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Seoung-Hyun Kim[a]; Huu-Hao Ngo[a]
[a] Faculty of Engineering, University of Technology, Sydney, Australia

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Adsorption Characteristics and pH-dependence of Metsulfuron-Methyl onto Activated Carbons

Seoung-Hyun Kim and Huu-Hao Ngo
Faculty of Engineering, University of Technology, Sydney, Australia

Abstract: The adsorption characteristics of metsulfuron-methyl (MM) onto powdered activated carbon (PAC) and granular activated carbon (GAC) were studied at varying solution pHs (4–9) and temperatures (20–40°C). The dependence of pH was observed in aqueous solution with MM. The film mass transfer and intraparticle diffusion coefficients were estimated from concentration decay curves obtained in the batch adsorber. The maximum adsorption capacity decreased with increasing pH and temperature. Among the PAC used, the coconut based PAC had the best adsorption capacity. The adsorption isotherms could be plotted using the Freundlich and Toth models with a reasonable degree of accuracy. The overall adsorption isotherm such as the modified-Toth model should be applied. The performances of the fixed-bed GAC system was also simulated by a model developed. The objective of the present study was to investigate the adsorption and pH dependence behavior of MM onto PAC and GAC in order to diminish the environmental risk of MM pollution.

Keywords: Metsulfuron-methyl, powdered activated carbon, granular activated carbon, adsorption, herbicide, synthetic organic compounds, wastewater treatment

INTRODUCTION

Metsulfuron-methyl (MM) ($C_{14}H_{15}N_5O_6S$) herbicide is widely used to control broad-leaved weeds in the world. However, this compound may persist in the environment for many months. After application they permeate into the soil

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Address correspondence to Huu-Hao Ngo, Faculty of Engineering, University of Technology, P. O. Box 123, Sydney, Broadway, Australia NSW 2007. Tel.: +61-2-9514-1693; Fax: +61-2-9514-2633; E-mail: huuhao.ngo@uts.edu.au

and can subsequently run off from cropland into rivers and lakes, causing surface water pollution. Removal of these potentially harmful compounds from water has emerged as an important issue of environmental protection (1). As one of the number of clean-up techniques, the adsorption of trace organic pollutants by granular activated carbon (GAC) packed fixed-bed columns has proved to be economical and effective. The application of this technique to herbicide removal has been cited as having great potential and is routinely used in the water treatment industry (2).

Many Synthetic Organic Compounds (SOCs) present in drinking water are of major concern because of their potential mutagenicity, carcinogenicity, and toxicity. These compounds are continuously produced in the form of pesticides, herbicides, solvents, and other products. SOCs enter drinking water by water runoff, through waste discharge, or chemical spills (3–5). Under these circumstances, the conventional solid/liquid separation technologies such as sedimentation, photocatalysis, microbiology, and filtration have been employed for drinking water production (6–8). Synthetic organic compounds are the products of a wide range manufacturing processes, and some are classified as hazardous to animal and human health. Occasionally, these compounds find their way into natural water sources by means of accidental spills, dumping, or leaching to groundwater aquifers (9). The US Environmental Protection Agency (U.S. EPA) has set maximum contaminant levels (MCLs) for several Volatile Organic Compounds (VOCs) and many other compounds are currently being added to the list (10).

This work presents the adsorption of MM onto powdered activated carbons (PACs) and granular activated carbon (GAC). The objectives of this study are to investigate the adsorption characteristics of MM onto activated carbons and to obtain the reliable information that will be applied in analyzing and simulating the adsorption and kinetics and dynamics of various adsorbents used in removing SOCs from wastewater.

EXPERIMENTAL METHOD

Materials

The commercial preparation of Metsulfuron-methyl (MM) group B herbicide (Australia Du Pont, 60%) was used in the present study. The adsorbents used were commercial PACs, purchased from James Cumming & Sons PTY LTD, Australia as shown in Table 1. The GAC F-400 was obtained from Calgon Carbon Corp. USA. Its surface area measured using the Brunauer, Emmett and Teller (BET) method and bulk density are $1112\,m^2/g$ and $748\,kg/m^3$ respectively. It had a mean pore diameter of 26.14 Å, total pore volume $7.27 \times 10^{-4}\,m^3/kg$, average particle diameter 5.9×10^{-4} m and coal-based activated carbon.

