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Modelado Estadístico de Adsorción de Metales Pesados en una Columna de Lecho Fijo

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Resumen

Las columnas de adsorción de lecho fijo son el método más aplicado a nivel industrial en el proceso de tratamiento de aguas residuales contaminadas. En este trabajo se propone un modelo matemático que describe las curvas ruptura del proceso de adsorción. El modelo fue aplicado para describir la adsorción del metal Cr (VI), altamente toxico, sobre el biopolímero quitosano, extraído de descartes pesqueros. Para ello se obtuvieron datos experimentales utilizando una columna a escala, a diferentes caudales y alturas del lecho, obteniendo en cada caso la curva de ruptura correspondiente y el tiempo de ruptura tb (tiempo de saturación de la columna). En base a estos datos se desarrolló un modelo matemático probabilístico con un enfoque bayesiano utilizando el programa R. El modelo propuesto representó una buena descripción general del proceso de adsorción y en todos los casos el tb experimental se encontró próximo o dentro del intervalo de credibilidad del modelo. Asimismo, estableciendo la concentración inicial del adsorbato y la velocidad de flujo, los parámetros del modelo obtenidos, se podrían usar para escalar la curva y el tiempo de ruptura para diferentes alturas del lecho. Por lo expuesto el modelo representa una opción para el diseño de columnas de adsorción de contaminantes.

Statistical Modelling of Fixed-Bed Columns for Heavy Metal Adsorption

Abstract

Continuous Fixed-Bed Column Adsorption for wastewater treatment provides the most practical application for the industry. The objective of this work was to develop a statistical model capable of simulating the dynamic behavior of the fixed-bed adsorption. The model was applied to describe adsorption mechanism of Cr(VI), one of the most toxic metals in water, onto chitosan flakes, obtained from the waste of crustacean industry. For the design of a column adsorption system, the basic information is the determination of the breakthrough curve and the breakthrough point time tb (Saturation time of the column). The experimental data were obtained using a glass column in which the chitosan particles were introduced. The continuous passage of Cr(VI) was carried out at different initial concentrations and bed heights. Then, the model projections were compared with experimental data in a Bayesian framework, programmed in software R. The proposed model represented a good description of the column adsorption. In all cases, the experimental tb was into or near to credibility interval. According to the model, setting initial concentration and flow velocity, the model parameters obtained can be used to scale up the breakthrough curve and the breakthrough time for different bed heights. Therefore, the model represents an option for the design of adsorption columns for wastewater treatment.

INTRODUCTION

Water pollution by heavy metals is considered one of the major environmental problem due to the adverse effects of these contaminants on ecosystems and on human health. The adsorption method is the most used for its versatility and low cost. Adsorption can be classified into static adsorption (batch adsorption) and dynamic adsorption (continuous adsorption). Although batch adsorption studies provide useful information on the application of adsorption to the removal of specific waste constituents, continuous column studies provide the most practical application of this process in wastewater treatment (Xu et al., 2013). A dynamic adsorption usually occurs in an open system where adsorbate solution continuously passes through a column packed with adsorbent.

For column adsorption, how to determine the breakthrough curve is a very important issue because it provides the basic but predominant information for the design of a column adsorption system (Xu et al., 2013). In these sense, computational simulation has proven to bring an advantage in terms of costs and time, helping to optimize the adsorption process. In general, the prediction of column dynamics behavior requires the simultaneous solution of a set of coupled partial differential equations (PDEs) representing material, energy, and momentum balances over a fixed bed with the appropriate boundary conditions. Because the simultaneous solution of a system of PDEs is tedious and time consuming, the use of simplified models capable to predict fixed-bed behavior is desirable (Saleh Shafeeyan et al., 2014).

