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Modeling of Fixed Bed Adsorption: Application to the Adsorption of an Organic Dye

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ABSTRACT

The modeling of the dynamics of adsorption of an organic dye (Rhodamine B) onto natural clay on a fixed bed from aqueous solutions was studied. The application of different models to describe the breakthrough curve shows that the models of Clark, Yoon and Nelson and Thomas give better results for the operating conditions. The Bohart and Adams model describes only the initial part of the breakthrough curve. The study of variation of parameters of the mass transfer zone for different operating conditions shows that the rate of mass transfer area increases with increasing initial concentration. The rate of saturation and the partial ability of the bed do not depend on operating conditions.

Key words: Adsorption, rhodamine B, fixed bed, clay breakthrough curve

INTRODUCTION

Currently, the rejections of textile industry are heavily charged in dyes. The rejections of these industries present a true danger to the man and his environment because of their stability and their low biodeterioration (Benguella and Yacouta-Nour, 2009). The traditional processes, in particular biological, do not ensure a satisfactory elimination. The techniques of adsorption gave good outputs of elimination of the organic molecules. The activated carbon was largely used because of its great capacity of adsorption of the organic species, but its use is very expensive, that's why, several authors preferred the use of clays for the removal of the organic dyes as their cost are less expensive than that of the activated carbon. The elimination of the organic dyes by clay was studied by several researchers (Almeida *et al*., 2009; El-Mouzdahir *et al*., 2007; Hong *et al*., 2009; Ghosh and Bhattacharyya, 2002). They showed that clays present an affinity of adsorption with respect to these species. In this context, a study of the adsorption of the dye model (Rhodamine B) on a fixed natural clay bed is carried out (made) throughout this work, in order to master the adsorption of the basic dyes on fixed-bed clay and to develop on this basis a modeling making it possible to predict the performances and the characteristics of the bed according to the operating conditions.

MATERIALS AND METHODS

The adsorbent: In this study, the adsorbent used is natural clay. The used clay is of smectite type. The minerals of this group are characterized by a structure of the interlayer type 2:1 of distance

Table 1: Chemical composition of natural clay

Chemical compound	% Mass
CaO	2.52
SiO_2	48.92
Al_2O_3	19.31
Fe_2O_3	13.13
SO_3	0.28
K_2O	1.06
MgO	2.53
Na_2O	1.21
ZnO	0.17
P_2O_5	0.19
TiO_2	1.63
ZnO	0.17

Table 2: Characteristics of Rhodamine B

Characteristics	Values
Chemical formula	$C_{28}H_{31}N_2O_3Cl$
Mass molar	479 g mol^{-1}
Maximum absorbance	555 nm
Ionization	Basic
Solubility	50 g L^{-1} with 20°C in water
Density	0.79 g cm^{-3}
Fusion temperature	210-211°C

Table 3: Properties of the column

Properties	Values
External diameter (mm)	22
Internal diameter (mm)	17
Height (mm)	200
Section (mm^2)	226.98
Volume (mm^3)	45396
Mass clay (g)	51

equal to 14 Å. The smectite is a consistent mineral, very soft, which is generally presented in compact mass, the stacking of the layers is disordered. This disorder and the weak load of the layers facilitates their spacing from where the adsorption of varied molecules. The analysis of our clay by the method of x-ray fluorescence gave the following results concerning their characterizing chemical compounds (Table 1).

The adsorbate: The dye used during our work is the Rhodamine B (CI No. 45170). It is an organic compound whose physicochemical properties are grouped in Table 2.

Fixed bed experiments and mathematical models: In this study, an adsorber, whose dimensions are shown in Table 3, was used. The dye is aspired from the dye tank by means of a feed pump. Then, it crosses the bed of the column filled with burnt clay mass. At the exit of the column, the solution is recovered with intervals of 15 min time to determine its concentration. Before carrying out discoloration, the clay bed was percolated by the distilled water instead of the dye during 2 to 3 h to ensure the damping and the swelling of clay.