Table 1. Characteristics of powdered activated carbons (PACs) tested

Specification	PAC WB	PAC CB	PAC HA
Iodine number, mg/g min	900	800	900
Ash content	6% max	5% max	3% max
Moisture content	5% max	8% max	10% max
Bulk density, kg/m^3	290 – 390	300 – 100	350 – 500
Surface area, m^2/g	882	915.23	1198.56
Nominal size	80% min finer than 75 micron	55% to 65% finer than 45 micron	75% min finer than 75 micron
Type	Wood based	Coal based	Coconutshell based
Product code	MD3545WB powder	MD3545CB powder	MD3545CO powder
Mean pore diameter Å	30.61	24.20	30.41
Micropore vol., cc/g	0.34	0.192	0.067
Mean diameter, μm	19.72	10.9	34.15

Adsorption Equilibrium and Batch Test Procedure

Adsorption equilibrium data were obtained by introducing known weights of PACs each 200 ml of mixed solution in Erlenmeyer flasks with stoppers and shaking in a constant temperature incubator at 20, 25, 30, and 40°C for about 5 days to give sufficient contacting time for equilibrium. All the flasks were shaken in a temperature-controlled shaker. NaOH and HCl solutions were used to control solution pH at 4, 5, 7, and 9, respectively to determine the adsorption isotherm. After equilibrium was reached, a sample was taken from each flask. The concentrations of individual component were measured using an UV-Visible spectrophotometer (Varian, DMS 100S) at 230 nm as MM has a significant high absorbance at this wavelength. The pH was measured using a pH meter (Orion, model 920A). The adsorbed amount (q) and error function ($E(\%)$) was calculated by following equation.

$$q = \frac{V(C_i - C_e)}{M} \tag{1}$$

$$E(\%) = \frac{100}{N}\sum_{n=1}^{N}\left[\frac{|q_{\exp} - q_{cal}|}{q_{\exp}}\right]_N \tag{2}$$

Where q is the adsorbed amount (mg/g), V is the volume (L) of solution, M is the amount of adsorbents (g), C_i is the initial MM concentration (mg/L), C_e is the equilibrium MM concentration (mg/L), the superscripts “exp” and “calc” are the experimental and calculated values and N is the total number of experimental data point.

Batch adsorption experiments were performed at 100, 200, 300, and 500 rotations per minute (rpm) with PAC adsorbents. Liquid samples were taken periodically by using an airtight precision syringe, withdrawing the solution from the vessel through the sample hole. The batch reactors were 1 L conical glass flask. In each flask, a known concentration of wastewater was mixed with the known amount of adsorbent. The purpose of these experiments is to investigate the MM removal with time and to find the equilibrium MM concentration. Experiments were carried out at a temperature of 25°C. All samples were filtered through 0.45 μm membrane prior to the concentration measurement.

Fixed-bed Experiments

The schematic diagram of apparatus for fixed-bed column studies is shown in Fig. 1. The adsorption fixed-bed column was made of glass with an inside diameter 0.01 m and length 0.3 m. GAC F-400 were packed into the

