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Modeling of Manganese (II) biosorption by a dead biomass in a fixed bed-column

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ABSTRACT/RESUME

Abstract: *The main objective of our study is to model Mn^{2+} adsorption kinetics on a "Pleurotus Mutilus" dead biomass in a fixed bed column, using a published mathematical model which describes experimental breakthrough curves obtained by varying the process parameters such as Mn^{2+} initial concentration, bed height and Mn^{2+} solution flow rate.*

I. Introduction

Pollution by heavy metals is a global environmental problem. The effluents from various industrial processes represent one of the largest sources of pollution [1]. Heavy metals are described as priority pollutants due to their high toxicity on ecosystems and water [2, 3].

This explains why removal of these metals same Mn^{2+} has become a primary concern for many researchers, and has been the subject of several studies. Among these, many are focused on the use of less expensive materials such as solid by products or natural products available in the environment [4].

Study of the sorption kinetics in the treatment of sewage containing manganese is important since it provides necessary data to the sizing of adsorption columns [5, 6].

Consequently, it is necessary to consider a quantitative approach before attempting the optimization of the process under study. Also, modelling of the dynamic behaviour of a fixed bed column helps to describe breakthrough curves [7].

On the other hand, modelling of the breakthrough curves is a very important step because it provides basic information for the design of an adsorption column.

There are two widely used approaches to obtain the breakthrough curve of a given system, by direct experimentation or using mathematical models. The experimental method can provide direct and concise breakthrough curve of a given system. Otherwise, mathematical modelling is simple and easily performed without the need of experimental apparatus, and because of this, has attracted a growing interest among researchers [8].

Currently, many mathematical models available in the literature are used to describe and predict the breakthrough curves of an adsorption column system [9, 10].

As one of the most common techniques of separation and purification, the fixed bed

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adsorption has been widely applied due to its high efficiency and ease of use and regeneration. Given the fact that the experimental determination of the adsorption performance in various conditions takes significant time, the development of mathematical models to predict adsorption in fixed beds is needed. The mathematical model used in this study was developed by Xu et al [8].

II. Materials and methods

II.1. Adsorbent

After extraction of pleuromutilin, fungal biomass *"Pleurotus Mutilus"* has the aspect oaf wet floc with yellowish color and characteristic odor. It undergoes various physico-chemical pretreatment designed to remove impurities and increase its adsorption capacity. Raw biomass was washed several times with distilled water to eliminate any impurities remaining after the antibiotic extraction process and dust due to exposure to air. Then it is dried in an oven at 50°C for 24 h, crushed, sifted and stored in polyethylene bottles. In our experimental tests, the particle used have a size ranging between 315 and 400 microns(µm).

II.2. Adsorption tests

The adsorption tests were performed in a laboratory glass column of 1.6 cm inner diameter and 18 cm of length.

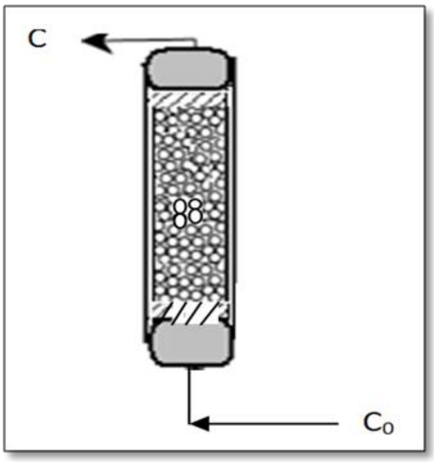

Figure 1. *Schematic of the experimental setup.*

The samples were analyzed using an atomic adsorption spectrophotometer AAS Perkin Elmer A600 with a wavelength 280.1 nm.

Model Description

II. 3 Model Description

Before making the necessary assumptions for the model formulation, the physical phenomenon involved in the process, namely transport by convection and axial dispersion which are the mass transfer mechanisms in the liquid phase, are considered.

Within the particle, molecules can diffuse by surface diffusion, porous diffusion or both at the same time.

II.4. Simplifying assumptions

In order to formulate the general model corresponding to the adsorption in a fixed-bed column, the following assumptions are made:

- The adsorption is isotherm,
- The bed particles are supposed to be spherical,
- An ideal plug flow is considered in the column,
- A local and rapid equilibrium is achieved between the two phases,
- The bed porosity is assumed to be constant,
- The flow rate is uniform throughout the column.

