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Experimental and Numerical Comparison of Dispersion and Sorption of Cr(VI) on Maize Cane Biomass

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Abstract. Computational and theoretical modelling has become an important tool for the characterization, development, and validation of packed beds. Relevant breakthrough curves would provide much valuable information on designing a fixed bed adsorption process in field applications. In this study, the hydrodynamic properties involved in the Navier–Stokes flow equation, such as velocity, pressure, and permeability, in a packed bed were investigated. Experiments in natural porous media such as maize cane biomass for determining the sorption of Cr(VI) are compared with numerical simulations. The relevant ordinary partial equations were solved in COMSOL Multiphysics Software friendly and efficiently. The close agreement between the experimental and numerical results suggests that the theoretical model of advection-hydrodynamic dispersion can be used to model the transport of Cr(VI) in unsaturated porous media composed of maize cane biomass.
Keywords: Numerical simulation; hydrodynamic dispersion; sorption; porous media.

Resumen. El modelado computacional y teórico se ha convertido en una herramienta importante para la caracterización, desarrollo y validación de lechos empacados. Las curvas de avance relevantes proporcionarían información muy valiosa sobre el diseño de un proceso de adsorción de lecho fijo en aplicaciones de campo. En este estudio, se investigaron las propiedades hidrodinámicas involucradas en la ecuación de flujo de Navier-Stokes, como la velocidad, la presión y la permeabilidad, en un lecho empacado. Los experimentos en medios porosos naturales como la biomasa de caña de maíz para determinar la sorción de Cr(VI) se comparan con simulaciones numéricas. Las ecuaciones parciales ordinarias relevantes se resolvieron en COMSOL Multiphysics Software de manera amigable y eficiente. La estrecha concordancia entre los resultados experimentales y numéricos sugiere que el modelo teórico de dispersión hidrodinámica por advección puede usarse para modelar el transporte de Cr(VI) en medios porosos no saturados compuesta por biomasa de caña de maíz.
Palabras clave: Simulación numérica; dispersión hidrodinámica; sorción; medios porosos.

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Introduction

Heavy metal ions ubiquitous in the environment but their increased levels in water are consequences of man–made activities. One of the most toxic metal ions in our environment that has raised global concern is chromium [1].

Chromium contamination of soil and groundwater is a significant problem worldwide and is becoming a serious threat to our environment. The predominant forms of chromium in nature are Cr(III) (trivalent chromium) and Cr(VI) (hexavalent chromium) as chromate ion, which have different physicochemical characteristics including mobility, toxicity and bioavailability [2]. The Cr(VI) is 10 – 100 times more toxic that the Cr(III) when both are introduced by oral ingestion [3]. The World Health Organization (WHO) reported that chromium is a priority pollutant and proposed a provisional guideline value of 0.05 mg L^{-1} for total chromium, mainly soluble Cr(VI), in drinking water [4,5].

A variety of methods and materials have been developed for the Cr(VI) removal including precipitation, membrane separation, or solvent extraction, neutralization and adsorption [6,7]. Among these techniques, biosorption using agricultural waste such as maize cane, has gained considerable attention because of high efficiency, low cost, more availability, and ease of handling [1,8]. These materials have been reported to possess good adsorption capability for Cr(VI) from aqueous system. The use of these waste material as adsorbent also reduces the cost of the Cr(VI) treatment process and makes the application of adsorption technology. The physicochemical and surface characteristics of this biomass and sorption properties, that make it a candidate to absorb Cr(VI) are reported by Marin-Allende et al., 2017 [9].

The computational fluid dynamics (CFD) is a useful tool for the modelling of flow and contaminant transport (hydrodynamics system). The main advantage of computational modelling may be that different physical domains can be coupled and solved efficiently. In fixed beds column, in general, several modes of transport and processes take place simultaneously. For instance, fluid flow, permeation, advection, hydrodynamic dispersion, diffusion, and the chemical reactions involved in adsorption. The CFD simulations can be applied by manually written codes or commercial software programs. Some commercial packages, such as COMSOL Multiphysics (Femlab, formerly COMSOL [10], Inc., Sweden) has become popular for various physics and engineering applications, geoenvironmental phenomena, or multiphysics in last decades since commercial packages are designed to be user friendly. The purpose of these programs is to allow researchers who may not be well versed in fluid dynamics to successfully model the channel fluid flow phenomena in an interdisciplinary field such as column adsorption [11].

