Simulation of breakthrough curves of selenium absorbed in two biomass filters using a dispersion and sorption model. Use for a hypothetical case

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A fixed bed study was carried out using the non-living biomasses *Eichhornia crassipes* and *Lemna minor* as a biosorbent for the removal of selenium from an aqueous solution. A 3D model, capable to represent the real system, was configured using the *Navier Stokes*, *Brinkman* and mass transport equations. Experimental and numerical results were compared to validate the model. Correlation factors up to R^2=0.95 were obtained in the validation model. Using the model, different systems were simulated obtaining relations between feed concentration and sorption capacity which increases when the inlet selenium concentration increases. A serial system of columns was configured with a flow rate of 2500 L/day and an inlet selenium concentration of 100 ppm capable of keeping an outlet concentration below 10 ppb during 27 days.

Keywords: Selenium; sorption capacity; inactive biomasses; breakthrough curves; modeling; simulation.

Un estudio de lecho fijo fue realizado utilizando biomasas no vivas de *Eichhornia crassipes* y *Lemna minor* como biosorbentes para remover selenio de soluciones acuosas. Un modelo 3D capaz de representar el sistema real fue configurado utilizando las ecuaciones de *Navier Stokes*, *Brinkman* y de transporte de masa. Resultados experimentales y numéricos fueron comparados para validar el modelo. Factores de correlación superiores a R^2=0.95 fueron obtenidos en la validación del modelo. Utilizando el modelo, diferentes sistemas fueron simulados obteniendo relaciones entre la concentración inicial y la capacidad de sorción, los cuales aumentan cuando la concentración de selenio alimentada aumenta. Un sistema serial de columnas fue configurado con un flujo de 2500 L/día, con una concentración inicial de selenio de 100 ppm, y capaz de mantener una concentración de salida debajo de 10 ppb durante 27 días.

Descriptores: Selenio; capacidad de sorción; biomasa no activa; curvas de rompimiento; modelado; simulación.

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1. Introduction

For many years, selenium has been a largely unrecognized pollutant, particularly in emerging nations, and has been overshadowed by issues involving contaminants such as industrial chemicals, heavy metals, pesticides, and air pollutants just to name a few [1].

Selenium is a natural trace element found in bedrock, but it is also introduced into the environment by anthropogenic activities, such as mining and combustion of fossil fuels. One of the primary human activities responsible for mobilizing selenium in the environment is the procurement, processing, and combustion of coal for electricity production [2-4].

An elevated exposure to this element can produce bad effects on human health such as dermatitis, bronchitis, pneumonia, fever, vomit, central nervous system and digestive system disorders, among others [5].

Its toxicity led the World Health Organization (WHO) and the EU to recommend a maximum selenium concentration in drinking water of 10 ppb, while the EPA sets a limit of 50 ppb [6]. In Mexico, up to now, there is no regulation for selenium in drinking water.

Dispersion plays a critical role in numerous processes and practical applications, including contaminant transport in groundwater, filtration, etc. Hydrodynamic dispersion in a porous medium occurs as a consequence of two different processes: i) molecular diffusion, which is originated from the random molecular motion of solute molecules, and ii) mechanical dispersion, which is caused by non-uniform velocities and the flow path distribution. Both processes cannot be separated in a flow regime [7,8]. To predict the breakthrough curves for sorption in fixed bed columns, most of them are models in 1D [9-13]. In this work a 3D model for the biosorption of selenium by *Eichhornia crassipes* (Ec) and *Lemna minor* (Lm) inactive biomasses were simulated using experimental results. The model was configured using the *Navier Stokes, Brinkman* and mass transport equations. With this model it is possible to obtain results for a 3D system which can be presented by images and animations by means of numerical simulation.

Therefore, the aim of this work is to evaluate the simulation as a tool that can represent the selenium sorption in Ec and Lm biomass comparing the experimental and simulated breakthrough curves.