Model of clark: Clark proposed a new simulation of the breakthrough curves (Clark, 1987). The model developed by Clark is based on the following hypotheses:

- On the use of a mass-transfer concept in combination with the Freundlich isotherm (Ayoob and Gupta, 2007)
- The flow is of piston type (Hamdaoui, 2006)

By using the laws of mass transfer and by neglecting the phenomenon of dispersion, Clark solved the system of equations of mass transfer and obtained the following relation (Sahel and Ferrandon-Dusart, 1993).

$$C=\left(\frac{C_0^{\,n-1}}{1+Ae^{-rt}}\right)^{\frac{1}{n-1}} \tag{1}$$

$$A=\left(\frac{C_0^{\,n-1}}{C_b^{\,n-1}}-1\right)e^{rtb} \tag{2}$$

Where:

$$r=\frac{K_T}{U}$$

n = Freundlich parameter

A and r are the constants of the model and are obtained starting from the following equation:

$$C^{n-1}=\left(\frac{C_0^{\,n-1}}{1+Ae^{-rt}}-1\right) \tag{3}$$

$$Ae^{-rt}=\left(\frac{C_0^{\,n-1}-C^{n-1}}{C^{n-1}}\right) \tag{4}$$

When linearizing this equation, we obtain:

$$LnA-rt=Ln\left(\frac{C_0^{\,n-1}-C^{n-1}}{C^{n-1}}\right) \tag{5}$$

Model of thomas: The Thomas model is one of the most general and widely used theoretical methods to describe column performance (Rozada *et al*., 2007). This model can be described by the following expression:

$$\frac{C_t}{C_0}=\frac{1}{1+\exp\left(\left(K_{th}/F\right)\left(q_{\infty}x-C_0V_{ef}\right)\right)} \tag{6}$$

where, C_0 and C_t are respectively the influent and effluent concentrations (mg L^{-1}), K_{th} is the Thomas rate constant (mL/mg/min), q_∞ is maximum capacity of adsorption (mg g^{-1}), X quantity of adsorbent in the column (g), V_{ef} is volume of solution (mL) and F is the feed flow (mL mn^{-1}).

The Thomas model which assumes Langmuir kinetics of adsorption-desorption and no axial dispersion is derived with the assumption that the rate driving force obeys second-order reversible reaction kinetics (Thomas, 1944; Wu and Yu, 2008; Ayoob and Gupta, 2007; Rozada *et al.*, 2007).

Model of Yoon-Nelson: The Yoon-Nelson model is not only less complicated than other models, but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent and the physical properties of the adsorption bed (Aksu and Gonen, 2004). This model assumes that (Yoon and Nelson, 1984):

- The rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent (Ayoob and Gupta, 2007)

The Yoon-Nelson equation for a single component system is expressed as (Yoon and Nelson, 1984):

$$\frac{C_t}{C_0 - C_t} = \exp\left(k_{YN} t - \tau k_{YN}\right) \quad (7)$$

where, K_{YN} is the rate constant (mn^{-1}), τ is time required for 50 % adsorbate breakthrough (mn) and t is time (mn).

Model of Adams-Bohart: To account for the adsorption of chlorine on a fixed bed activated carbon in a dynamic model, Bohart and Adams established the fundamental equation describing the relationship between C/C_0 and time. The modeling conceived by these authors was in the beginning planned for gases and it was transposed later to the liquids by quite simply replacing the terms in pressure by terms of concentration, since it is the same definition even of the chemical activity of an aqueous solution in solution in a diluted medium (Sahel and Ferrandon-Dusart, 1993; Bohart and Adams, 1920).

To solve the equations of the model, certain assumptions were put forth:

- The concentrations are weak $C \ll C_0$
- When: $t \to \infty$: $q \to N_0$ with: N_0 maximum capacity of adsorption
- The speed of adsorption is limited by the external mass transfer

The resolution of the conservation equations of the matter leads to:

$$\mathrm{Ln}\left(\frac{C}{C_0}\right) = KC_0 t - KN_0 \frac{Z}{U} \quad (8)$$

where, C_0 and C: are, respectively the concentrations initial and instantaneous aqueous solution in the solution (g L^{-1}), K is the kinetic constant (L/g/min), N_0 is capacity of adsorption (g L^{-1}), Z is the bed depth in the column (m), t is time (mn) and U and the speed of gas out (m sec^{-1}).