II.5. Mass balance

Based on the above assumptions, the overall mass balance of a control volume A. dz of the fixed bed is given as follows in figure 2:

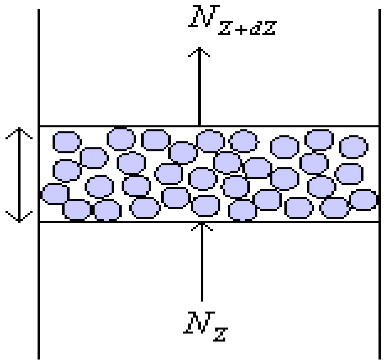

Figure.2. *Mass balance of a volume element of the fixed bed.*

Mass balance: Input ± chemical reaction = Output + Accumulation

Mathematical model:

The mass balance results in the following equation:

$$\left(\varepsilon D_L \frac{\partial^2 c}{\partial z^2}\right) AdZ + \left(-U\frac{\partial C}{\partial Z}\right) AdZ = \varepsilon \frac{\partial C}{\partial t} AdZ + \rho(1-\varepsilon)\frac{\partial q}{\partial t} AdZ \quad \textbf{(1)}$$

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Where,q: is the solute concentration (mg/g), representing the amount adsorbed, it is determined by the adsorption isotherm.
C: is the solute concentration in phase transferred into the liquid phase (mg/m^3)
A: is the cross section area of the column (m^2).

Z: is the height of the adsorbent bed (m).
D_L: is the axial dispersion coefficient (m^2/s).
ε : Is the bed porosity
t: is the time of operation.
U: Is the average superficial velocity of the liquid (m/s)
ρ : Is the bulk density of the bed particles (g/m^3).
After simplification, we obtain the final equation of the overall balance governing the transfer of a solute during adsorption on a fixed bed column:

$$U_0\left[\frac{\partial C}{\partial Z}\right]_t + \left[\frac{\partial C}{\partial t}\right]_Z + \rho\frac{(1-\varepsilon)}{\varepsilon}\left[\frac{\partial q}{\partial t}\right]_Z = D_L\left[\frac{\partial^2 c}{\partial Z^2}\right] \quad \textbf{(2)}$$

Where
U_0: is the interstitial liquid velocity in (m/s), it is given by [11]:

$$U_0 = \frac{F}{A\varepsilon} = \frac{U}{\varepsilon} \quad \textbf{(3)}$$

F: is the liquid volume flow rate (m^3/s).

Langmuir isotherm

The expression for the adsorption isotherm is as follows:

$$q_e = \frac{q_m b c_e}{1+b c_e} \quad \textbf{(4)}$$

Where
C_e : is the concentration of solute in the liquid phase at equilibrium in (mg/l).
b : is the affinity adsorption.
q_m : is the maximum adsorption capacity (mg / g).
q_e : Is the adsorption capacity in equilibrium (mg /g).

Freundlich isotherm

The expression for the adsorption isotherm is:

$$q_e = k_{Fr}\,(C_e)^{\frac{1}{n}} \quad \textbf{(5)}$$

Where k_{Fr} and n are the Freundlich parameters
According to the impact of diffusion is negligible when the bed height exceeds fifty times the diameter of the particle, which is the case in our study [12]. Hence, the diffusion term is neglected. So overall mass balance of the species adsorbed is reduced to

$$U_0 = \left[\frac{ac}{az}\right]_t + \left[\frac{ac}{at}\right]_z + p\frac{(1+\varepsilon)}{\varepsilon}\left[\frac{aq}{at}\right]_z = 0 \,\textbf{(6)}$$

The adsorption rate can be described by the model of the linear driving force in terms of the overall mass transfer coefficient in the liquid phase in the following form [13]:

$$\rho\frac{\partial q}{\partial t} = \varepsilon K_L a(C - Ce) \quad \textbf{(7)}$$

Where:
a: is the interfacial area of the adsorbent bed in (m^2/m^3).
K_L : is the overall mass transfer coefficient in the liquid phase (m/s).
C_e: is the solute concentration in the liquid phase at equilibrium in (mg / m3).
C: is the solute concentration in the liquid phase at time t in (mg / m3). [14]

$$a = \frac{6(1-\varepsilon)}{dp}\varepsilon \quad \textbf{(8)}$$

d_p : is the particle diameter (m).

II.6. Resolution of the model equation

Writing the mass balance leads to a system of partial differential equations. We can greatly simplify the model by linearization through an operating point taking into account the preceding simplifying assumptions.

Equation (6) can be written in a more simplified form using the variable combination method by reducing the number of variables.