The simplest form that represents the sorption phenomenon for a contaminant transport model, assumes that the time scale associated with the diffusion is smaller than timescales associated to macroscopic fluid transport processes. This assumes that the equilibrium prevails locally, so the change of the sorption concentration at each point reflects instantaneously by changing the solution concentration and the relationship between sorption concentration and solution concentration was calculated with a lineal isotherm due to the correlation between the experimental data and the model.

The breakthrough curves are used to illustrate the main features of the biosorption column dynamic function. These curves can be calculated using different equations [14]. This work presents a 3D model that is able to calculate the selenium transport as a function of time and obtain the breakthrough curves using the fluid dynamic equations, and a lineal isotherm.

2. Methodology

2.1. Experimental

2.1.1. Sampling and biomass preparation

The aquatic weeds (Ec and Lm) were collected from two different sampling sites. The Ec from the Lerma River at the sampling point named Mexico-Toluca highway and the Lm from the pond of Ixtlahuaca. Both sites are located in the Estado de México, México where its presence is abundant. The plants were kept in ice up to the laboratory, and then were washed with tap water and with a 0.01 M HCl solution to remove impurities.

After washing, they were exposed to solar light to remove excess humidity before drying for 24 h at 80°C in a stove. When dry, they were milled and meshed to obtain homogeneous particles of size 2 mm.

With this biomass, glass columns of different dimensions were packed manually, maintaining the mass amount in every column according to Table I.

The biomasses used in this work were characterized by Marin [20], the main physical and chemical characterizations are as follows:

The biomasses are color brown and have a porous structure with free spaces. The Ec biomass has a specific surface area of 1.3521 m^2/g with an active site density of 0.00904 sites/nm^2. The Lm biomass has a specific surface area of 0.6395 m^2/g with an active site density of 0.00832 sites/nm^2.

2.1.2. Chemical composition of the biomasses

The Ec biomass is composed of: Carbon 49.22%, Oxygen 39.67%, Potassium 3.21%, Calcium 3.12%, Chlorine 2.49%, Sodium 0.73%, Sulfur 0.45%, Aluminum 0.42%, Phosphorous 0.40%, Magnesium 0.29%, Silicon 0.14%.

The Lm biomass is composed of: Carbon 47.53%, Oxygen 40.49%, Calcium 3.45%, Iron 2.58%, Silicon 2.37%, Aluminum 1.61%, Manganese 1.14%, Phosphorous 1.02%, Potassium 0.99%, Sulfur 0.23%, Sodium 0.12%.

2.1.3. Selenium sorption and determination

The sorption of selenium by the biomass packed columns was performed by passing 300 mL of 0.02 ppm selenium solution using a peristaltic pump at a flow rate of 2 mL/min. At the outflow, 30 fractions of 10 mL were taken. Subsamples of these fractions were diluted with 6M HCL and treated in a microwave oven, to reduce Se (VI) to Se (IV) according to the methodology proposed by Brunori [15], for selenium determination. Finally, total selenium was determined with a Hydride Generator coupled with Atomic Absorption Spectrometry.

2.2. Modeling and validation

Considering that more than a few factors, such as, inlet concentration, temperature, adsorbent dose, etc. significantly affect the biosorption capabilities [16], the model was used to simulate the validated system with variations of the factors showed in Table II.

TABLE II. Factors

	Nomenclature
ρ	liquid phase density (kg/m^3)
k	porous media permeability (m/s)
v	velocity field in free flows (m/s)
ε, θ_s	porosity
p	pressure (Pa)
t	time (min)
μ, η	liquid phase viscosity (Pa*s)
v_0	velocity field in porous media (m/s)
D_h	hydrodynamic dispersion tensor
C, c	solute concentration in liquid phase (Kg/m^3)
q, C_{pi}	solute retained amount in the solid phase (mg/g)
ρ_b	average density of porous media(Kg/m^3)
C_in	inlet concentration (Kg/m^3)
k_p	constant of lineal isotherm
n	unitary vector normal to boundary
U	velocity by Eqs. 1 and 3

TABLE I. Characteristics of columns and packing.