In column adsorption, concentrations of the solute in fluid phase and of the solid adsorbent phase change with time and with position in the fixed bed, as adsorption proceeds (Geankoplis, 1993). Taking into account this kind of process, a statistical model may be suitable to describe the probability that the solute is adsorbed at different heights of the column, as well as the proportion of solute adsorbed as a function of time. The statistical model can be confronted with experimental data and adjusted using tools of classical statistics, as well as Bayesian statistics. Bayesian inference in particular, is being used in different areas of science like economic, health, biological and engineering studies (Gelman et al., 1992, Condit, 2007). Bayesian statistic natively incorporates the idea of confidence, it performs well with sparse data, and the model and results are highly interpretable and easy to understand. It is simple to use what you know about the process along with a relatively small or messy data set to project what you should expect about the process in the future.

One of the heavy metals that has been a major focus in wastewater treatment is hexavalent chromium Cr(VI) (Hena, 2010). The use of chromate and dichromate has many industrial applications such as in textile, electroplating, leather tanning, cement preservations, paints, pigments and metallurgy industries. Cr(II), Cr(III) and Cr(VI) are the three oxidation states for chromium in nature, but only the last two are stable (Aydın and Aksoy, 2009). Chromium is considered as a priority hazardous pollutant and the European Union defined severe environmental regulations to set the maximum level of hexavalent chromium allowed in industrial and civil wastewaters (200 g L^{-1}), as well as in superficial and underground water bodies (5 g L^{-1}) (Di natale et al., 2015). The United States Environmental Protection Agency has laid down the maximum contaminant level for Cr (VI) into inland surface waters as 0.1 mg/L and in domestic water supplies to be 0.05 mg/L (Sivakami et al., 2013). Commonly techniques to remove chromium from industrial wastewaters include precipitation, membrane filtration, solvent extraction, ion exchange, activated carbon adsorption electro deposition and biological processes (Di natale et al., 2015). In the past, activated alumina, active carbon, polymeric hybrid, and natural solids have been used as adsorbents for the removal of heavy metals from water. In the last years, the use of biopolymers as adsorbents is an emerging technique because they are cheap, abundant and environmentally safe. Chitosan is a natural polymer obtained from crustacean waste and has proved to be an effective chromium hexavalent (Cr(VI)) adsorbent (Dima et al., 2015).

The objective of the present work was to develop a statistical model capable of simulating the dynamic behavior of a fixed bed adsorption. The model proposed was applied to describe adsorption mechanisms of Cr(VI) onto chitosan flakes.

EXPERIMENTAL STUDIES

Chitosan production

Shrimps shells (*Pleoticus muelleri*) were used for the extraction of chitosan. The shells were provided by the seafood industries from Puerto Madryn, Patagonia-Argentina. Chitosan particles (CH) were obtained by deacetylation of chitin according to technic proposed by Dima et al (2015).

Fixed-bed column adsorption studies

The fixed-bed column studies were performed using a laboratory-scale glass column with an internal diameter of

2 cm and a length of 25 cm. Column was packed with 0.27, 0.42 and 0.72 g of CH to obtain defined bed heights of the adsorbent (0.7, 1.5 and 2 cm of bed depths respectively). Cr(VI) solution at pH=4 and at different initial concentrations (C_0= 90, 150 and 200ppm) was fed continuously at the bottom of the column with a flow rate of 3 ml/ min using a pump. Exit chromium solution (effluent solutions) (Ct) was collected at regular time intervals, until saturation. The effluent concentration was measured by 1,5- diphenylcarbazide method using a UV–visible spectrophotometer operated at 540 nm. The obtained data were included in a breakthrough curve (Ct/C_0 vs time) for further analysis.

Column data analysis

As the adsorbate solution travels through the column, the adsorption zone (where the bulk of adsorption takes place) starts moving out of the column and the effluent concentration starts rising with time. The time necessary for the effluent concentration to reach a specific breakthrough concentration of interest is called the breakthrough point time (tb) (Chen et al., 2012).