Error analysis: The squares of the differences between the experimental data and the data obtained by calculating from the models can be obtained as the following formula:

$$\delta = \sqrt{\frac{\sum\left[\left(\frac{C}{C_0}\right)_{cal} - \left(\frac{C}{C_0}\right)_{exp}\right]}{N}} \tag{9}$$

where, $(C/C_0)_{cal}$ is the ratio of effluent and influent RB concentrations obtained from calculation according to dynamic models and$(C/C_0)_{exp}$ is the ratio of effluent and influent RB concentrations obtained from experiment.

RESULTS AND DISCUSSION

Choice of models: The dynamic behavior of the column is approached by the following models: Bohart and Adams, Thomas, Yoon-Nelson and Clark (Fig. 1).

We deduce from this first comparison that the models of Clark, Thomas and Yoon-Nelson correctly smooth the experimental curve of opening, whereas the model of Bohart and Adams describes only the initial part of the curve of opening, in accordance with the made approximation ($C \ll C_0$).

The method of least square confirms this conclusion by the absolute error analysis carried in Table 4.

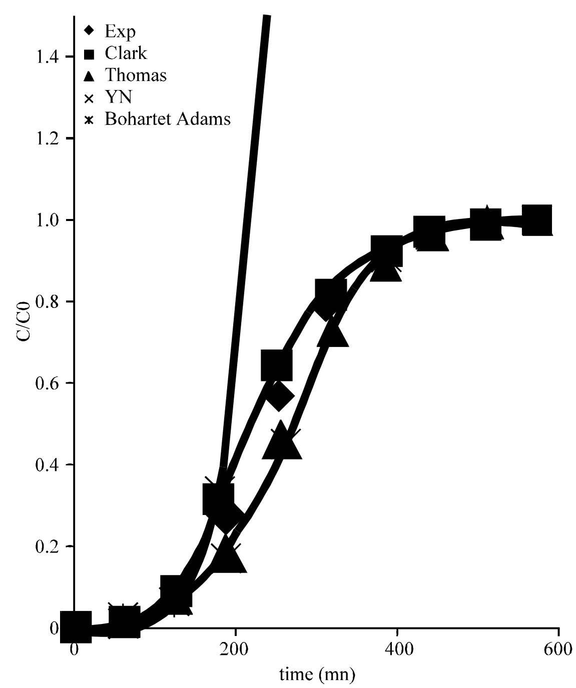

Fig. 1: Comparison between the curve of experimental opening and the curves predicted by the models

Table 4: The error analysis

Absolute error	Clark	Bohart and Adams	Thomas	Yoon and Nelson
δ	0.02932	14.3654	0.0527	0.057

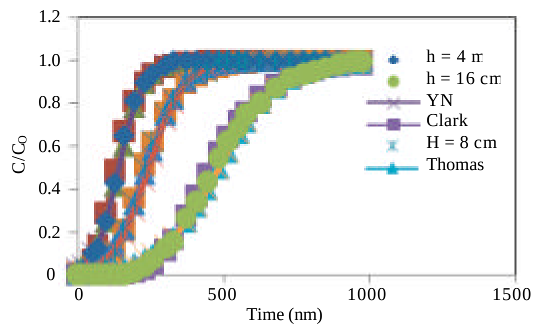

Fig. 2: Breakthrough curves : the effect of different bed depths on RB adsorption (C_0 = 80 mg L^{-1}, Q = 0,18 L mn^{-1})

According to this table, one finds that the model of Clark gives the best result. Several studies found the same result (Bohart and Adams, 1920; Han *et al.*, 2009).

Fixed bed adsorption experimental results and modeling

Effect of different bed depths on breakthrough curve: The sorption performance of natural clay was tested at various bed heights bed depths, 16, 8 and 4 cm at flow rate of 0,18 l mn^{-1} and initial concentration of 80 mg L^{-1}. The breakthrough curves at different bed depths are shown in Fig. 2.

Effect of initial concentration on breakthrough curve: The experiments of two different initial concentration, 50 and 20 mg L^{-1}, were operated at the same bed depth (8 cm) and flow rate (0, 18 L mn^{-1}), respectively. The results are shown in Fig. 3.

Effect of flow rate on breakthrough curve: The experimental conditions chosen to study the effect of the flow rate were : inlet concentration of RB 80 mg L^{-1} ; bed depth, 8 cm and feed flow rates 0, 06, 0,18 and 0,3 L mn^{-1}. The breakthrough curves at various flow rates are shown in Fig. 4.

