.512 x 10⁻⁵ m/s. The determined values are well within the range reported by other researchers (Summers and Roberts, 1987; Weber, 2004).

Dispersion Coefficient Calculation

Dispersion coefficient (*D_z*) was calculated using the following equation (Hutzler et al., 1986):

$$\frac{D_z}{D_l} = 0.67 + 1.15 \left[\frac{V_s d}{D_l} \right]^{1.2} \quad (15)$$

A typical value of *D_z* for a GAC particle size (*d*) of 0.105 mm was 5.0 x 10⁻⁷ m²/s.

Estimation of Surface Diffusivity (*D_s*)

Batch experiments for the adsorption of raw water NOM onto GAC were conducted to estimate the values of *D_s*. The results are shown in Figure (2) for each GAC particle size (0.105, 0.162, 0.230 and 0.353 mm). The determined values for *D_s* were 1.90, 2.1, 2.2 and 2.4x10⁻¹⁵ m²/s for each GAC particle size, respectively. The results showed linear dependence between the surface diffusivity and GAC particle size, being consistent with the assumption made when developing the RSSCT mathematical model (Crittenden et al., 1986b).

Estimation of GAC Sphericity (*ψ*)

The necessity of introducing a sphericity shape factor

is due to the inadequacy of the particle spherical shape assumption. Its value was found to be significant in predicting the actual GAC column performance. The predicted value was found to match the experimental results very well for a sphericity factor value of 0.7. This value was reached after successive trials to minimize the least square error between the predicted values and the experimental results. Other researchers adopted ψ values of 0.69 and 0.62 for GAC of 12 x 40 and 8 x 30 standard mesh size respectively (Michele and Johannes, 2004).

Theoretical and Experimental Breakthrough Curves

Comparison of experimental and predicted breakthrough curves are shown in Figures (3, 4 and 6). Figure (3) illustrates breakthrough curves for different EBCTs (0.5, 1.0, 2.0 and 3.0 min; corresponding to large-scale EBCT of 5, 10, 20 and 30 minutes, respectively). From the figure, it can be seen that breakthrough at $C/C_o=0.05$ for the longer EBCT occurs at a larger treated-bed-volumes value than the shorter EBCT. This was expected because as EBCT increases, contact time between the adsorbate and the adsorbent also increases giving the organic matter more opportunity to be adsorbed onto the GAC. However, doubling the EBCT generally does not double the treated water volume. It can also be noticed that there is good agreement between experimental results and model prediction.

Figure (4) shows experimental breakthrough curves at various particle sizes and model prediction. GAC particle size plays an important role in the amount of NOM adsorbed from raw water. The number of treated-bed-volumes for smaller GAC particle size is higher than that for larger particle sizes. This can be justified as follows: with a smaller particle size, the diffusion pathway from the external surface of the particle to its inside is shorter and the external particle surface area per unit mass of adsorbent is larger - both of which enhance adsorption rate (Matsui, 2004). The predicted values for this case

were, also, in close agreement with the experimental results.

In order to test the effect of reducing raw water pH on the nature of the adsorption process, four AEI tests were conducted. The experimental results are shown in Figure (5). From the figure, it can be concluded that as raw water pH decreases, adsorption capacity (measured in terms of AEI parameter K) increases while the exponent ($1/n$) value decreases. This increase in the adsorption capacity can be explained as follows: NOM is predominately negatively charged; therefore, decreasing the pH renders the negatively charged organic molecules more neutral. A neutral molecule is inherently less soluble in water than a charged molecule and, consequently, more adsorbable. In addition, at low water pH, NOM is more coiled due to less negative-charge repulsion allowing for greater access to GAC pores (Clark and Boutin, 2001). The numerical values of K and ($1/n$) are listed in Table (3).

Experimental breakthrough results for different raw water pH values along with predicted ones using the obtained values for K and ($1/n$) are illustrated in Figure (6). It is clear that the increased adsorption capacity did not reflect a significant effect on the breakthrough behavior. Changing the pH from 7.9 to 6.5 increased K by more than 36%, while it increased the number of treated bed volumes by only 11.5%. It can, also, be noticed that the prediction model curves match the experimental results very well.

CONCLUSIONS

A mathematical model to predict the performance of fixed bed GAC column to remove or reduce the concentration of NOM in raw surface water was built, and its numerical algorithm was developed. Good agreement was achieved between predicted values and experimental results conducted using RSSCT for a range of EBCT, GAC particle size and raw water pH.

Nomenclature

<i>Symbol</i>	<i>Description</i>	<i>Unit</i>
C	Bulk adsorbate concentration	g/m^3
C_e	Equilibrium adsorbate concentration	g/m^3
C_o	Influent concentration	g/m^3
C_p	adsorbate concentration within the pores	g/m^3
d	Geometrical mean diameter of GAC particles	mm
D_l	liquid diffusivity coefficient	m^2/s
D_s	Surface diffusion coefficient	m^2/s
D_z	Dispersion coefficient	m^2/s
$EBCT$	Empty Bed Contact Time	s
K	Freundlich adsorption isotherm capacity constant	$(\text{mg/g}) (\text{mg/l})^{-1/n}$
$1/n$	Freundlich adsorption isotherm rate constant	-
k_f	Liquid film mass transfer coefficient	m/s
L	Column length	m
MW	Molecular mass of adsorbate	Dalton
M	Mass of GAC used in batch reactor	g
q	Amount of adsorbate adsorbed per unit mass of GAC	mg/g
r	Radial coordinate	m
R	GAC particle radius	m
Re	Reynolds number = $V_s d / \nu \varepsilon$	-
Sc	Schmidt number = ν / D_l	-
V	Water volume in batch reactor	m^3
V_s	Superficial water velocity	m/s
Z	Axial coordinate	m

Greek letters

ε	packed bed porosity	-
ρ_a	apparent density of GAC	g/m^3
ν	kinematic viscosity	m^2/s
ψ	Sphericity, ratio of the surface area of equivalent-volume sphere to actual surface area of particle.	-

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