Column	Length (cm)	Diameter (cm)	*Eichhornia* (g)	*Lemna* (g)	Bed height (cm)
1	22	2.0	7.1	6.9	19
2	15	1.5	1.7	1.5	11
3	10	1.0	0.7	0.5	8

2.2.1. Equations

In the last century, the *Navier Stokes* equations were frequently applied; they have been used by physicians and engineers in different fields of hydraulic, meteorology and aeronautic, and their validity has been well established. These are basic equations of physics [17] and can represent the flow in the columns [18], therefore we use them to calculate the free flow in unpacked zones.

The *Navier Stokes* (1) and continuity (2) equations are written in the form:

$$\rho \frac{\partial v}{\partial t} + (v + \nabla)v = -\nabla p + \mu \nabla^2 v + \rho g \qquad (1)$$

$$\frac{\partial \rho}{\partial t} = -(\nabla \cdot \rho v) \qquad (2)$$

The *Brinkman* equation describes the velocity of the fluid moving through a porous media using the kinetic potential of the fluid velocity. This equation extends the *Darcy's* law to describe kinetic energy dissipation by velocity as the *Navier Stokes* equation [18] and it was used to calculate the velocity field in the porous system.

The *Brinkman* (3) and the modified continuity (4) equations were used to calculate the velocity field, and are given by the equations.

$$-\nabla p - \frac{\mu}{k} v_0 + \mu \nabla^2 v_0 + \rho g = 0 \qquad (3)$$

$$\varepsilon \frac{\partial p}{\partial t} = (\nabla \cdot \rho v_0) \qquad (4)$$

In a dynamic system, the transport velocity controls the effective sorption velocity in the inner surfaces, more than the sorption reactions [19].

The general equation of mass transport calculates the mass transport through the media; nevertheless, it is necessary to obtain a second equation that estimates the relationship between the solution concentration and the sorbed amount.

Selenium transport and its sorption through the biomasses are calculated by solving the transport Eq. (5) and a lineal isotherm (6), respectively:

$$\varepsilon \frac{\partial c}{\partial t} + \rho_b \frac{\partial c_p}{\partial c} \frac{\partial c}{\partial t} + \nabla \cdot [-\varepsilon D_L \nabla c + vc] = 0 \qquad (5)$$

$$c_p = K_p c \qquad (6)$$

2.2.2. Solution

To solve the model, the following considerations and parameters were used:

1. The biomass was considered as a porous macroscopic media.

2. The selenium solution was considered as an incompressible fluid.

TABLE III. Parameters used in Eqs. (1) to (6), *[20]

	Parameters	Value
P	Density of aqueous solution	1000 Kg/m^3
ρ_b	Density of *Eichhornia crassipes**	570 Kg/m^3
ρ_b	Density of *Lemna minor**	109 Kg/m^3
ε	Porosity*	15 %
K	Permeability*	1.4e-3 m/s
Kp	Constant of lineal isotherm	0.017445 m^3/Kg
$\alpha1$	Longitudinal dispersivity	0.5 m
$\alpha2$	Transversal dispersivity	0.005 m
$\alpha3$	Transversal dispersivity	0.005 m
μ	Viscosity of aqueous solution	0.001 Pa*s
C_in	Inlet concentration	2e-5 Kg/m^3

3. The fluid velocity through the biomass packed columns was considered constant through time.

4. The sorption capacity at the initial time is equal for all the biomasses.

In Table III we show the parameters that characterize the biomasses and fluids and were used to solve the model.

The Eqs. (2) and (3) were solved with the following initial and boundary conditions: Every limit except the upper and lower limits are homogeneous: *Dirichlet* condition ($U = 0$). The upper limit is: *Dirichlet* condition $U = -U_0 n$. For the lower limit we used a pressure condition: $p = p_0$, where $p_0 = 0$.