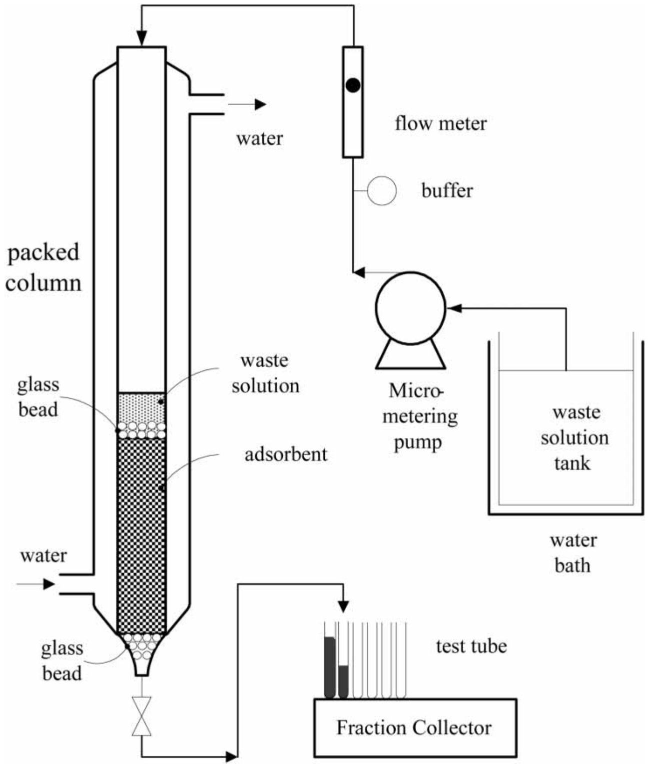

Figure 1. Experimental set-up of fixed-bed column experiments.

fixed-bed column and sustained by glass beads. A precision micro pump regulated the flow rate. The solution was introduced downward into the column. To prevent channelling and to enhance distribution of the solution through the fixed-bed column, the two layers of small glass beads were packed in the top and bottom of the column. All the packing procedures were conducted under water to avoid the generation of bubbles in the fixed bed. After the start of experiments, samples were taken at the determined time intervals and liquid samples were taken periodically by a fraction collector. Stock solutions were prepared in a glass-made tank of 3 L volume, and it was placed in a constant-temperature water bath. The flow was controlled at a constant rate using a micrometering pump and the rate was determined with a rotameter during a run. In order to maintain the column at a constant temperature 25°C, a water bath with a temperature controller was installed and the column was also jacketed. The heating medium was water circulated by a constant temperature circulator.

THEORETICAL APPROACH

Adsorption Isotherm

The adsorption isotherm models listed in Table 2 can be classified as two-parameter models such as Langmuir and Freundlich models and three-parameter model such as the Toth model. Since adsorption is one of the fundamental surface phenomena, it is important to have a satisfactory description of an equilibrium state in order to successfully represent the kinetic and dynamic adsorption behavior of any species from the fluid to the solid phase (11). In general, the three-parameter models fitted the experimental data better than the two-parameter models (12). Their parameters for single adsorption isotherms are showed in Table 2.

The Langmuir model, based on monolayer, uniform, and finite adsorption site assumptions, did not fit all the experimental data well (13). The Freundlich model, an empirical equation for heterogeneous surface, fitted all the experimental data quite well (14). Although the Freundlich model fitted individual set of data quite well, only the Toth model could give good correlations for varying solution pHs and temperatures. In the Toth model, q_m represents the

Table 2. Various adsorption isotherm models used to fit the experimental data

Model	Equation	Parameters
Freundlich	$q = k \cdot C^{1/n}$	k, n
Langmuir	$q = q_m \cdot b \ \cdot C_e/1 + b \cdot C_e$	q_m, b
Toth	$q = q_m \cdot C/(1/K + C^m)^{1/m}$	q_m, K, m

maximum adsorption capacity, K the adsorption equilibrium constant, and m the dissociation parameter. The effect of solution pH and temperature on the parameters q_m, K, and m will be discussed separately (15).

The modified Toth model used to predict the adsorption isotherms at varying pHs is as follows (16).

$$q = \frac{(a + b \cdot pH + c \cdot pH^2) \cdot C}{(1/K + C^m)^{1/m}} \tag{3}$$

where the a, b, and c are the constants to get the overall equilibrium information, C is the equilibrium MM concentration. According to equation (3), the maximum adsorption capacity is expressed as a quadratic function of the solution pH. The choice of the pH-dependent function is arbitrary without any physical meanings. Since the simple linear function could not give good fit to all the data, the quadratic function was used (Fig. 2). The average absolute deviations for the MM at pH 4, 5, 7, and 9 are 5.88, 6.2, 3.76, and 4.33%, respectively.

