Desalination and Water Treatment
www.deswater.com

21 (2010) 247–254
September

doi: 10.5004/dwt.2010.1540

Removal of metsulfuron methyl by granular activated carbon adsorption

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Received 3 October 2009; accepted 5 March 2010

ABSTRACT

The removal of metsulfuron methyl (MSM) from aqueous solution (a sulfonyl urea herbicide) was investigated by adsorption both in batch and fixed bed processes. Coal based granular activated carbon (GAC) was used as an adsorbent. The adsorption equilibrium, isotherms and kinetics of MSM were studied and the data was fitted into various mathematical models. The adsorption equilibrium was fitted by Langmuir and Freundlich isotherms. Homogeneous surface diffusion model (HSDM) kinetic equation with Langmuir and Freundlich adsorption isotherm model was successfully applied to predict the adsorption kinetics data for various concentrations of MSM. The average mass transfer coefficients (k_f) were 2.125×10^{-5} and 2.198×10^{-5} m/s with the Langmuir and Freundlich adsorption isotherm model, respectively. The Bohart-Adams, Thomas, and Yoon and Nelson empirical models were attempted to fit long term column adsorption data. Overall, the Thomas model was found to best simulate the fixed bed adsorption of MSM.

Keywords: Adsorption; GAC; Modelling; MSM

1. Introduction

Approximately 2.5 million tonnes of pesticides are used world wide to protect crops from pests, weeds and plant pathogen pests [1]. Most herbicides are recalcitrant (not bio-degradable) and some are classified as endocrine disrupting chemicals (EDC). Their fate and transport in soils is of primary concern, as they pose a major threat to water resources [2].

Sulfonylurea herbicides are the largest major group of soil-applied herbicides. This group includes chemicals that are ionisable (under acidic pH) and frequently found in ground and surface waters worldwide [3]. The sulfonylurea herbicides derived its name due to a characteristic middle urea bridge joined to a sulphonamide and a triazine groups (Fig. 1(a)). Mesulfuron methyl (MSM) belongs to this category of herbicides. The molecular structure of MSM is shown in Fig. 1(b). It is marketed in Australia by Dupont under the name of ''Brush off.''

Herbicide adsorption on activated carbon was studied by a number of researchers. The influence of surface properties of activated carbon on the adsorption of molinate herbicide was studied by Coelho et al. [4]. The adsorption of molinate depended upon the hydrophobicity of the surface of activated carbon [4]. Adsorption of alachlor and metolachlor (anilidic herbicides) on two commercially available activated carbons (Norit W 52 and Gro-Safe) was investigated and the results suggested a high affinity of herbicides on activated carbon [5]. The adsorption of MSM on granular activated carbon (GAC) has been studied in both batch and stirred tank adsorbers. Two kinetic parameters, film mass transfer and interparticle diffusion coefficients, were

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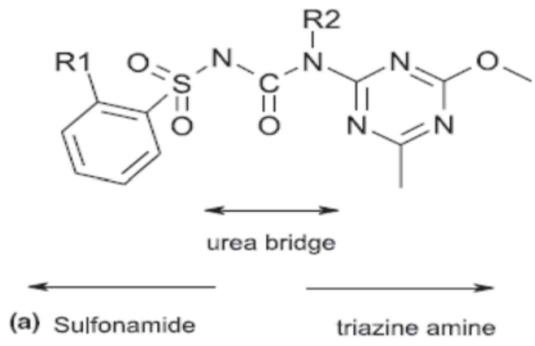
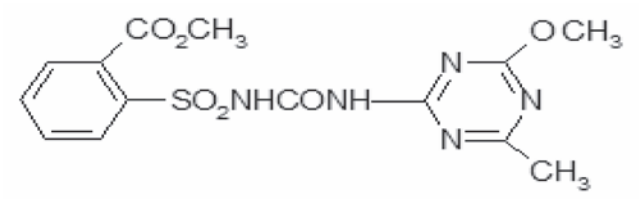


a). MeS showing urea bridge



b). Molecular structure

Fig. 1. Mesulfuron methyl (MSM).

estimated from concentration decay curves obtained in the batch adsorption. Based on these kinetic parameters, the concentration profiles measured in the stirred tank adsorber were simulated [6]. Adsorption and photocatalysis of MSM on powdered activated carbon (PAC) and TiO_2 was investigated by Kim et al. [6]. Areerachakul et al. [7] experimentally studied the long term GAC column performance in adsorbing MSM. However, these studies did not mathematically model the column adsorption.