The Eq. (5) was solved with the following initial and boundary conditions:

The upper and lower limits are *Dirichlet* conditions:

$$n(-\theta_s D_L \nabla_c + uc) = U * C_{in}$$

and

$$-n(-\theta_s D_L \nabla_c + uc) = U * c,$$

respectively.

The other limits are considered as a wall with the homogeneous *Dirichlet* condition:

$$-n(-\theta_s D_L \nabla_c + uc) = 0.$$

The solution of the model was obtained with the COMSOL Multiphysics software, version 3.5a. This software uses the finite element method to solve the partial differential equations. The final mesh elements are constituted by 161,764 elements.

2.2.3. Validation

In order to validate the established model, numerical and experimental results were compared to obtain a correlation and to analyze if the model can represent a real system. Every case in Table I was compared.

TABLE IV. Dimensions of simulated columns

Column	Diameter (cm)	Length (cm)
A	16	50
B	16	70
C	16	150
D	12	150
E	10	150

2.3. Simulation

a) Different feed inlet selenium concentrations.

Using the same geometry and dimensions of the laboratory's system, were simulated five cases with different inlet concentrations (0.025, 0.05, 0.1, 0.15, 0.2 ppm), keeping the same flow and initial conditions. Thereafter, the sorption capacity was calculated using the numerical results.

b) Columns with different dimensions.

Using the same geometry but different dimensions, columns with the dimensions in Table IV were simulated with an inlet volume of 250 L/day, keeping similar boundary and initial conditions. Subsequently, the sorption percent was calculated using the numerical results.

c) A hypothetical case

While most available biomasses have the capability to sequester heavy metals from solutions, not all of them fit as alternative adsorbents in real wastewater treatment plants. Several vital characteristics are available and need to be listed to render the materials valuable enough as an industrial sorbent [16]: Such characteristics are:

1. High adsorption capacity

2. Available in large quantities at one location

3. Low economic value and less useful in alternative products

4. Attached metals can be easily recovered while biosorbent is reusable

Based on the above and the results of the simulation of columns with different dimensions, a hypothetical case was simulated using the column with the best sorption percentage.

This case consists of a serial system of four columns type C in Table IV; it was fed with 250 L/day and an inlet selenium concentration of 100 mg/L, its objective is to keep a discharge concentration below to the allowable limits proposed by the WHO (C< 10 ppb) [21].

3. Results and discussion

3.1. Dispersion and sorption

The results of the simulation are presented in Fig. 1 and 2.
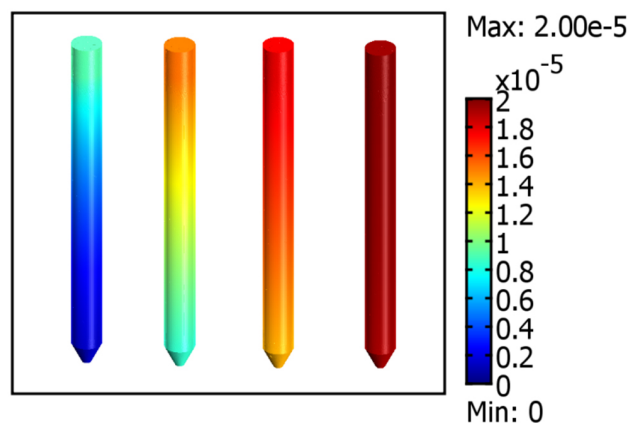

FIGURE 1. Dispersion of selenium through the column 1 in Table I for 15, 50, 80, and 160 minutes respectively.
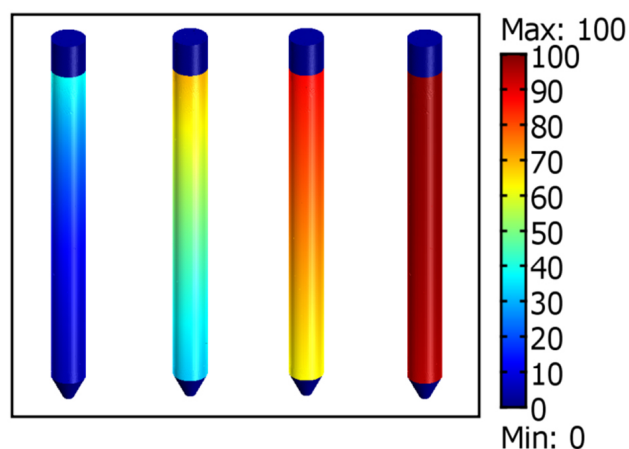

FIGURE 2. Sorption percent of selenium through the column 1 in Table I for 15, 50, 80, and 160 minutes respectively.