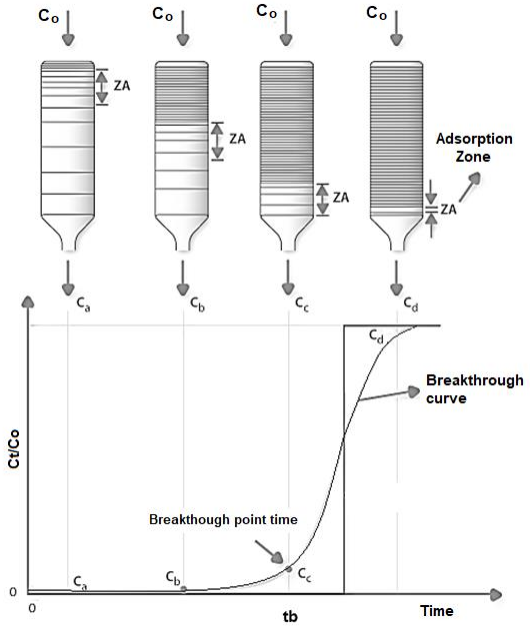

Fig. 1. Scheme of the adsorption zone progress through a fixed bed column and breakthrough curve in the continuous system

In the present work, the breakthrough point time (tb) for the column operation was defined as the time necessary for the Cr(VI) concentration at the exit (Ct) to be 0.1% of the feed concentration (C_0). Breakthrough curves were plotted in terms of the ratio of concentrations (Ct/C_0) vs. time (t) for different operating conditions (Chen et al., 2012). The breakthrough curves showed the performance of the fixed bed column. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and dynamic response of an adsorption column (Chen et al., 2012). The column performance was investigated by calculating the breakthrough time and adsorption capacity. The adsorption capacity (qb) was calculated according to Lara et al (2016):

$$qb = \frac{Q_v tb C_0}{1000m} \quad (1)$$

where qb is the bed capacity at breakthrough point (mg/g), tb is the breakthrough point time (ie to reach Ct/C_0=0.1), m is the bed mass (g), C_0 is the initial adsorbate concentration (mg/L), and Q_v (m^3/min) is the volumetric fluid

STATISTICAL MODELLING

Bayesian statistical methods use Bayes' theorem to compute and update probabilities after obtaining new data. This theorem describes the conditional probability of an event based on data as well as prior information or beliefs about the event. In Bayesian inference, Bayes' theorem can be used to estimate the parameters of a probability distribution or statistical model. Since Bayesian statistics treats probability as a degree of belief, Bayes' theorem can directly assign a probability distribution that quantifies the belief to the parameter or set of parameters.

General adsorption model

Let us assume that we have a column of height *h* and a solute is starting to flow at time t = 0, with a linear flow v. To model the adsorption process in the column, the solute is considered to be adsorbed by the adsorbent at height x at time t, with a probability distribution $F_a(x,t)$ and density $f_a(x, t)$. The distribution $f_a(x, t)$ is modeled as a combination of two processes: the displacement of the adsorption zone and the trajectory of the solute through the unsaturated zone. The displacement of the front of the adsorption zone is modeled through a probability density $f_d(x, t)$ that represents the probability that the adsorption front is at the height x at time t. The solute path is modeled through a density $f_r(x)$ that represents the probability that the solute travels a distance *x*, from an available adsorption zone until it is adsorbed. Taking into account these processes $f_a(x, t)$ can be calculated as:

$$f_a(x,t) = \int_0^x f_d\left(x - y, t - \frac{y}{v}\right) f_r(y)dy \tag{2}$$

representing the multiplication of the probability that the solute exceeds the adsorption front at the height x - y, at time t – (y / v), by the probability that then, moving at speed v, it travels a height y until it is absorbed at the height x at time t.

For a given time t, the complement of the cumulative probability $1 - F_a(x,t)$ represents the concentration profile in the fluid, that is the relative concentration C/C_0 at a height x, when x varies between 0 and h (Geankoplis, 1993). Then $C(t) = 1 - F_a(h,t)$ is the function that represents the breakthrough curve, and the breakthrough time of the model is t= tb such that C(tb) = 0.1.