The main objective in this research is to evaluate the behaviour of the Cr(VI) sorption in natural porous media such as maize cane biomass through the experimental and simulated breakthrough curves.

Experimental

The work model consists of a cylindrical container in three dimensions (3D), using porous biomass of maize cane as a fixed bed column. The column of internal diameter 0.5 cm and length 15 cm with a cross-sectional area of 0.78 cm^2, is installed in a vertical position. In order to obtain homogeneous porous packaging, the column was placed in a vertical position. The filling of the column with material granular sorbent (biomass), is poured into the column partially by layers of 3 cm, by adding water to prevent the formation of air bubbles and lightly shaking the column to ensure a good compaction. Tests are conducted under a continuous flux of dissolved solute [40 mg L^{-1} of Cr(VI) solution] as an influent for the sorption studies. The flow is described by the average linear velocity or seepage velocity (v=q/n), which transports the dissolved solute by advection-dispersion. The solute continuously moves down the column at seepage velocity v. Solute samples were collected at the outlet of the column in glass tubes.

Numerical Solution using COMSOL software

COMSOL software (COMSOL [10] Multiphysics program, Version 3.5ª) was used as a numerical software package to solving sets of ordinary and/or partial differential equations for modelling predicting and

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optimizing the performance of water treatment process, adsorption, operations, flow behaviour, etc. The numerical solution by COMSOL software is performed based on the finite element method. The software runs the finite elements analysis together using adaptive meshing refinement and error control by a variety of numerical solvers.

The simulation is performed assuming the biomass is as porous and permeable material, and saturated, with a high surface area for capture of retention of Cr(VI) as polluting potential. The velocity field into the cylindrical container was obtained by solving the Navier Stokes and continuity equations. The speed of the porous media was obtained by solving the Brinkman and continuity equations. The dispersion, convection and sorption of biomass were obtained by solving the transport equation. The equations were solved by the finite element method. The COMSOL Multiphysics post processing was used to analyze the simulation results. The analysis is performed by the generation of images of the process and its animation.

Generating of the geometry

The experimental device (Fig. 1) consists of the following elements:

The geometry is based on the experimental device used in the laboratory, in which the biomass is packed in a cylindrical container with the dimensions indicates in Fig. 1.

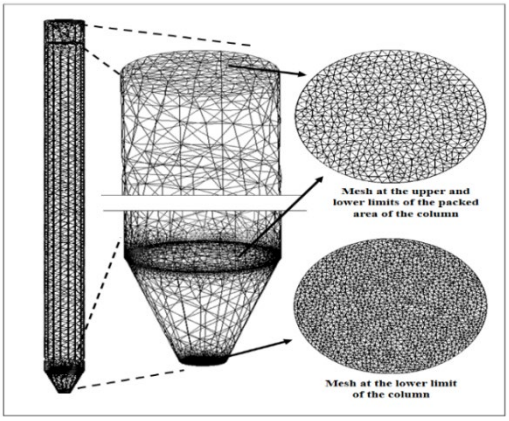

Fig. 1. Mesh for the simulation.

The system is divided into three zones; Zone 1 is the feed injection zone, in this area there is no biomass and the feed flow is constant. In zone 2 the biomass is present, in this zone the interaction between the biomass and Cr(VI) solution occurs, this is considered a saturated porous system. In zone 3, there is no biomass here; it is when the Cr(VI) concentration value in the eluates is measured, to determine the concentrations of Cr(VI) sorbed in the biomass, Fig. 2.