In Fig. 1 we show the dispersion of selenium through the column at different times. The selenium concentration in the solution changes through the column and its value increases with time. For the final time (160 min), the selenium concentration in the solution through the column and the inlet concentration are equal. This represents that the selenium concentration in the solution doesn't change by sorption effects after the final time.

In Fig. 2 we show the selenium sorption percentage in the biomass at different times. It can be also observed how the selenium sorption occurs only in the biomass. In Fig. 2, the change occurs only in the packed zone, showing the selenium sorption values as percentages in relation to the maximum selenium sorption capacity.

When the sorption percent is 100, the column is saturated. At this time, the column is saturated and the inlet concentration is the same to the outlet concentration because the biomass does not sorb anymore. From these results, the outlet concentration was taken and compared with the experimental results.
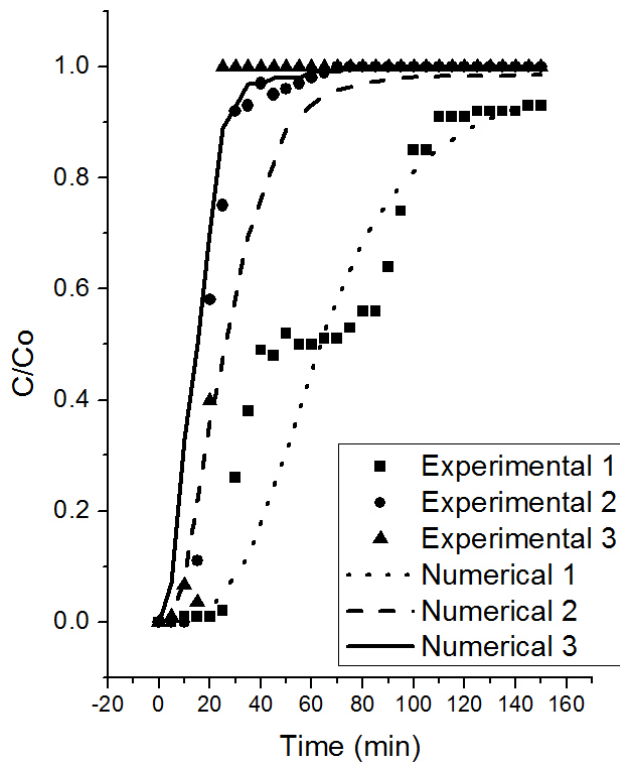
FIGURE 3. Comparison of experimental and numerical break-through curves of columns from Table I and packed with *Eichhornia crassipes*. Column 1■, column 2●, column 3▲.
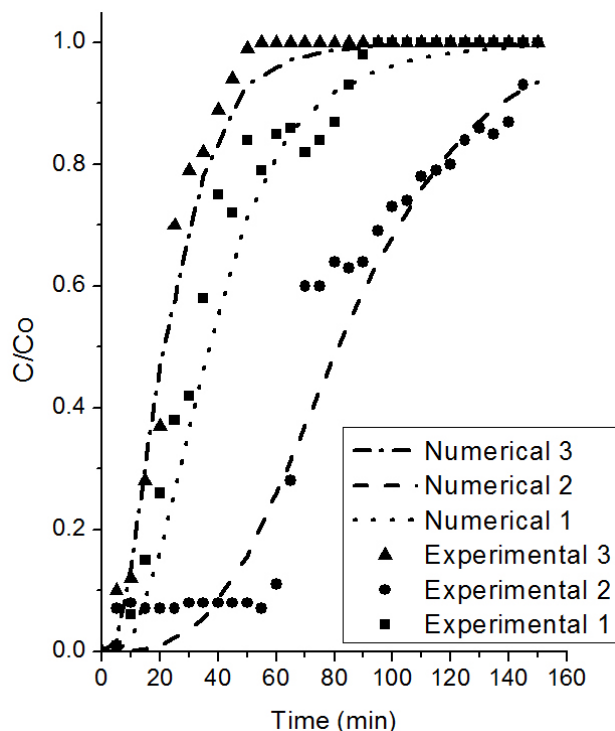