Normal Model

As a first simplification we will assume that the column extends between −∞ and + ∞ beyond the region occupied by adsorbent between 0 and h. We will model the probability distributions with normal densities $f_N(x|\mu, \sigma)$ having mean μ and standard deviation σ that depend on certain parameters to be estimated. Specifically, for the displacement of the adsorption zone we will consider a normal density with mean $v_d t$ and standard deviation σ_d, $f_d(x, t) = f_N(x|v_d t, \sigma_d)$, where v_d corresponds to the linear velocity of the adsorption zone displacement and $v_d.t$ is the mean height of the adsorption front. For the distance of the solute displacement, until it is absorbed, we will consider a normal density with mean μ_r and standard deviation σ_r, $f_r(x) = f_N(x \mid \mu_r, \sigma_r)$. With these considerations, and integrating Eq. (2) from −∞ to x, $f_a(x, t) = f_N(x \mid \mu_a, \sigma_a)$, with a mean:

$$\mu_a(t) = v_d t + \mu_r\left(1 - \frac{v_d}{v}\right) \tag{3}$$

and standard deviation

$$\sigma_a = \sqrt{\sigma_d^2 + \sigma_r^2\left(1 - \frac{v_d}{v}\right)^2} \tag{4}$$

Since σ_a^2 is a linear combination of σ_d^2 and σ_r^2 these two variances cannot be estimated independently (that is, deviations for each particular process cannot be obtained). Then, a single parameter σ_a is considered to describe the standard deviation associated with both processes. Therefore, the breakthrough curve projected by this model is given by the function

$$\begin{aligned} C\left(t|v_{d,}\mu_r, \sigma_a\right) &= 1 - f_N(x|\mu_a(t), \sigma_a) \\ &= \frac{1}{2} + \frac{1}{2}\,\mathrm{erf}\left(\frac{\mu_a(t) - h}{\sqrt{2}\sigma_a}\right) \\ &= \frac{1}{2} + \frac{1}{2}\,\mathrm{erf}\left(\frac{v_d t + \mu_r\left(1 - {}^{v_d}/_{v}\right) - h}{\sqrt{2}\sigma_a}\right) \end{aligned} \tag{5}$$

where erf is the error function.

Considering a change of variables in eq (5), given by

$$\tilde{v}_d = s.v_d$$

$$\tilde{\mu}_r = \frac{s\left(\mu_r\left(1-{}^{v_d}/_{v}\right)-h\right)}{\left(1-s\frac{v_d}{v}\right)-h} \quad (6)$$

$$\tilde{\sigma}_a = s\sigma_a$$

it follows that $C(t|v_d, \mu_r, \sigma_a) = C(t|\tilde{v}_d, \tilde{\mu}_r, \tilde{\sigma}_a)$. Therefore there are infinite combinations of the parameters that produce the same function C(t), and as a consequence v_d, μ_r, and σ_a cannot be simultaneously estimated from the data of the experimental breakthrough curve. Then assuming $\mu_r = 0$ (since it is considered that the adsorption kinetics of the solute is instantaneous when it meets the available adsorbent), a model with two independent parameters is obtained. The applied model is then:

$$C\left(t|v_{d,}\sigma_a\right) = 1 - F_N(h|v_d.t, \sigma_a) = \frac{1}{2} + \frac{1}{2}\,\mathrm{erf}\left(\frac{v_d t - h}{\sqrt{2}\sigma_a}\right) \quad (7)$$

The parameters of the model are: v_d the speed of movement of the adsorption zone and σ_a the standard deviation of the position of the adsorption zone front. Likewise, the breakthrough point of this model can be calculated by solving:

$C\left(tb|v_{d,}\sigma_a\right) = 1 - F_N(h|v_d.tb, \sigma_a) = 0.1$, that is , $F_N(h|v_d.tb, \sigma_a) = 0.9$, resulting:

$tb = \frac{1}{v_d}\left(h - \sigma_a \Phi^{-1}(0.9)\right)$, were Φ^{-1} is the Probit function (8)

Parameters Estimation

A Bayesian approach was used in which, based on prior probability distributions of the parameters and a likelihood function, the projections of the model are compared with the experimental data to obtain posterior distributions of the parameters (Gelman et al., 1992). Given the conditions of the column: initial concentration C_0, linear flow rate v and height *h*, and given a series of experimental observations of the output relative concentration $\{x_i\}$, taken at times $\{t_i\}$ respectively, a normal likelihood function was used to confront it with the projections of the model. The logarithm of the likelihood function was calculated as

$$LogL(v_d, \sigma_a|\{x_i, t_i\}) = \sum_i \log\left(f_N(x_i|C(t_i|v_d, \sigma_a), \tau)\right) \quad (9)$$

where τ corresponds to a new parameter that represents the observation error associated with the model. In order to estimate the posterior parameters distributions, uniform prior distributions were assumed within certain admissibility intervals for each parameter. The intervals considered were: [0, v = 0.95] for v_d, [0, 2] for σ_a, and [0, 0.1] for τ. A Gibbs sampler was adopted, that is a Markov chain Monte Carlo (MCMC) algorithm for obtaining a sequence of posterior observations, which are approximated from the multivariate posterior probability distribution (Carlin et al., 1992, Condit el al., 2007). The result is a posterior sample of the values of each parameter, from which posterior samples of the breakthrough curves and the breakthrough time tb are obtained according to Eqs (7) and (8). Then, median and credibility intervals of 90% were calculated from posterior samples. Gibbs sampling was programmed in R (R Core Team 2019), using a metropolis algorithm. For this sampling, 100,000 simulations were run, discarding the first 10000 as burn-in and thinning the remaining by sampling every 10th (in order to refine the sampling and avoid autocorrelation), finally producing 9000 posterior samples.

RESULTS AND DISCUSSION

According to Eq (1) there was a good capacity of adsorption (qb) of Chromium (VI) onto chitosan particles. Likewise, a decrease in qb with the initial chromium concentration was observed (Table 1).

Table 1. Adsorption capacity (qb), estimated values of parameters (v_d, σ_a) (median and 90% credible interval), and fit error (RMSE) as a function of column height and initial chromium concentration

C_0	Bed height (h)	qb	Experimental tb (min)	v_d	σ_a	RMSE	Model tb (min)	BDTS tb (min)
90	0.7	108	100	0.004 (0.003-0.005)	0.140 (0.116-0.169)	0.044	136 (125-145)	103
150	0.7	102	57	0.008 (0.007-0.009)	0.206 (0.178-0.242)	0.031	56 (51-60)	40

200	0.7	15	6	0.025 (0.024-0.026)	0.466 (0.419-0.520)	0.056	4 (1-7)	0.4
90	1.5	163	260	0.004 (0.003-0.005)	0.215 (0.189-0.245)	0.029	291 (280-300)	252
150	1.5	84	76	0.012 (0.011-0.013)	0.524 (0.468-0.588)	0.027	71 (64-76)	119
200	1.5	37	26	0.016 (0.014-0.017)	0.843 (0.747-0.948)	0.039	27 (19-33)	40
90	2.0	128	341	0.005 (0.004-0.005)	0.311 (0.260-0.367)	0.019	355 (337-371)	346
150	2.0	123	196	0.007 (0.006-0.008)	0.493 (0.445-0.548)	0.035	201 (192-210)	169
200	2.0	62	74	0.017 (0.016-0.018)	0.637 (0.574-0.705)	0.028	71 (66-75)	65

According to Gibbs sampler used for the model proposed, posterior estimates of the breakthrough curve fit to the experimental data well (Figure 2), indicating that the statistical model with two parameters is adequate to describe the adsorption process in general. The error parameter of the model was τ = 0.036 posterior median, with (0.033, 0.040) 90% credible interval.