The objectives of this study were: (i) to investigate the batch adsorption kinetics of MSM on GAC for different concentrations of MSM and pH. (ii) To investigate dynamic column adsorption of MSM. The adsorption column represented the permeable reactive barrier. (iii) To calibrate and validate simple empirical adsorption models using the long term column adsorption experimental data.

2. Mathematical formulations used in this study

2.1. Adsorption isotherm

A satisfactory description of the equilibrium state between two phases (solid and liquid) is important for a successful representation of the dynamic behaviour of the adsorption system. The adsorption equilibrium of solute (adsorbate) from the bulk solution onto the surface of an adsorbent (solid media) is quantified by adsorption isotherms.

The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites and is given in the following equation:

$$q = \frac{q_m bC}{1 + bC}, \tag{1}$$

where q is the amount of solute adsorbed per gram of adsorbent (mg/g), C is the equilibrium concentration of solute in the bulk of the solution (mg/L), q_m is saturation amount of organic adsorbed (mg/g) and b is a constant (L/mg).

The Freundlich isotherm describes heterogeneous surface adsorption. The energy distribution for adsorptive sites (in Freundlich isotherm) follows an exponential type function which is close to the real situation. The rate of adsorption/desorption varies with the strength of the energy at the adsorptive sites. The Freundlich isotherm is expressed by the following equation:

$$q = k_F C^{1/n}, \tag{2}$$

where the constants k_F and n relate to sorption capacity of the adsorbent and the deviation form linear sorption.

2.2. Batch adsorption kinetics

The homogeneous surface diffusion model (HSDM) has been used to study the GAC adsorption kinetics, Eqs. (3)–(6) [8]. HSDM 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; (iii) the adsorbate diffuses along the inner surface of the carbon particles until it reaches its adsorption site

$$\frac{\partial q}{\partial t} = D_s\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right). \tag{3}$$

Initial and boundary conditions:

$$t = 0; \quad q = 0, \tag{4}$$

$$r = 0; \quad \frac{\partial q}{\partial r} = 0, \tag{5}$$

$$r = r_p; \quad D_s\, \rho_p \frac{\partial q}{\partial r} = k_f(C - C_s), \tag{6}$$

where q is surface concentration at any radial distance (r) from the center of the activated carbon particle during adsorption, mg/g; D_s is the surface diffusion coefficient (the rate of diffusion of the target compound along the surface of the carbon), m^2/s; k_f is the external mass transfer coefficient, m/s; ρ_p is the apparent density of the activated carbon, kg/m^3; C is the bulk phase concentration, mg/L; C_s is the concentration on the external surface of PAC particles, mg/L. Using the isotherm parameters and the above equations, one can calculate the k_f and D_s values.

The HSDM was applied to the adsorption kinetics of a batch reactor. These equations were solved by an orthogonal collocation method using finite element technique. The partial differential equations of the batch system were first transformed into ordinary differential equations. The resulting equations were then integrated numerically in the time domain.

2.3. Fixed bed adsorption

In this study we investigated only the use of simple empirical equations as they can easily be used to find the length of the barrier that is necessary to remove the required quantity of MSM. Recently, Srivastava et al. [9] have discussed the theory associated with several empirical models that have been used for the prediction of breakthrough time in fixed bed adsorption. The Bohart-Adams model (BDST) is used for the description of the initial part of the breakthrough curve in the fixed bed [10]

$$\ln\left(\frac{C_0}{C}-1\right)=\ln\left[\exp\left(kN_0\frac{L}{U}\right)-1\right]-k\,C_0t, \qquad (7)$$

where k is adsorption rate constant for a fixed bed (l/min mg), N_0 is the adsorptive capacity of adsorbent (mg/l), L is the height of the column bed (cm), and U is the linear flow velocity of the feed to the bed (m/min). Hutchins [7] linearized this equation to give bed depth service time (BDST)

$$t=\frac{N_0}{C_0U_0}L-\frac{1}{kC_0}\ln\left(\frac{C_0}{C}-1\right). \qquad (8)$$

Thomas model assumes plug flow behavior in the bed, and uses the Langmuir isotherm for equilibrium, and second-order reversible reaction kinetics. This model is suitable for adsorption processes where the external and internal diffusion limitations are absent [11]

$$\ln\left(\frac{C_0}{C}-1\right)=\frac{k_Tq_0m_c}{Q}-k_T\,C_0t, \qquad (9)$$

where k_T is the Thomas rate constant (l/min mg), q_0 is the maximum solid-phase concentration of the solute (mg/g), m_C is the mass of adsorbent in the column (g) and Q is the volumetric flow rate (l/min).