Estimation of breakthrough curves

Model of clark: The adsorption isotherm of clay can be described by the Freundlich isotherm. The Freundlich constant (n) was used to calculate the parameters in the Clark model. The values of A and r in the Clark model are shown in Table 5. As seen in this later as both flow rate and influent dye concentration increased, the values of r increased. From the experimental results and data regression, the model proposed by the Clark model provided good correlation on the effects of influent RB concentration, flow rate and bed depth.

These results are similar to those found by other researchers working on different sorbate-sorbent systems (Ayoob and Gupta, 2007; Han *et al.*, 2009; Ayoob *et al.*, 2007).

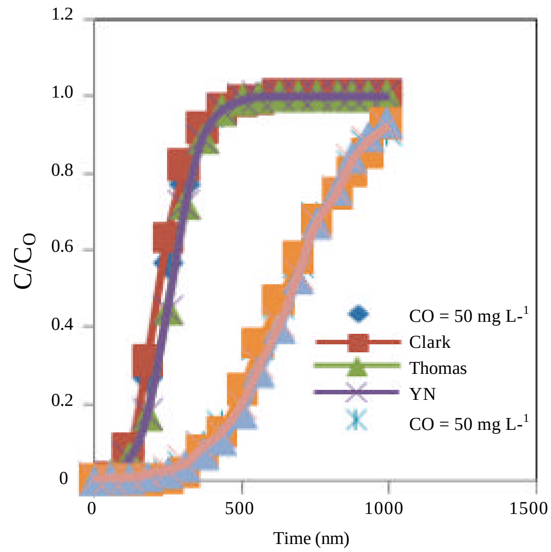

Fig. 3: Breakthrough curve : the effect of influent concentration on RB adsorption (H = 8 cm, Q = 0,18 l mn^{-1})

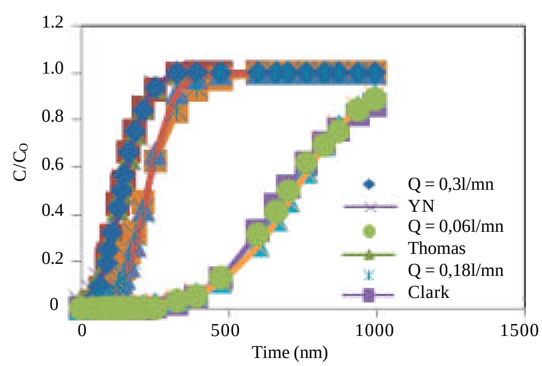

Fig. 4: Breakthrough curves : the effect of flow rate on RB adsorption (C_0 = 80 mg L^{-1}, H = 8 cm)

Model of Yoon-Nelson: This model is very simple and does not require any data concerning the characteristics of the adsorbent and the bed. The parameters of this model are gathered in Table 6.

From Table 6, the rate constant K_{YN} increased with increasing both flow rate and RB influent concentration (Ayoob and Gupta, 2007; Han *et al.*, 2009). The data in Table 6 also indicate that values of τ are similar to the experimental results.

Model of thomas: The Thomas model is one of the most general and widely used methods in column performance theory. The parameters of the model of Thomas are also listed in Table 7. It is shown in Table 7 that as the influent concentration increased, the value of q_e increased but the value of Kth decreased. With flow rate increasing, the value of q_e decreased while the value of Kth increased. As the bed depth increased, the value of q_e increased significantly but the value of Kth decreased significantly (Han *et al.*, 2009; Aksu and Gonen, 2004).

Table 5: Parameters of the Clark model at different conditions

Operating conditions			Parameters of the model			Absolute error
Q (L mn^{-1})	C_0 (mg L^{-1})	H (cm)	r (min^{-1})	A	R^2	δ
0.3	80	8	0.019	0.884	0.9972	0.0017
0.18	80	8	0.013	1.257	0.9928	0.0016
0.06	80	8	0.0052	2.510	0.9926	0.0040
0.18	80	16	0.0079	2.494	0.9949	0.0014
0.18	80	4	0.0188	0.786	0.9952	0.0120
0.18	20	8	0.0053	2.854	0.9983	0.0051
0.18	50	8	0.014	1.460	0.9927	0.0100