FIGURE 4. Comparison of experimental and numerical break-through curves of columns from Table I and packed with *Lemna minor*. Column 1■, column 2●, column 3▲.

3.2. Validation

In Figs. 3 and 4 we present the breakthrough curves obtained using the numerical results and the experimental data for the biomass packed columns 1, 2 and 3 of the Table I.

The correlation factor (R^2) between the experimental data and the numerical results in Fig. 3 are 0.9041, 0.8581, and 0.9129 for column 1, 2 and 3, respectively. The correlation factor (R^2) between the experimental data and the numerical results in Fig. 4 are 0.9770, 0.9508 and 0.9825 for column 1, 2 and 3, respectively.

Hasan [22] reported correlations of $R^2 = 0.936$ and $R^2 = 0.968$ using the Thomas and Yoon-Nelson model respectively by selenium sorption in agro-industrial waste.

Akzu [14] reported correlations to biosorption of phenol by immobilized activated sludge in a continuous packed bed using several models, obtaining a $R^2 = 0.989$ with the Thomas model, $R^2 = 0.987$ with the Yoon Nelson model.

According to the good correlations, the model can be used to predict the breakthrough curves of selenium sorption systems with different dimensions and porous media.

3.3. Concentration

When the model was validated with the experimental results, it was then used to obtain the relationship between sorption capacity and inlet concentration, using the breakthrough curves made from the numerical results of the system and that presented the best correlation factor.

The absorption capacity was calculated with the following equations which were used by Akzu [14] and Hasan [22]:

$$q_{\text{total}} = QA = Q \int_{t=0}^{t=t_{\text{total}}} C_{ad} dt \qquad (7)$$

$$C_{ad} = C_o - C \qquad (8)$$

The relationship between sorption capacity and inlet concentration is shown in Fig. 5.

The results in Fig. 5 show that the effect of the inlet concentration on the sorption capacity is positive and directly proportional. In other words, if the inlet concentration increases, the sorption capacity also increases.

Hasan [22] obtained similar selenium sorption results for the agro-industrial waste 'wheat bran' where a lower inlet concentration gave a lower sorption capacity. Hul [23] found that the sorption capacity is dependent of the inlet concentration.