Yoon and Nelson [12] developed a model based on the assumption that the rate of decrease in the probability of adsorption of adsorbate molecule is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough on the adsorbent.

$$\ln\left(\frac{C_0}{C}-1\right)=k_{YN}t-t_{0.5}k_{YN}, \qquad (10)$$

where k_{YN} is the Yoon–Nelson rate constant (min^{-1}).

3. Experimental

3.1. Chemicals

In this study, MSM was used as the model contaminant. MSM ''Brushoff'' was obtained from DuPont, Australia. The main characteristics of the GAC used are presented in Table 1. The GAC was sourced from James Cummings and Sons Pty Ltd, Australia.

3.2. Adsorption

Batch equilibrium adsorption experiment: GAC was sieved and washed with Milli Q water and dried at 105°C. Batch adsorption experiments were performed in amber coloured bottles (110 ml capacity) to ensure the mechanism of removal was only adsorption and not the result of any photo-oxidation. A known amount of GAC (from 50 to 3,000 mg/L) was added to each bottle. A 100 ml aliquot of 50 mg/L MSM was added to all bottles. The adsorption of MSM on GAC was studied at pH 3, 4.5, 7, and 10, respectively, at room temperature (23–24°C). The samples were placed on a shaker for continuous mixing in the dark at 100 rpm for 120 h. After equilibrium was reached 10 ml of aliquot was withdrawn and filtered through 0.2 μm filter disks and the residual MSM was analysed by UV spectrophotometer at 232 nm. A relatively high concentration of MSM was used as the minimum detection limit (MDL) was 0.1 mg/L

Table 1
Characteristics of granular activated carbon (GAC)

Specification value	Value
Nominal size	12 x 40 Mesh
Finer than 40 Mesh (0.42 mm)	4% max
Coarser than 12 Mesh (1.7 mm)	5% max
Iodine number (mg/g min)	1,000
Hardness (%)	80-85
Moisture content (%)	2% max
Bulk density (kg/m^3)	600
Type	Coal based