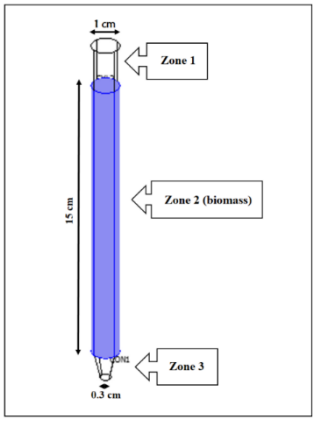

Fig. 2. Geometry, dimensions, and zone subdomains used for the simulation.

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The flow in the interstitial access from the biomass is calculated by solving the equation governing the water flow and continuity which is written in the form:

$$\rho \frac{\boldsymbol{Dv}}{\boldsymbol{D}t} = -\boldsymbol{\nabla} p + \mu \boldsymbol{\nabla}^2 \boldsymbol{v} + \rho \mathbf{g} \tag{1}$$

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

where ρ in the density [M L^{-3}], v is the velocity [L t^{-1}], t is the time [t], p is the pressure [M $L^{-1}t^{-2}$], μ is the viscosity [M $L^{-1}t^{-1}$] and g is the gravity [L t^{-2}]. The equation used for the free flow in this simulation is obtained from equation (1), which is written as follows:

$$\left(-\boldsymbol{\nabla} \cdot \mu(\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T)\right) + \rho \boldsymbol{v} \cdot \boldsymbol{\nabla v} + \boldsymbol{\nabla} p = 0 \tag{3}$$

where the density is considered constant and in the steady state equation the time dependent terms are eliminated [12]. For the flow through the biomass (porous system), the Brinkman and the modified continuity equations for the porous systems are:

$$-\boldsymbol{\nabla} p - \frac{\mu}{k}\boldsymbol{v} + \mu \boldsymbol{\nabla}^2 \boldsymbol{v} + \rho \mathbf{g} = 0 \tag{4}$$

$$\varepsilon \frac{\partial p}{\partial t} = -(\boldsymbol{\nabla} \cdot \rho \boldsymbol{v}) \tag{5}$$

where k is the permeability [L t^{-1}], ε is the porosity (the ratio between porous volume and total container volume). The equation used for the porous media flow in this simulation is obtained from equation 4, which is written as follows:

$$\left(-\boldsymbol{\nabla} \cdot \frac{\mu}{\varepsilon}(\boldsymbol{\nabla v} + (\boldsymbol{\nabla v})^T)\right) - \left(\frac{\mu}{k}\boldsymbol{v} + \boldsymbol{\nabla} p\right) = 0 \tag{6}$$

where the density is considered constant and for steady state equation the time dependent terms has been eliminated. The steady state equations (2, 3, 5 and 6) are solved according with the experimental methodology. Cr(VI) transport and its sorption through the biomass are calculated by solving the transport equations. The Freundlich isotherm solution is written as follow:

$$\varepsilon \frac{\partial \mathrm{c}}{\partial t} + \rho_b \frac{\partial c_p}{\partial c}\frac{\partial c}{\partial t} + \boldsymbol{\nabla} \cdot [-\varepsilon D_L \boldsymbol{\nabla} \mathrm{c} + \boldsymbol{v}\mathrm{c}] = \mathrm{R_L} + \mathrm{R_p} + \mathrm{S_c} \tag{7}$$

$$c_p = K_F c^N \quad , \quad \frac{\partial c_p}{\partial c} = N K_F c^{N-1} \tag{8}$$

where ε is the porosity, c is the solute concentration [M L^{-3}], t is the time [t], ρ_b is the density of the porous medium [M L^{-3}], cp is the concentration of the solute sorbed in the biomass (the mass amount of solute sorbed per unit of biomass), v is the velocity [L t^{-1}], D_L is the hydrodynamic dispersion tensor, KF and N are constants of Freunlich isotherms (COMSOL 2008). The equation used for flow and transport in porous medium in this simulation is obtained from equation (7), which is written as follows:

$$\varepsilon \frac{\partial \mathrm{c}}{\partial t} + \rho_b \frac{\partial c_p}{\partial c}\frac{\partial c}{\partial t} + \boldsymbol{\nabla} \cdot [-\varepsilon D_L \boldsymbol{\nabla} \mathrm{c} + \boldsymbol{v}\mathrm{c}] = 0 \tag{9}$$

where the reaction terms are removed if there are no chemical reaction.