Table 6: Parameters of the model of Yoon-Nelson

Operating conditions			Parameters of the model			Absolute error
Q (L min^{-1})	C_0 (mg L^{-1})	H (cm)	K_{YN} (mn^{-1})	τ_{th} (min)	τ_{exp} (min)	δ
0.3	80	8	0.0252	141.37	139	0.049
0.18	80	8	0.0238	225.21	231	0.050
0.06	80	8	0.0081	721.63	702	0.051
0.18	80	16	0.0099	485.54	465	0.046
0.18	80	4	0.0243	142.34	113	0.025
0.18	20	8	0.0080	732.3	715	0.018
0.18	50	8	0.0019	261	255	0.057

Table 7: Parameters of the model of Thomas

Operating conditions			Parameters of the model		Absolute error
Q (L min^{-1})	C_0 (mg L^{-1})	H (cm) K_{th}	(L mg^{-1} mn^{-1})	q_e (mg g^{-1})	δ
0.3	80	8	$3.013\ 10^{-4}$	162.15	0.0010
0.18	80	8	$2.97\ 10^{-4}$	167.73	0.0220
0.06	80	8	$1.013\ 10^{-4}$	173.30	0.0054
0.18	80	16	$1.24\ 10^{-4}$	194.40	0.0480
0.18	80	4	$3\ 10^{-4}$	153	0.0270
0.18	20	8	$4.3\ 10^{-4}$	66.36	0.0520
0.18	50	8	$3.88\ 10^{-4}$	98.70	0.0330

Evaluation of basic design parameters of adsorption column: The formation and movement of adsorption zone can be mathematically described and evaluated (Ayoob *et al.*, 2007; Bhakat *et al.*, 2007).

Partial capacity of the adsorbent bed: The partial capacity of the adsorbent bed determines the adsorbent's removal efficiency, denoted F, it is defined as the amount actually involved in adsorption phenomenon compared to the total amount of adsorbent. It can also be defined as the amount of adsorbate actually eliminated from the potential disposal of the adsorbent inside the zone transfer. It is calculated by the ratio:

$$F = \frac{A_Z}{A_{max}} = \frac{\int_{t_b}^{t_s} (C_0 - C)\,dt}{C_0 (t_s - t_b)} \tag{10}$$

Table 8: Parameters for the fixed bed clay column

C_0 (mg L^{-1})	F (%)	tz (h)	Hz (cm)	Uz (cm mn^{-1})	% Saturation
20	95	8.41	4.71	0.495	92.18
50	91	3.53	3.53	1.345	95.26
80	94	4.20	4.20	1.653	90.38

where, C_0 is the initial concentration of RB in water (mg L^{-1}); C is the concentration of solute RB at any instant in the effluent (mg L^{-1}); Az is the amount of RB that has been removed by the adsorption zone from breakthrough to exhaustion (mg) and Amax is the amount of RB removed by adsorption zone if completely exhausted (mg), t_s is the saturation time and t_b: the breakthrough time.

The height of the mass transfer zone: It is in this portion of the bed, practically, that most of the transfer phenomenon. Take place it determines the rate of removal of adsorbate by the adsorbent. It is an effective parameter to quantify the overall rate of exchange which is calculated by the equation below:

$$H_Z = \frac{H_b(t_s - t_b)}{t_b + F(t_s - t_b)} \tag{11}$$

where, H_b is the height of the adsorbent bed

The speed of the mass transfer zone: The speed of the mass transfer zone depends on the capacity of the adsorbent and allows us to calculate the velocity saturation of the bed. It is directly related to the height of the mass transfer zone. It is given by:

$$U_Z = \frac{H_Z}{t_Z} = \frac{H_Z}{t_s - t_b} = \frac{H_b}{t_s - t_f} \tag{12}$$

where, t_z is the time required for the adsorption zone to travel its own length when established, t_f is The time required for the formation of the transfer zone.

The value of t_f can be calculated as:

$$t_f = (1 - F)t_Z \tag{13}$$

The percentage of saturation of the column to the breakthrough: Fix a breakthrough concentration C_b = 0.2C_0 and a saturation concentration Cs and C_0 = 0.9, than calculate all parameters at different initial concentrations for a bed height H = 8 cm and a flow rate Q = 0.18 L min^{-1}. The calculation results are given in Table 8.

We note that the speed of the mass transfer area increases with the initial concentration after increasing the driving force that controls the adsorption process. The rate of saturation and the partial capacity of the bed do not depend on operating conditions.