3.4. Simulations of columns with different dimensions

Columns in Table IV were simulated and with their breakthrough curves the holding percent in each one was calculated with the Eq. (7), (8), (9), and (10).
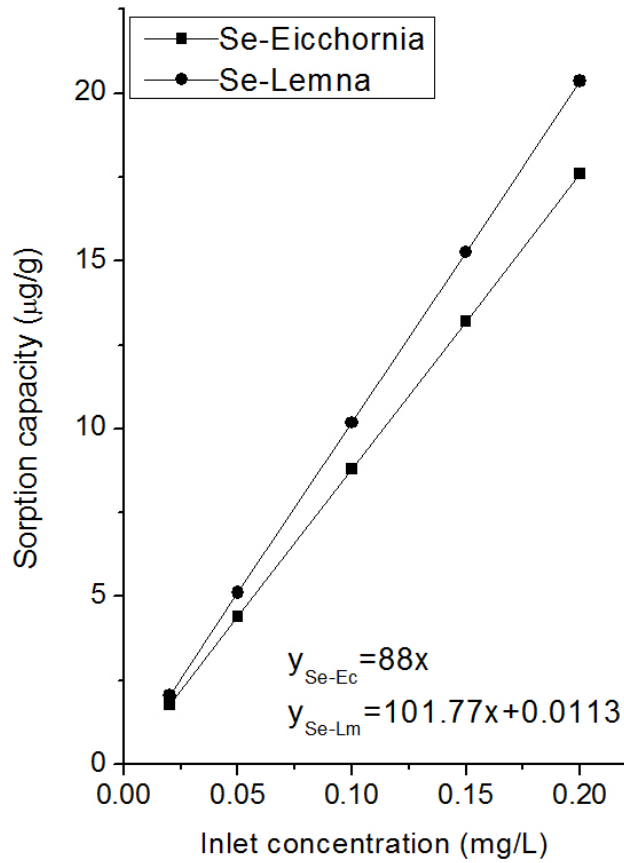
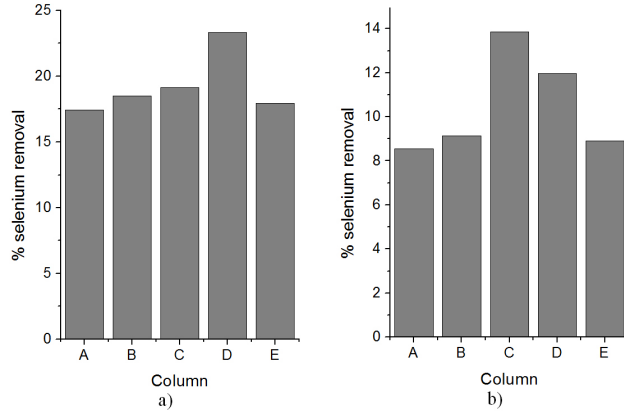FIGURE 5. Relation between inlet concentration (mg/L) and sorption capacity (μg/g).

FIGURE 7. Frontal view of the serial system in the hypothetical case.

FIGURE 6. Selenium removal percent in biomass packed columns of a) *Eicchornia crassipes* and b) *Lemna minor*.

$$m_{\text{total}} = \frac{c_0 Q t_{\text{total}}}{1000} \qquad (9)$$

$$\%\text{removal} = \frac{q_{\text{total}}}{m_{\text{total}}} * 100 \qquad (10)$$

Percent removals of selenium in biomass packed columns are presented in Fig. 6.