The root-mean-square error (RMSE) was used to measure the error fit, that is the differences between predicted and experimental points: $= \sqrt{\frac{\sum(C_{exp}-C_{Predicted})^2}{N}}$. The root mean square error of the breakthrough curve range between 0.019 and 0.056 for the 9 columns analyzed (Tabla1).

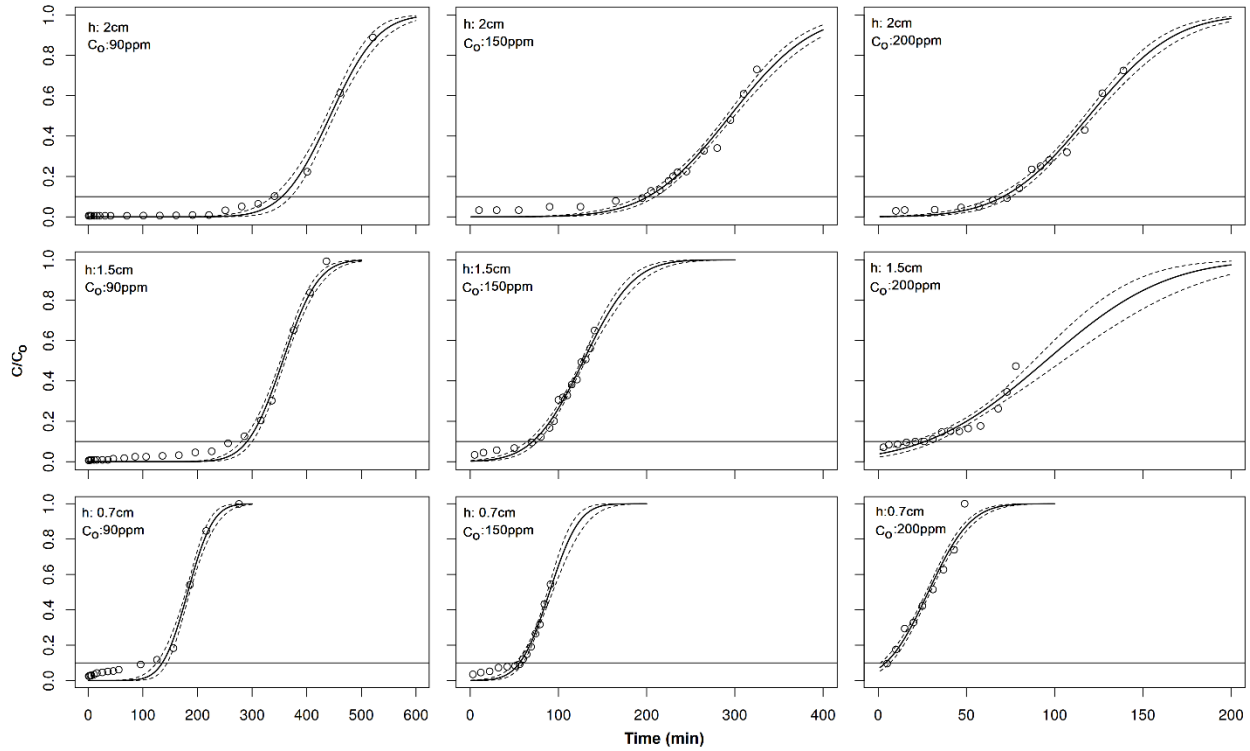

Fig. 2. Breakthrough curve as a function of height of the column and the initial chromium concentration. Experimental data (Points). Model breakthrough curve (Full lines). Credible interval (Dotted lines)

According to the model proposed, estimated values of both parameters (v_d, σ_a) increased along with the initial concentration (Figure 3). This is the expected behavior since more concentration implies more solute per time unit traveling in the column. On the other hand, no clear trend between estimated parameters and bed height (h) was observed (Figure 3 and Table1). Moreover, according to Geankoplis (1993) the breakthrough curve slope (that represents the mass-transfer zone width) depends on the fluid velocity and is essentially independent of column height. This independence of h is clearly observed in the model parameters for low concentration (90 ppm) with near identical estimated values of v_d and very close values of σ_a for the different bed heights (Table1, Figure 3).