The Gibbs free energy change of the adsorption process is related to the equilibrium constant by the following equation.

$$\Delta G = -RT \ln K \tag{4}$$

Where R is the gas constant and T is the absolute temperature. According to thermodynamics, the Gibbs free energy change (ΔG) is also related to the entropy change (ΔS) and the heat of adsorption at constant temperature by the following equation.

$$\Delta G = \Delta H - T\Delta S \tag{5}$$

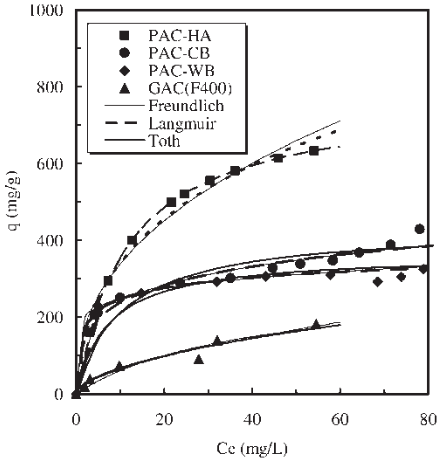

Figure 2. Adsorption isotherms of MM at varying activated carbons. (Temp = 298.15 K, pH = 4.0).

Combining equations 2 and 3 leads to

$$K = \exp\left(\frac{\Delta S}{R} - \frac{\Delta H}{RT}\right) \tag{6}$$

The modified Toth model, whose parameters also shown in Fig. 3, used to predict the adsorption isotherms at varying solution temperatures is as follows (16).

$$q = \frac{q_m \cdot C}{(e^{-\Delta S/R+\Delta H/RT} + C^m)^{1/m}} \tag{7}$$

Kinetic Studies

The material balance in the batch reactor can be described by (17–20)

$$\frac{dC}{dt} = -\frac{M}{V}\frac{dq}{dt} \tag{8}$$

In addition, the homogeneous surface diffusion model has been used in the study of adsorption kinetics from Equations (7) to (10). The homogeneous surface diffusion model consists of a three-step process:

i. the adsorbate diffuses through a stagnant liquid film layer surrounding the carbon particle;
ii. the adsorbate adsorbs from the liquid phase onto the outer surface of the carbon particle;

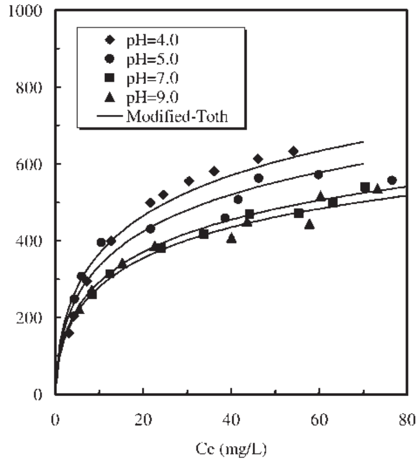

Figure 3. Experimental and modified Toth model predicted adsorption isotherms of MM at varying solution pHs by PAC-HA.

iii. the adsorbate diffuses along the inner surface of the adsorbent particle until it reaches its adsorption site (20–23).

$$\frac{\partial q_t}{\partial t} = D_s\left(\frac{\partial^2 q_t}{\partial r^2} + \frac{2}{r}\frac{\partial q_t}{\partial r}\right) \tag{9}$$

The above equation can be numerically solved by setting the initial and boundary conditions:

$$t = 0, \quad q_t = 0 \tag{10}$$

$$r = 0, \quad \frac{\partial q_t}{\partial r} = 0 \tag{11}$$

$$r = R_p, \quad D_s \rho_p \frac{\partial q_t}{\partial r} = k_f (C - C_s) \tag{12}$$

Where R_p is the particle radius (m), D_s is the intraparticle diffusion coefficient (m^2/s), k_f is the external film mass transfer coefficient (m/s), and ρ_p is the particle density (kg/m^3). The values of k_f and D_s can be computed using the isotherm parameters and the above equations. The adsorption kinetic data obtained from different temperatures and adsorbents were analyzed by homogeneous surface diffusion model (HSDM) which was useful for design purpose.