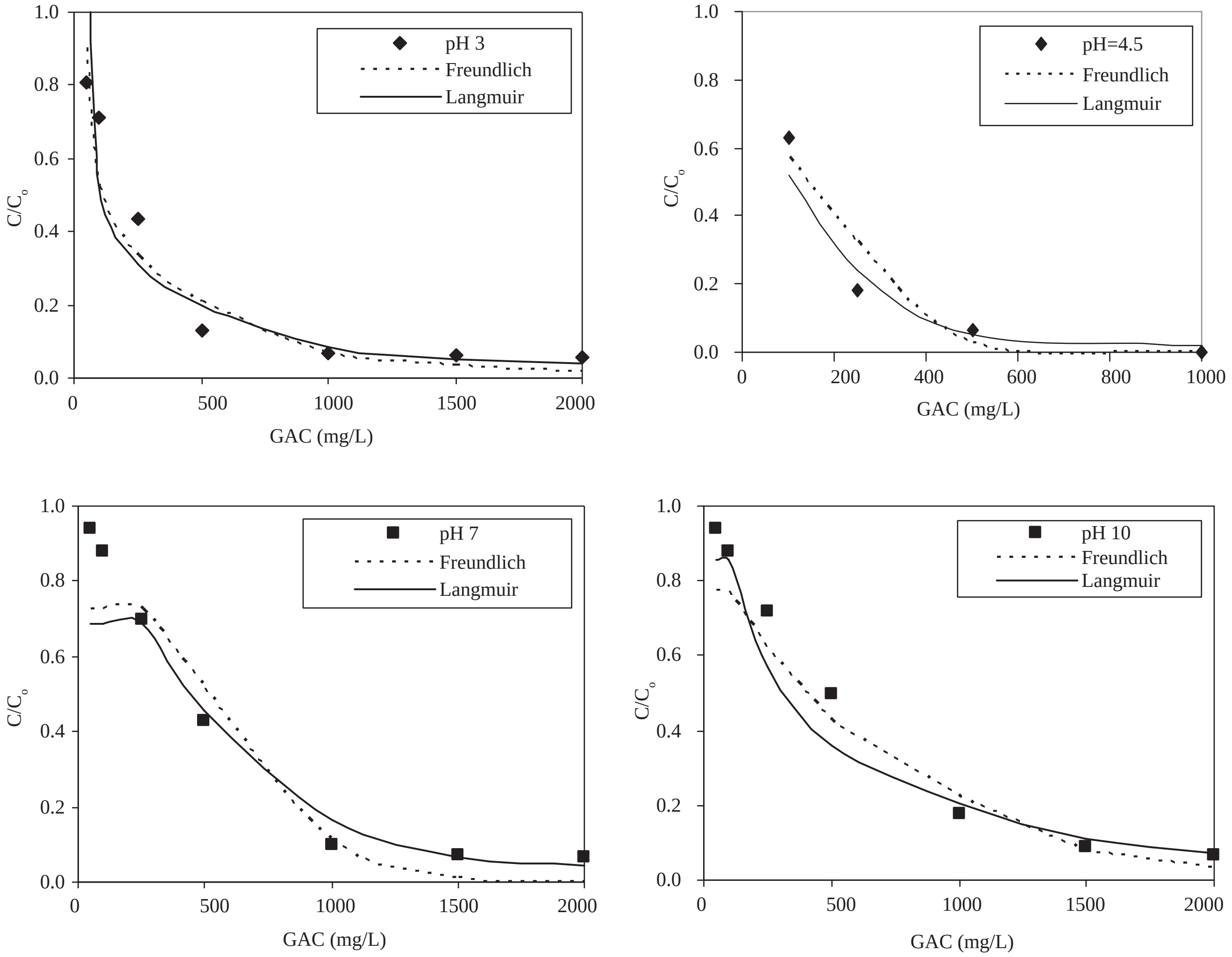


Fig. 2. Concentration decay (C/C_0) of MeS concentration at different pH (MSN concentration (C_0) = 50 mg/L). Also plotted are Freundlich and Langmuir isotherm model describing the adsorption equilibrium of MSM by GAC.

3.3. *Batch kinetic adsorption experiment*

Kinetic studies were performed in a jar test. Different amounts of GAC (100, 250, 500 and 1,000 mg) were added to four different beakers containing 1 L solution of 10 mg/L MSM. All studies were conducted in duplicate. The solution was stirred at 130 rpm. 10 ml of the solution aliquots were drawn at regular time intervals for UV analysis.

3.4. *Column equilibrium adsorption experiments (fixed bed)*

Perspex column with an internal diameter of 2 cm and a height of 30 cm were used for fixed bed adsorption studies. Three different GAC bed heights of 5, 10 and 20 cm were used in column studies. The column had ports for influent feeding, effluent collection and backwashing. The GAC bed was operated at a constant filtration rate of 1 m/h with a Master flex pump. The influent concentration of MSM was 10 mg/L and its pH was 4.5. The filter was backwashed for approximately 5 min every 24 h of the filter run to eliminate any filter bed clogging. The backwash rate was controlled by allowing up to 30% bed expansion. The backwashing did not desorb MSM that was already adsorbed. The influent and effluent concentration of MSM was measured at regular intervals by UV at 232 nm after filtering through 0.2 µm filter disks.

4. Results and discussion

4.1. *Adsorption equilibrium studies*

The adsorption isotherm studies were investigated using GAC as an adsorbent and MSM as an adsorbate. The removal of MSM by adsorption was a function of the amount of GAC available as shown in Fig. 2. The MSM removal was greater than 90% for an amount of

GAC of 0.5–1 g and for an initial MSM concentration of 50 mg/L. The adsorption of MSM onto the GAC was also a function of the solution pH (Fig. 2). The content and chemical characteristics of soils organic matter and pH were two important factors that affected the adsorption of MSM on soils and the adsorption capacity was generally higher at lower pH.