CONCLUSIONS

On the basis of the experimental results of this investigation, the following conclusion can be drawn:

- The adsorption of RB was depended on the flow rate, the intel RB concentration and bed depth
- The initial region of breakthrough curve was defined by the Adams-Bohart model at all experimental condition studied while the full description of breakthrough could be accomplished by the Thomas, Yoon-Nelson and Clark models
- The study of variation of the parameters of the mass transfer zone for different operating conditions shows that the rate of mass transfer area increases with the initial concentration. The rate of saturation and partial capacity of the bed do not depend on operating conditions

REFERENCES

Aksu, Z. and F. Gonen, 2004. Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves. Process Biochem., 39: 599-613.

Almeida, C.A.P., N.A. Debacher, A.J. Downs, L. Cottet and C.A.D. Mello, 2009. Removal of methylene blue from colored effluents by adsorption on montmorillonite clay. J. Coll. Interf. Sci., 332: 46-53.

Ayoob, S. and A.K. Gupta, 2007. Sorptive response profile of an adsorbent in the defluoridation of drinking water. Chem. Eng. J., 133: 273-281.

Ayoob, S., A.K. Gupta and P.B. Bhakat, 2007. Analysis of breakthrough developments and modeling of fixed bed adsorption system for As(V) removal from water by Modified Calcined Bauxite (MCB). Sep. Purif. Technol., 52: 430-438.

Benguella, B. and A. Yacouta-Nour, 2009. Elimination des colorants acides en solution aqueuse par la bentonite et le kaolin. Comptes Rendus Chimie, 12: 762-771.

Bhakat, P.B., A.K. Gupta and S. Ayoob, 2007. Feasibility analysis of As(III) removal in a continuous flow fixed bed system by modified calcined bauxite (MCB). J. Hazard. Mater., 139: 286-292.

Bohart, G.S. and E.Q. Adams, 1920. Some aspects of the behavior of charcoal with respect to chlorine. J. Chem. Soc., 42: 523-544.

Clark, R.M., 1987. Evaluating the cost and performance of field-scale granular activated carbon systems. Environ. Sci. Technol., 21: 573-580.

El-Mouzdahir, Y., A. Elmchaouri, R. Mahboub, A. Gil and S.A. Korili, 2007. Adsorption of methylene blue from aqueous solutions on a moroccan clay. J. Chem. Eng. Data, 52: 1621-1625.

Ghosh, D. and K.G. Bhattacharyya, 2002. Adsorption of methylene blue on kaolinite. Applied Clay Sci., 20: 295-300.

Hamdaoui, O., 2006. Dynamic sorption of methylene blue by cedar sawdust and crushed brick in fixed bed columns. J. Hazard. Mater., 138: 293-303.

Han, R., Y. Wang, X. Zhao, Y. Wang, F. Xie, J. Cheng and M. Tang, 2009. Adsorption of methylene blue by phoenix tree leaf powder in a fixed-bed column: Experiments and prediction of breakthrough curves. Desalination, 245: 284-297.

Hong, S., C. Wen, J. He, F. Gan and Y.S. Ho, 2009. Adsorption thermodynamics of methylene blue onto bentonite. J. Hazard. Mater., 167: 630-633.

Rozada, F., M. Otero, A.I. Garcia and A. Moran, 2007. Application in fixed-bed systems of adsorbents obtained from sewage sludge and discarded tyres. Dyes Pigm., 72: 47-56.

Sahel, M. and O. Ferrandon-Dusart, 1993. Adsorption dynamique en phase liquide sur charbon actif: Comparaison et simplification de differents modeles. Revue des Sciences de l'eau, 6: 63-80.

Thomas, H.C., 1944. Heterogeneous ion exchange in a flowing system. J. Am. Chem. Soc., 66: 1664-1666.

Wu, J. and H.Q. Yu, 2008. Biosorption of 2,4-dichlorophenol from aqueous solutions by immobilized *Phanerochaete chrysosporium* biomass in a fixed-bed column. Chem. Eng. J., 138: 128-135.

Yoon, Y.H. and J.H. Nelson, 1984. Application of gas adsorption kinetics. I. A theoretical model for respirator cartridge service life. Am. Ind. Hyg. Assoc. J., 45: 509-516.