It is interesting to note that the model proposed can be used to scale the height of the column. Assuming

independence from the bed height h and for a given column condition: initial concentration (C_0) and flow linear velocity (v), model parameters, v_d and σ_a, can be used in Eqs (7) and (8) to scale the breakthrough curve and the breakthrough point time for other height values, at least as a first approximation.

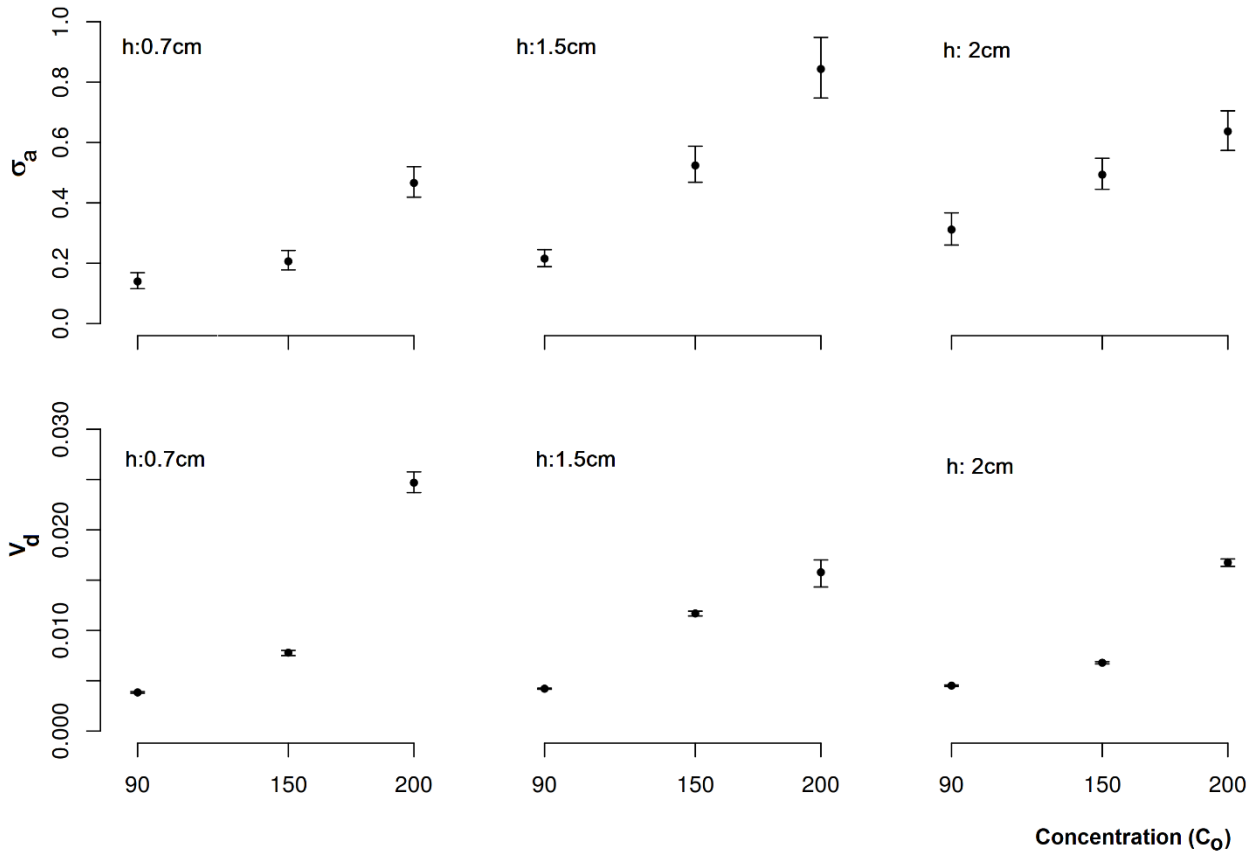

Fig. 3. Performance of Bayesian model parameters (v_d, σ_a) as a function of initial chromium concentration, for different bed heights