Various isotherm models including the Langmuir and the Freundlich models which are the most common isotherm models that describe the equilibrium between the two phases viz. solid and liquid were used. These isotherm models are widely accepted because of their simplicity. The isotherm parameters were optimized to give the best fit with the experimental data.

In the Freundlich model the parameter n was greater than 1.0 for all pH indicating MeS was adsorbed favorably by the GAC. The parameter k_F relates to the adsorption density and it had a peak value at a pH of 4.5. This relates to the results shown in Fig. 2 where the highest adsorption was at pH 4.5. In the Langmuir model the parameter b had the highest value and correspondingly the parameter q_m was lowest at pH of 4.5. This again relates to the highest adsorption was at pH 4.5.

Fig. 2 shows the employed isotherm equations equally fitted the experimental isotherm data ($r^2 > 0.97$) satisfactorily. In addition, as listed in Table 2, the parameter n values, which reflect the degree of heterogeneous and the adsorption intensity of adsorbent, were larger than 1.0 for all pHs. This result clearly indicates that the textural structure of coal based GAC are highly heterogeneous and the MSM adsorption is also highly favourable.

To investigate the adsorption behaviour of MSM on GAC, dimensionless equilibrium separation parameter (R) was also popularly used for the Langmuir type adsorption isotherm model.

$$R = \frac{1}{1 + bC_0},$$

Table 2
Adsorption isotherm parameters of MSM onto the GAC in terms of pH

pH	Langmuir		Freundlich	
	q_m	b	k_F	n
3	245.2	0.055	24.0	1.82
4.5	41.9	1.470	25.0	4.42
7	67.0	0.250	24.5	4.00
10	70.0	0.140	20.0	3.33

where R is the dimensionless constant separation factor, b is the Langmuir isotherm constant and C_0 is the initial concentration of MSM solution. The R value generally represents the type of adsorption isotherm; (1) irreversible (R=0), (2) linear (R=1), (3) unfavourable (R>1.0) and (4) favourable (0<R<1.0).

The values of R obtained in this work were 0.645 (pH 3), 0.022 (pH 4.5), 0.286 (pH 7) and 0.42 (pH 10), respectively. This result also revealed that the adsorption of MSM follows closely the favourable natures, which are well in agreement with the result of Freundlich isotherm.

4.2. Batch adsorption kinetics

Fig. 3 shows the kinetics of adsorption at different initial concentrations of GAC. The adsorption was rapid in the first few minutes of solution–adsorbent contact and it reached the equilibrium state after approximately 20 min. The amount of MSM adsorbed increases with increase in the initial GAC concentration. The estimated mass transfer coefficients used to predict the kinetic data are given in Table 3 for different GAC concentration. These experimental data were successfully predicted by HSDM model with both the Freundlich and Langmuir adsorption isotherms. These values of k_f and D_s were of the same order of magnitude to those obtained by Kim et al. [13] for MSM adsorption on GAC. It should be noted that the GAC used in this study was different from than used by Kim et al. [10].

4.3. Column adsorption

The column experiments were performed with three different GAC bed depths of 5, 10 and 20 cm. The shallow bed depths were chosen to obtain faster decay in concentration of MSM during the study period of 50 days. The variation of C/C_o with time is shown in Fig. 4. The reduction in C/C_0 was smaller for larger column bed heights. Further for a bed depth of 20 cm the value C/C_0 remained low at 0.3 even after 40 days of continuous operation.

4.4. Modelling

The experimental adsorption breakthrough curves were obtained at three different bed depths (5, 10, and 15 cm) and the same initial concentration (10 mg/l) and filtration rate (1 m/h), respectively. The fit between experimental data and the linearised forms of the Bohart-Adams (BDST) model **(**Eq. (8)**)**, Thomas model (Eq. (9)), and Yoon and Nelson (Y&N) model (equation 10) are shown in Fig. 4. The model parameters were