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Constants

The values of the constants were obtained according with the results from the physicochemical characterization of the biomass and the interaction between the Cr(VI) as a solute-biomass to determine the sorption rate, Table 1.

Table 1. Values of the constants obtained by experimental procedures [5].

Constants		Value
ρ_s	Biomass density	0.072 kg m^{-3}
ε	Porosity	0.76%
k_s	Permeability	1.4e^{-4} m s^{-1}
K_F	Freundlich constant	0.907 mg g^{-1}
N	Freundlich isotherms exponent	2.015
α1	Longitudinal dispersivity	0.03 m
α2	x Transversal dispersivity	0.005 m
α3	y Transversal dispersivity	0.005 m
C_{in}	Feed concentration	0.04 kg m^{-3}
V_{max}	Feed velocity	0.45 mL min^{-1}

Definition of initial and boundary conditions

The initial and boundary conditions are the follow: for t = 0, c = 0 and cp=0 and the boundary conditions are shown in Fig. 3, where r=sqrt(x^2+y^2+z^2), R is the radius of the cylinder, Fig. 2, v is the velocity, n is a unit vector normal to the plane, N is the total flux of Cr(VI), V_{max} is the feed velocity (Table 1), Uchns is the velocity calculated by the Navier Stokes equation, Cin is the initial concentration of Cr(VI) (Table 1), p is the pressure, c is the Cr(VI) concentration in the solution, cp is the solute concentration sorbed in the biomass, z is the coordinate in the xyz plane and t is the time.

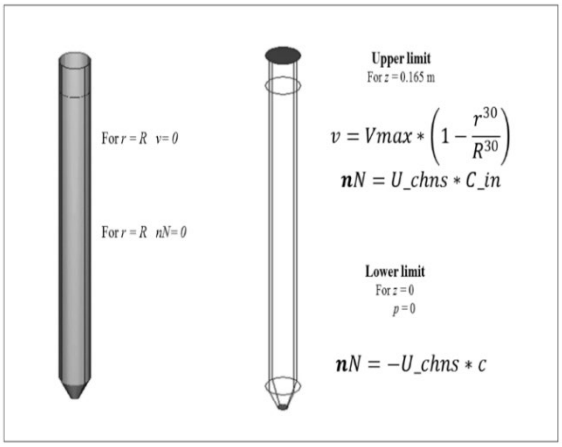

Fig. 3. Initial and boundary conditions for the Cr(VI) sorption simulation.

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Mesh and running solution

The quality of the mesh plays a significant role to achieve accurate results without unnecessary computational demand. The cell shape and cell size have an important effect on the accuracy and stability of the numerical solution. The very fine meshes can obtain more accurate results of solution but will cost higher computer memory and central processing unit time [11]. The mesh elements are prism and we use for the Navier-Stokes equation a total of 34,393 elements (Fig. 1). The finite element method is one of the most popular mathematical techniques used in decades, and it is employed in popular modeling software is commonly used to solve partial differential equations in systems possessing complex geometries [13].

Results and discussion

The Reynolds number value is 23, which were obtained by solving the fluid flow equations. The values indicate that the flow is in the laminar regime, as also reported by Basak, 1977 [14]. In Fig. 4 we present the velocity field at the entrance of the system and in the region occupied by the biomass that is represented as a porous system. The velocity field is deviates when the Cr(VI) solution gets in contact with the biomass because the porosity change and the permeability is modified.

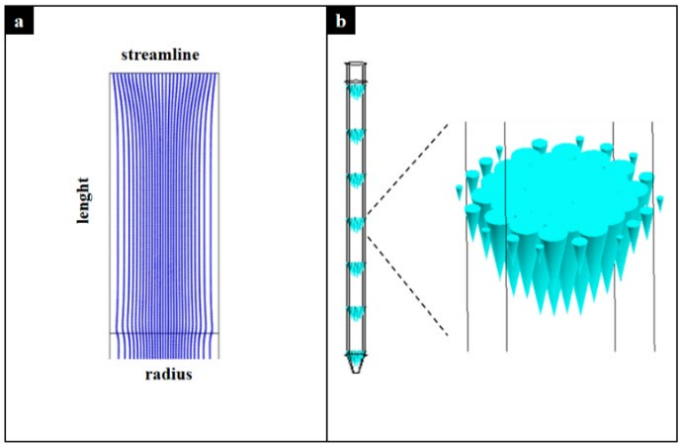

Fig. 4. Flow lines simulation on column.