Adsorption Dynamics

The dynamic model for adsorption of MM in the fixed-bed charged with GAC adsorbents was formulated according to the following general assumptions:

1. The system is isothermal,
2. The shape of activated carbon particles is spherical,
3. Fixed-bed column is homogeneously packed
4. Pore size distribution is homogeneous,
5. The pore structure inside particles is uniform,
6. The metsulfuron-methyl concentration gradient is neglected,
7. The fluid physical properties are constant,
8. The flow pattern is a plug flow with a constant linear velocity along the column,
9. The concentration profile inside the particle is following to the parabolic type (24–28). The governing equations from the assumptions stated above can be written as follows.

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - \frac{(1-\varepsilon_b)}{\varepsilon_b}\frac{3k_f}{R_p}(C - C_s) \tag{13}$$

Where

C = concentration in bulk solution, mg/L
C_s = concentration inside particle, mg/L
D_L = axial dispersion coefficient, m^2/s
v = velocity of the fluid, m/s
z = bed depth, m
ε_b = bed porosity

The mass balance for the mobile phase and the relevant initial and boundary conditions in the fixed-bed has been discussed as follows.

Initial condition, C = 0

Boundary condition,

$$\text{At } z = 0 \text{ is } D_L \frac{\partial C}{\partial z} = -v(C_{z=0^-} - C_{z=0^+}) \tag{14}$$

$$\text{And at } z = L \text{ is } \frac{\partial C}{\partial z} = 0 \tag{15}$$

Wakao's correlation was used to determine the axial dispersion coefficient (29).

$$D_L = 2vR_p\left(\frac{20}{R_e S_c} + \frac{1}{2}\right) \tag{16}$$

Where R_e and S_c are Reynolds and Schmidt number, respectively. The estimated value of the axial dispersion coefficient, D_L, is $1.0 \times 10^{-6}\ m^2/s$. The batch reactor and fixed-bed adsorption model with HSDM was solved numerically by applying the orthogonal collocation method to discretize the equations. Discretization was done for the spatial variable, resulting in a set of time derivative ordinary differential equations (ODEs) for the adsorbate concentration (26, 27). The resulting sets of ODEs were solved using the subroutine LSODA (30, 31).

RESULTS AND DISCUSSION

Adsorption Isotherm

The adsorption isotherms of MM in various adsorbents are shown in Fig. 2 and Table 3. It shows that the Freundlich and the Toth equation are adequate for fitting equilibrium data and PAC HA (coconut shell based) is the best for the removal of MM. The functional groups or adsorption sites of PAC are affected by the solution pH. Therefore, the maximum adsorption capacity may be expected to vary with the solution pH while the adsorption equilibrium constant and the dissociation parameter remain unaffected by the solution pH.

The adsorption isotherms of MM solutions onto PACs at varying pHs and temperatures were experimentally determined. In case of pH-dependence, the adsorption isotherm parameters are $K = 0.818$, $m = 0.321$, $a = 2380$,

Table 3. Adsorption isotherm parameters of MM on activated carbons at 298.15 K

	Parameters	PAC-HA	PAC-CB	PAC-WB	F-400
Freundlich	k	129.9	144.8	175.4	15.88
	n	2.41	4.47	6.82	1.66
	E(%)	4.4	3.75	4.44	15.99
Langmuir	q_m	771.1	436.01	365	294
	b	0.085	0.093	0.135	0.0258
	E(%)	6.2	8.3	9.5	22.3
Toth	q_m	4390	1890	463	15800
	K	0.742	2.02	2.28	0.393
	m	0.229	0.146	0.309	0.179
	E(%)	5.6	0.94	4.97	16.76

$b = -273$, and $c = 15.4$. In case of temperature dependence, the adsorption isotherm parameters are $\Delta S = -6.025$, $\Delta H = -2302$, $q_m = 45050$, and $m = 0.101$. There was a good agreement between experimental data and prediction data satisfactory as shown in Figs. 3 and 4.