As expected, the percent of selenium removal increases with an increment in the bed height, but the results are different when the diameter changes.
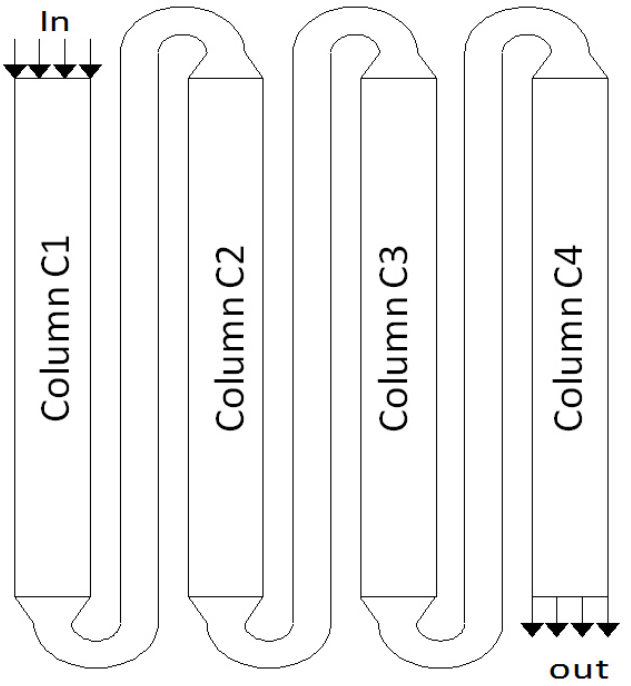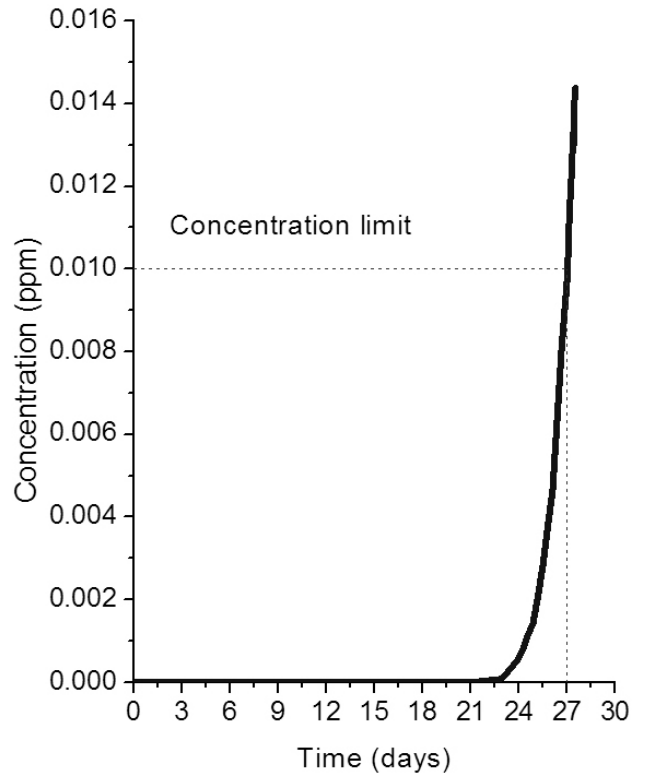

FIGURE 8. Outlet concentration of the system in the hypothetical case.

For columns packed with *Lemna mi*nor, the removal percent increases with an increment in the diameter, but for columns packed with *Eicchornia crassipes* the highest removal percent value is in the column with a diameter of 12 cm. This is because of the existence of an optimal column diameter value between 16 and 10 cm to remove selenium, associated to the intrinsic characteristics of the material. This can be attributed to the fact that when there was an increase in bed height, the axial dispersion decreased the mass transfer and as a result, the diffusion of the selenium ions into the sorbent increased. Thus, the solute had enough time to be sorbed by the biomass. Similar results were reported by Hasan [22] where was also observed that the sorption capacity as well as removal percentage efficiency of wheat bran for both Se(IV) and Se(VI) increased with the increase in bed height.

The D packed column of *Eicchornia crassipes* in Table IV presents the best removal percent of selenium, therefore, this was considered for the simulation of the hypothetical case.

3.5. Hypothetical case

In Fig. 8 is shown the outlet concentration as a function of time, resulting from the simulation of the proposed case. In the figure we mark the drinking water limit for selenium, as proposed by the WHO [21]. The results indicate that with this configuration the system can achieve an outlet concentration below the limit of about 27 days.

4. Conclusions

The biosorption of selenium from an aqueous solution on non-living biomasses of Ec and Lm was investigated at dynamic conditions for biomass packed columns. A 3D model was configured to represent the system of the biomass packed column and we obtained breakthrough curves from the simulations.

The results showed that the model can represent the sorption system with correlations up to $R^2 = 0.98$.

The increase in initial selenium concentration resulted in higher uptakes. The increase in the sorption capacity as a function of the inlet concentration can be representing by $C_p = 0.88C_i$ and $C_p = 101.77C_i + 0.0113$ for a Se-Ec and a Se-Lm system, respectively.

According to the results, the selenium sorption depends on the inlet concentration and the column dimensions.

A serial system of four biomass packed columns was configured and from the simulations it was possible to calculate the outlet concentration and to compare with the limits recommended by the WHO [21].

A serial system of four columns packed with *Eichhornia crassipes* and 16 cm radio and 150 cm length is capable of keeping an outlet concentration below 10 ppb during 27 days with a selenium inlet concentration of 100 ppm.

Acknowledgements

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