The input and output speed is shown in Fig. 5. The results indicate that the velocity is greater in the center and zero on the walls. In the first case (Fig. 5**(a)**), the velocity field is uniform; the Cr(VI) solution is injected at a constant rate around the entire surface.

Fig. 5**(b)** shows speed values larger than the maximum speed entry value due to the decrease in the cross-sectional area, as well as a more uniform profile. The multiple core measurement at the outlet column permitted an estimation of the velocity fluctuations. Due to different steady state infiltration rates, the water content distribution in the non-living biomass column varied with depth. In the central region, the velocity is greater than near the walls, this behaviour is correlated with Fig. 4 that indicates that in the core the velocity is greater and so the Cr(VI) sorption is probably lower due of the lower Cr(VI)-biomass interaction time. On the other hands, on the walls, the biomass has more interaction time with the solute, because the velocity of interaction is lower, or the interstitial water is saturating the pores.

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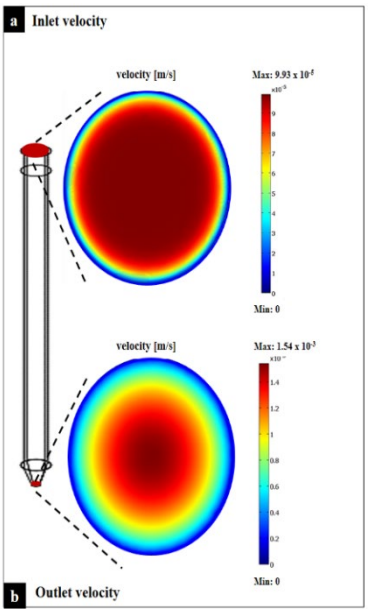

Fig. 5. Input and output velocity field.

The velocity field of the porous biomass is shows in Fig. 6. These results indicate that the pores of the biomass were saturated by the Cr(VI) solution, and then the fluid velocity diminishes through the biomass column, causing that the outlet velocity also decreases. Thus, higher values are obtained at the fluid outlet due of the pressure difference between the input and output of the porous medium.

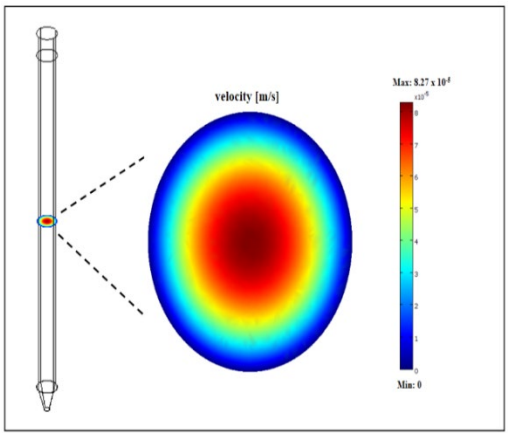

Fig. 6. Cr(VI) solution; velocities in biomass.

Solving the transport equation using the velocity field obtained previously, it was simulated the Cr(VI) transport system and its sorption onto maize cane biomass. Fig. 7 shows the biomass saturation time evolution during the Cr(VI) solution transport through the system at 5, 30, 60, 90 and 125 minutes. In the same Fig. 7 it was observed that the Cr(VI) concentration is not present at the bottom of the column, but it increases when it is transporting through the maize cane biomass. At 60 minutes is observed the Cr(VI) transport, the Cr(VI) is sorbed on the biomass, in the upper of the biomass column; the system is getting saturated depending upon the

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Cr(VI) concentration transport. The Cr(VI) concentration in the solution increases because the biomass is reaching its Cr(VI) saturation or the Cr(VI) concentration in the solution decreases through the biomass because it is sorbed by the biomass. Finally, at 125 minutes the biomass reaches its Cr(VI) saturation, the concentration is constant; the biomass is saturated and already does not sorbs Cr(VI) from solution.