Kinetic Experiments

Figure 5 shows the kinetics of adsorption at different mixing intensity (rpm) of MM. The rate of adsorption was rapid in the initial minutes of

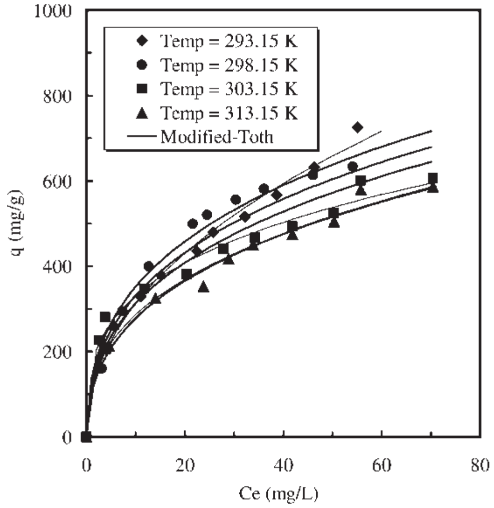

Figure 4. Experimental and modified Toth model predicted adsorption isotherms of MM at varying temperatures. (PAC-HA., pH = 4.0).

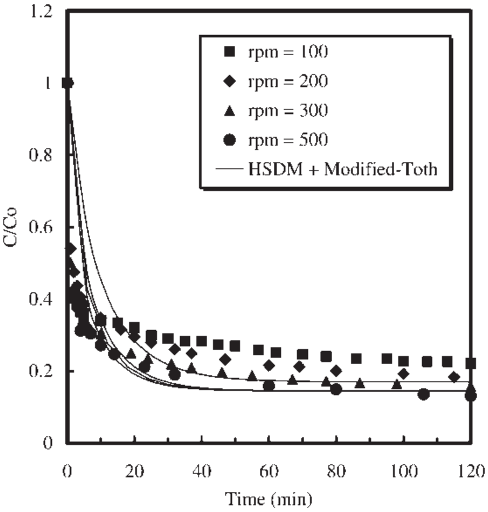

Figure 5. Batch experiments and simulation data in terms of the mixing intensity (rpm) in PAC-HA. (MM initial conc. = 57 mg/L, PAC amount = 300 mg/L).

solution–adsorbent contact and after ~10 min it became equilibrium state and it showed the same concentration decay curve in more than 300 rpm. The lumped effective mass-transfer parameters of the adsorption rate, external film mass transfer coefficients (k_f), and the effective intraparticle surface diffusion coefficients (D_s), was derived from the experimental concentration histories by an iterative two-parameter search technique predicted on the minimization of the sum of squares of residuals in Fortran PowerStation 4.0. In order to predict the kinetic data, the estimated mass transfer and diffusion coefficients were used to be 0.39×10^{-4}, 1.48×10^{-4}, 1.53×10^{-4}, 3.0×10^{-4} m/s for a different mixing intensity of 100, 200, 300, and 500 rpm, respectively. It was found that increasing the operation rpm improved the mass transfer coefficients (k_f). The intraparticle surface diffusion coefficient (D_s) was 9.8×10^{-13} m^2/s.

Effect of Flow Rate in Fix-bed Experiments

Fixed-bed with a 7 cm GAC F-400 bed height were operated at different flow rates of 3, 5, and 9 cm^3/min to study the effect of the flow rate on MM removal efficiency. The efficiency of MM removal decreased with an increase of flow rate (Fig. 6). The film mass transfer controls the overall transfer rate in this experiment. The estimated film mass transfer coefficients for MM are in the range of 6.4×10^{-6}, 7.0×10^{-6}, and 7.6×10^{-6} m/s at different flow rate of 3, 5, and 9 cm^3/min.

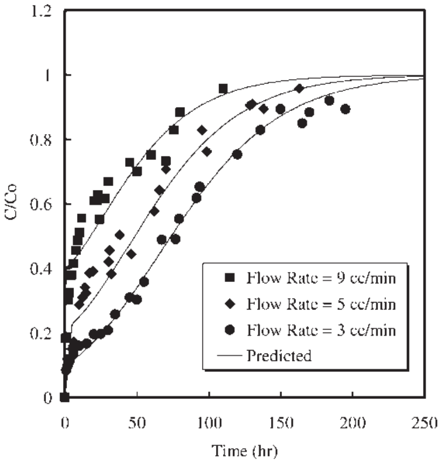

Figure 6. Breakthrough curves of MM with the variation of flow rate. (MM initial conc. = 30 mg/L, bed height = 7 cm, flow rate = 3, 5, 9 cm^3/min).