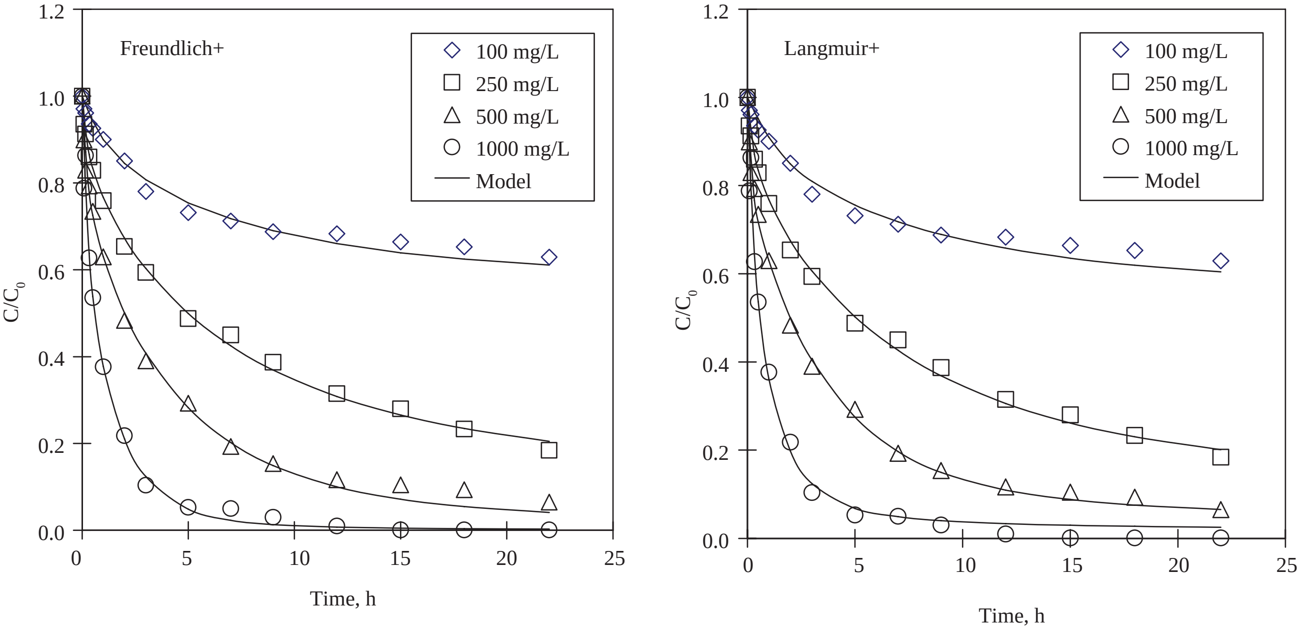


Fig. 3. Variation of C/C_0 of MSM with time in batch system with model results (where C_0 and C are the influent and final residual MeS concentration (mg/L)). Experimental values are shown by data points, and model predictions are represented by lines. (pH = 4.5). $^+$ HSDM model used in conjunction with the Freundlich and Langmuir adsorption isotherms.

optimized to give the best fit with the experimental data. The values of the parameters used are given in Table 4. Overall the fit of the Thomas model was the best for fixed bed adsorption of MSM as indicated by the r^2 values. For fixed bed adsorption in the short term the Yoon and Nelson (Y&N) model performed slightly better. However, as time progressed beyond 20 days the model performed poorly.

As can be seen in Fig. 4, the adsorption breakthrough time (or slope of breakthrough curve) increases with larger bed depths. This result closely related with time to diffuse into GAC and increment of adsorption surface area. A larger bed depth provides larger ratio of surface area/contact time).