According to the constant wave pattern approach, the wave travels with a constant flux speed U_c We make a change of variable to set the adjusted time given by:

$$\tau = t - \frac{z}{Uc} \quad \textbf{(9)}$$

τ : is a relative time that represents the difference between the elapsed time (since the launch of the test) and the residence time of the local fluid.

By combining the variables, we obtain the final equation of the model describing the adsorption kinetics in the mass transfer zone:

$$t = t_{\frac{1}{2}} + \frac{\rho q}{\varepsilon KLa\, C_0}\left[Ln2x - \frac{1}{n-1}Ln\frac{1-x^{n-1}}{1-2^{1-n}}\right] \quad \textbf{(10)}$$

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Where:
C_0 : is in equilibrium with q_0, $x = C/C_0$, $t_{1/2}$ is the time when half of the initial concentration is adsorbed, q_0 and C_0 are the initial concentrations in the solid and liquid phases respectively.

The overall mass transfer coefficient value of K_L in the liquid phase is determined from the Sherwood number representing the appropriate dimensionless number characterizing the transfer in the liquid film; it is similar to the Nusselt number in the case of heat transfer. The Sherwood number is given by the following equation [14].

$$Sh = \frac{K_L\, d_p}{D_m} \quad (11)$$

Where:
D_m is the molecular diffusion coefficient of the adsorbate (m^2/s).

The correlation [15] is widely applied to fixed bed reactors:

$$Sh = 2.0 + 0.6\, Sc^{\frac{1}{3}}\, Re^{\frac{1}{2}} \quad (12)$$

Where: Re and *Sc* are the Reynolds and Schmidt numbers respectively.
This equation shows that the Sherwood number tends to a limit value of 2.0 for low speeds.

III. Results and Discussion

We have performed several experiments in order to study the influence of different operating parameters on the Mn^{2+} adsorption kinetics on *"Pleurotus Mutilus"* biomass. The selected operating parameters were the initial concentration, the height of the fixed bed and the feed flow rate. Experimental breakthrough curves and those derived from the modeling process are shown below (fig. 3 and 4).

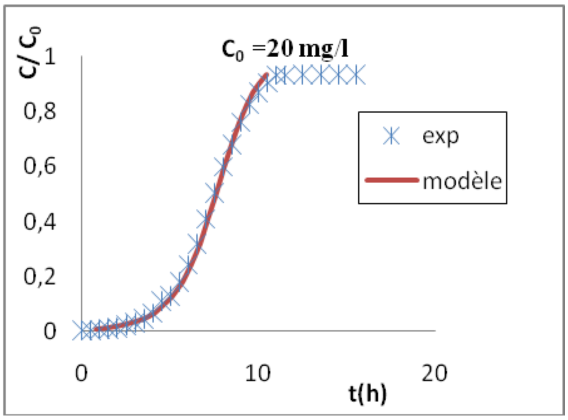

Figure 3. *Breakthrough curves in the adsorption of Mn^{2+} on "Pleurotus Mutilus" biomass.*
(T = 25 ° C, C_0 = 20 mg /L, Q = 20 mL/min, H = 10.6 cm).

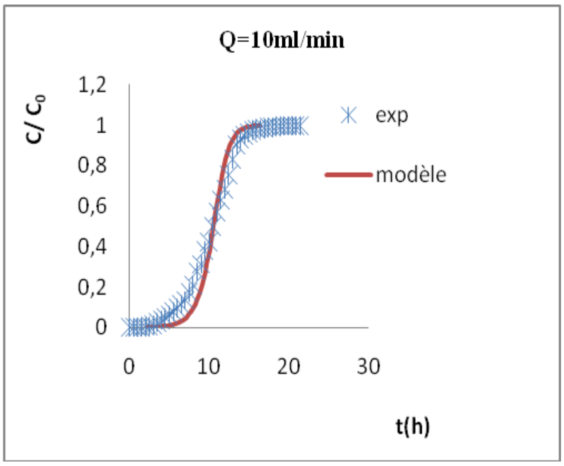

Figure 4. *Breakthrough curves in the adsorption of Mn^{2+} on "Pleurotus Mutilus" biomass.*
(T=25°C, C_0=50 mg/l, Q=10 ml/min, H=10,6 cm).

To check the influence of feed flow rate on the continuous adsorption kinetics, we have studied the evolution of the overall volumetric coefficient (K_{La}) estimated from empirical correlations according to the liquid superficial velocity and the evolution of $t_{1/2}$ as obtained from our model according to the inverse of the superficial liquid velocity.