Effect of Bed Height in Fix-bed Experiments

The effect of adsorbent depth in the adsorption of MM in water was studied. GAC fixed-bed adsorption experiments were performed at bed height of 5, 7, and 10 cm. The flow rate in fixed-bed experiments was kept 3 cm^3/min. The

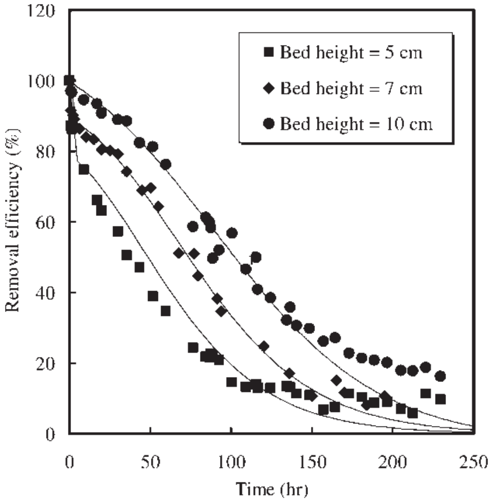

Figure 7. Variation of MM removal efficiency of GAC fixed-bed adsorption for different bed height (MM initial conc. = 30 mg/L, bed height = 5, 7, 10 cm, flow rate = 3 cc/min).

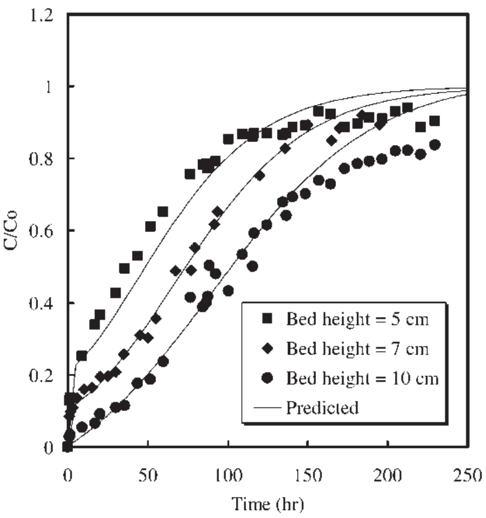

Figure 8. Breakthrough curves of MM with the variation of flow rate. (MM initial conc. = 30 mg/L, bed height = 5, 7, 10 cm, flow rate = 3 cc/min).

relative overall mass transfer coefficient at different depths was observed to be 6.4×10^{-6} m/s. The experimental and simulated MM breakthrough curves by adsorption modelling and the removal efficiency are shown in Figs. 7 and 8, respectively. As expected, the fixed-bed column with greater depth gave a later breakthrough than that with a shallower depth. As the GAC depth increases, the contact time between MM solute in wastewater and GAC medium increases, thus increasing the amount of MM solute retained in GAC medium.

CONCLUSIONS

From the experiments and model simulation on the adsorption of MM onto PACs in batch adsorber and GAC adsorbent in fixed-bed adsorber, several conclusions could be made.

- The adsorption isotherm data of MM on PACs and GAC could be fitted well with the Freundlich and Toth equations.
- In case of varying pHs and temperatures, the modified Toth model was used to apply the overall system.
- From the kinetic studies in a batch adsorber, the rate of adsorption was rapid in the initial minutes of solution-adsorbent contact and after ~ 10 min it became equilibrium state and it showed the same concentration decay curve in more than 300 rpm.

- The efficiency of MM removal decreased where the flow rate increased in fixed-bed experiments. The film mass transfer controls the overall transfer rate in this experiment.
- The fixed-bed column with greater depth gave a later breakthrough than that with a shallower depth. As the GAC depth increases, the contact time between MM solute in wastewater and GAC medium increases, thus increasing the amount of MM solute retained in GAC medium.

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