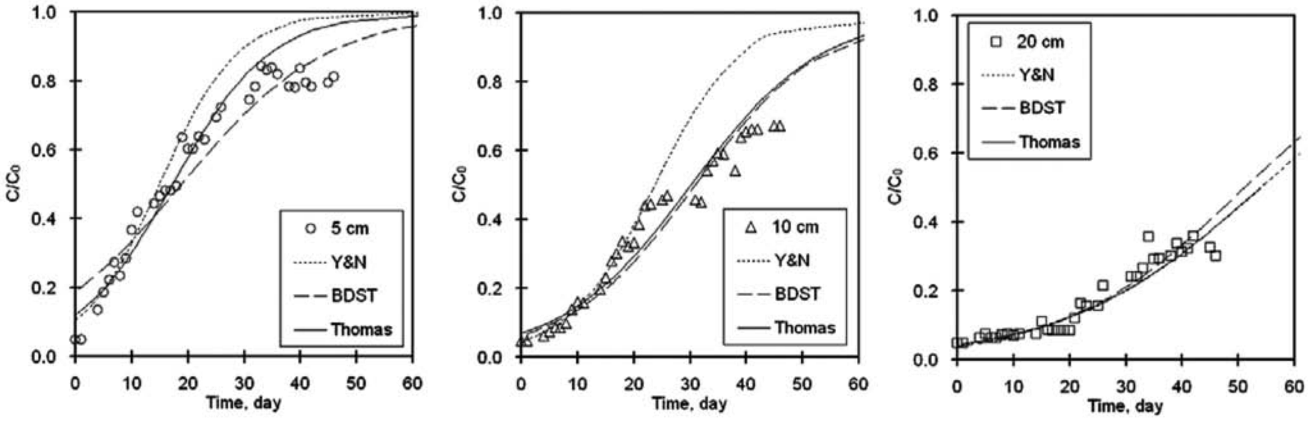
4.5. Simulation

The Thomas model was used to estimate the thickness of a hypothetical permeable reactive barrier and its service time. It should be noted that in deriving this estimate the assumptions made include the use of single media, a single component solute and the prevalence of continuous saturated conditions. Two estimates were derived. The first was for a relative high concentration of ground water pollutant of 10 mg/L. In this case a permeable reactive barrier of 1.5 m thickness would reduce the concentration of pollutants (MSM) in the effluent to below 0.05 mg/L and would be able to do so for a period of 325 days. In the second case, if the concentration of ground water pollutant

Table 3
Coefficients used to model batch adsorption kinetics of MSM onto the GAC (pH = 4.5)

Conc. of GAC (mg/L)	Langmuir$^+$		Freundlich$^+$	
	D_s (m^2/s)	k_f (m/s)	D_s (m^2/s)	k_f (m/s)
100	1.953E−13	1.427E−05	1.847E−13	1.697E−05
250	8.010E−14	2.586E−05	8.116E−14	2.826E−05
500	4.420E−14	2.52E−05	5.105E−14	2.31E−05
1,000	5.101E−14	1.97E−05	5.169E−14	1.96E−05
Average*	9.266E−14	2.125E−05	9.216E−14	2.198E−05

* Average value for D_s and k_f of different concentrations of GAC.
$^+$ HSDM model used in conjunction with the Freundlich and Langmuir adsorption isotherms.



a) 5 cm b) 10 cm c) 20 cm

Fig. 4. Percent MSM removed at varied bed depths (L), $C_0 = 10$ mg/l, U = 1 m/h, pH = 4.5, Experimental values are shown by data points, and model predictions are represented by lines.

Table 4
Estimated parameters for semi-empirical models for the fixed bed adsorption of MSM

Model	Parameter	5 cm	10 cm	20 cm
Yoon & Nelson	k (1/min)	1.00E−04	9.00E−05	4.00E−05
(Y&N)	$T_{0.5}$ (day)	14.9	23.7	53.9
	r^2	0.58	0.72	0.92
BDST	k (1/mg. min)	1.86E+05	1.65E+05	2.28E+05
	r^2	0.77	0.93	0.93
Thomas	k (1/mg. min)	8.00E−06	6.00E−06	4.00E−06
	r^2	0.80	0.93	0.92

was relatively low and about 1 mg/l, a permeable reactive barrier of 1.5 m thickness would reduce the concentration of pollutants in the effluent to 0.05 mg/L and would do so for a period of 3,785 days. In reality these estimates will be influenced by variations in chemical and hydraulic conditions that exist in the field.

5. Conclusion

The removal of MSM from the aqueous solution was initially investigated by batch GAC adsorption. The GAC adsorption removed more than 90% of MSM for initial concentrations of 50 mg/L. The adsorption of MSM onto the GAC was a function of the solution pH. The highest adsorption was at pH 3. On an overall basis, both the Freundlich and Langmuir isotherms were reasonable in describing the MSM adsorption equilibrium by GAC. HSDM with Langmuir and Freundlich adsorption isotherm model was successfully applied to predict the batch adsorption kinetics data in various concentrations of MSM. Simple empirical models such as the Bohart-Adams [10,14], Thomas [11] and Yoon and Nelson [12] were used to predict the column adsorption results. Although all the models were able to fit the experimental data, the Thomas model was found to best simulate the fixed bed adsorption of MSM.

Acknowledgement

This project was funded by Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) (project number 2-5-05-05/6).

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