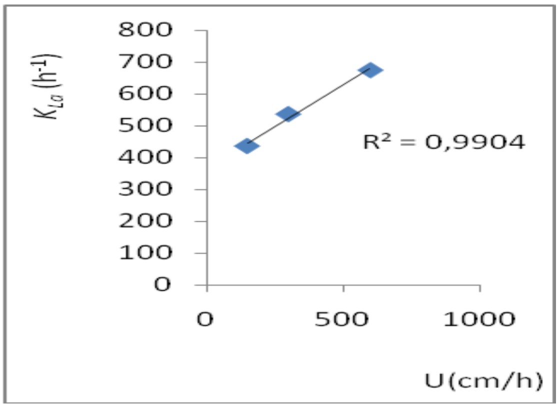

Figure 5. *Effect of superficial velocity on the overall volumetric coefficient (K_{La}) in the liquid phase.*

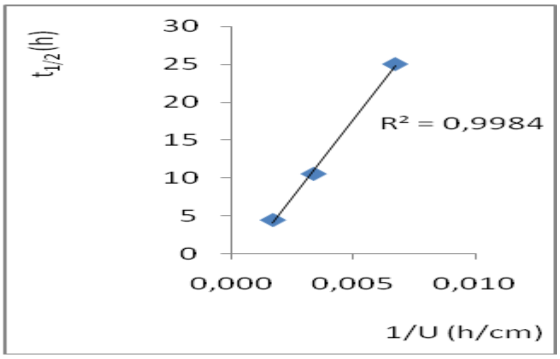

Figure 6. *Effect of superficial velocity on the half adsorption time $t_{1/2}$*

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According to these figures, we find a good linear fits between both $t_{1/2}$ and K_{La} and the liquid superficial velocity with correlation coefficients above 0.99 in both cases. Moreover, we note that the half adsorption decreases with increasing superficial velocity, whereas the overall volumetric coefficient (K_{La}) increases slightly, when the superficial velocity increases.

III.1. Validation of the mathematical model

Validation of the model consists to plot the curve f (x) versus time using experimental data

.

$$f(x) = \left[Ln2x - \frac{1}{n-1} Ln\frac{1-x^{n-1}}{1-2^{1-n}}\right] \quad (13)$$

Table 1 shows the selected operating conditions as well as the obtained experimental volumetric.

Table 1. Experimental conditions and results related to the adsorption of Mn^{2+} on "Pleurotus Mutilus" biomass in fixed bed column.

Experimental conditions	**Initial concentration effect**					**Flow rate effect**			**Bed height effect**		
Flow rate (ml/mn)	20	20	20	20	20	20	10	5	20	20	20
Initial concent. (mg/l)	50	40	30	20	10	50	50	50	50	50	50
Bed height (cm)	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6	10.6	13.6	16.6
Bed porosity	0.288	0.288	0.288	0.288	0.288	0.288	0.288	0.288	0.288	0.288	0.288
Temperature (K)	298	298	298	298	298	298	298	298	298	298	298
$t_{1/2}$ (h) exp.	4.71	5.58	6.58	7.67	11.20	4.70	9.14	24.71	4.70	8. 05	9,54
$t_{1/2}$ (h) calculated	4.40	5.40	6.40	7.60	11	4.40	10.50	25	4.40	8.00	10
$(K_La)_{exp}$ (h^{-1})	867.64	773.95	793.65	733.57	519.15	867.64	473.78	395.68	867.64	510.74	562.61
$(K_La)_{cal}$ (h^{-1})	674.82	674.82	674.82	674.82	674.82	674.82	537.37	437.4	674.82	674.82	674.82
% error	**22.22**	**12.81**	**14.97**	**8**	**29.99**	**22.22**	**13.42**	**10.54**	**22.22**	**32.13**	**19.94**

As can be seen, the model equation fits fairly well the evolution of the outlet concentration versus time in the mass transfer zone, whereas outside the mass transfer area domain, that is to say, in the zone of saturation ($C/C_o > 0.9$), we note a small difference between the values expressed by the model and experimental values, which may be due to the validation of empirical correlations used for estimating ($K_{L.}$ a) cal.

IV. Conclusion

The mathematical model enabled us to make the best description of the kinetics of continuous adsorption (for (C / C_0) <0.9) with a more or less significant shift in the saturation zone (for (C / C_0) > 0.9). Two important parameters ($t_{1/2}$) and (K_L.a) have been estimated by the model. The parameters are directly linked to the operating conditions namely the initial concentration, the height of the bed and the feed flow rate.

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