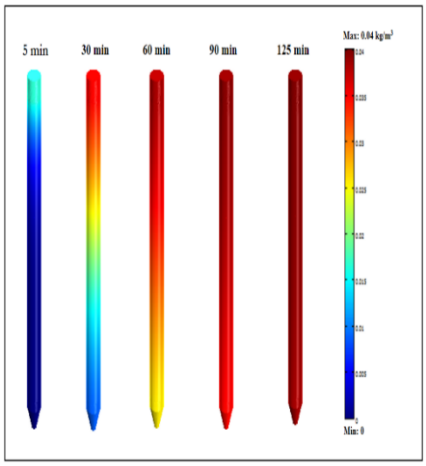

Fig. 7. Transport of the chromium (VI) solution in biomass, through the time, (kg m^{-3}).

Various mathematical models have been developed to predict the dynamic behaviour of sorption column studies [15, 16]. In this case, the experimental and simulated breakthrough curves for Cr(VI) sorption are shown in Fig. 8. Comparison between experimental and simulated breakthrough curves showed good agreement of predicted software COMSOL values, which indicates that the chosen models are suitable for explain the Cr(VI) sorption during the interaction between the biomass and the Cr(VI) solution.

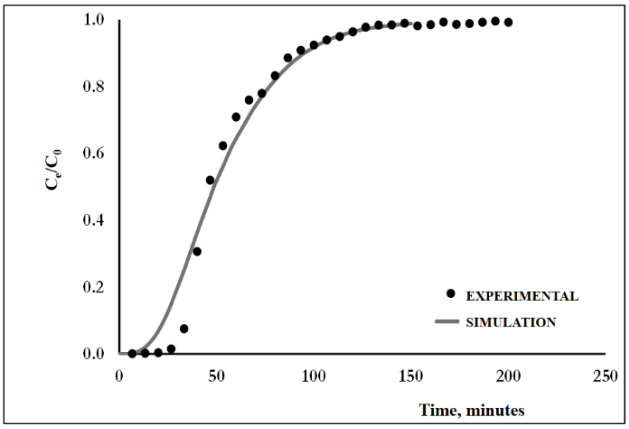

Fig. 8. Experimental and predicted breakthrough curves of Cr(VI) sorption in a fixed column of biomass (*maize cane*) in vertical flux.

According to breakthrough curves obtained with maize cane biomass, the point of rupture and saturation in the vertical flow for experimental and simulated system are given in Table 2. This indicates a greater capacity of sorption in vertical flow and that the COMSOL simulation is able to represent the dynamic conditions observed in a biomass-column test for Cr(VI).

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Table 2. Breakthrough and saturation points of process sorption in maize cane biomass.

Biomass	Process	Procedure	Breakthrough point, minutes	Saturation point, minutes
Maize cane	Sorption	Experimental	12	125
		Simulated	27	125

Conclusions

Model the transport of Cr(VI) in unsaturated porous media composed of maize cane biomass enhances our understanding of the fundamental physical behaviour of hydrodynamic flows and mass transfer in the channels of packed beds. Performing computational modelling reduces the time needed to design and develop adsorption systems because many physical parameters can be tested theoretically prior to the device fabrication. Data obtained from simulations can be used to validate experimental data, thereby providing a theoretical explanation of the performance of a system. Cr(VI) concentration measurements as obtained from experiments during the solute-biomass interaction were used for the simulation of the hydrodynamic dispersion. COMSOL software was proved to be an effective numerical tool to describe the transport and adsorption phenomena of the Cr(VI) adsorption in fixed bed column. Good agreement between the experimental results and the predicted theoretical breakthrough curves was observed. The computational fluid dynamics prediction can be used for analysing the experimental study of the Cr(VI) sorption process in packed bed.

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