The applied model assumed that the adsorption kinetics of the solute is instantaneous when it meets the available adsorbent (μ_r = 0). This assumption is consistent with the observed results for chromium - chitosan system in batch studies (Dima et al., 2015). On the other hand, if we consider a positive value of μ_r this would correspond to a displacement of the breakthrough curve, eq (5), and will only produce a proportional increase in v_d and σ_a parameters (eq 6) (without changes in the general parameters performance).

Comparison with other adsorption models

Different mathematical models have been used to describe and predict the breakthrough curves and breakthrough point time of an adsorption column. Mathematical equations such as Yoon–Nelson, Thomas, Bohart–Adams and BDTS (Bed-Depht Service Time analysis) are usually used to match experimental and model data (Chen et al., 2012, Mohan et al., 2017).

Thomas model assumes plug flow behavior in the bed, and uses 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. The linearized form of Thomas model can be expressed as follows:

$$\ln\left(\frac{C_0}{Ct}-1\right)=\frac{K_{TH}q_0m}{v}-K_{TH}C_0t \qquad (10)$$

where: K_{TH} (mL/min mg) is the Thomas rate constant; q_0 (mg/g) is the equilibrium of the adsorbate uptake per g of the adsorbent; C_0 (mg/L) is the initial chromium concentration; Ct (mg/L) is the outlet concentration of chromium at time t; m (g) the mass of adsorbent, v (mL/min) the flow rate and t total (min) stands for flow time.

On the other hand, the Bed-Depht Service Time analysis (BDTS) model is a widely used model, which is based on Bohart -Adams equation. The BDST model gives a simple relationship between breakthrough point time (tb) and bed height (h) in terms of BDTS parameters.

To compare these models with the statistical model proposed in the present work the evaluation of the breakthrough curves using the Yoon–Nelson, Thomas and Bohart-Adams models was carried out. The entire breakthrough curve was best predicted by Thomas model (eq.10), while the Bohart-Adam model described satisfactorily the initial portion of the curves. The RMSE for these models ranged between (0.03-0.17) for Thomas model and between (0.02-0.11) for Bohart-Adam model. These RMSE values are in the range, or are higher, than the RMSE values calculated for the Bayesian model proposed (Table 1). In contrast, the Yoon –Nelson model was the one that least fit the experimental data in comparison with the other applied models, showing the higher RMSE values (0.09-0.69).

It can be observed, that in all cases, the tb experimental was into or near to credibility interval of model proposed tb, while BDTS model only predict the tb well at low concentrations (Table1).

CONCLUSIONS

A statistical model capable of simulating the dynamic behavior of the fixed-bed adsorption was developed. The model was applied to describe adsorption of Cr(VI), one of the most toxic metals in water, onto chitosan flakes, obtained from the waste of crustacean industry.

Experimental data, for different operating conditions, were obtained using a glass column. Then, assuming normal distributions, the model projections were compared with experimental data in a Bayesian framework.

The proposed statistical model represented a good description of the adsorption column. The root mean square error (error fit, RMSE) of the model was in the range, or even lower than the error fit calculated for the other models described in the literature. In all cases, the experimental breakthrough point time (tb) was into or near to model credibility interval.

As a first approximation, setting the initial concentration and the flow linear velocity, the model parameters v_d and σ_a can be used to scale the breakthrough curve and the breakthrough point time for different bed height values.

Further analysis and investigations over the model and the Bayesian posterior estimators are needed to study its applicability to other column configurations. Therefore, the model represents an option for the design of adsorption columns for wastewater treatment.

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