Modeling the mass transfer in biosorption of Cr (VI) y Ni (II) by natural sugarcane bagasse

I. L. Rodríguez Rico¹ · R. J. Cabrera Carrazana² · N. Kumar Karna³ · I. Iáñez-Rodríguez⁴ · M. Calero de Hoces⁴

Received: 4 May 2017 / Accepted: 26 March 2018 / Published online: 4 April 2018
 © The Author(s) 2018

Abstract

The Cr (VI) and Ni (II) ion biosorption process by natural sugarcane bagasse in a fixed bed column was investigated. The characteristic removal parameters such as retention capacity, removal percent and unused bed length were experimentally determined at different operating conditions. Overall mass transfer coefficient was investigated and reported for the studied biosorption system. The breakthrough curves were simulated using Matlab2010a software to check the validity of the obtained overall mass transfer coefficients. Experimental data fitted well with predicted data ($R^2=0.94$). A statistical analysis was performed using the software Statgraphics Centurion-X v15.2.06 to compare the simulated and experimental data. No significant differences were observed between experimental and simulated data. The best operating conditions for Cr (VI) removal were 15 mg/L of inlet concentration and 1.5 g of biosorbent. For Ni (II) removal the best results were obtained with 25 mg/L of inlet concentration and 1.5 g of solid. The results obtained through the breakthrough curve showed high removal percentages (94.70 and 97.90% for chromium and nickel, respectively). Moreover, results indicated that sorption of these metals was irreversible and it was controlled by the mass transfer at the external film.

Keywords Biosorbent · Heavy metals · Pollution · Wastewaters

Nomenclature

V_{ef} Effective volume (ml)
 F Volumetric flow (mL/min)
 t Time (min)

t_b Break-point time (min)
 t_s Saturated point time (min)
 C_o Initial concentration (mg/L)
 C Concentration in the time to the exit of the column (mg/L)
 C_R Concentration of retained metal (mg/L)
 m_{total} Total amount of heavy metal sent to column (g)
 m_{ads} Total amount of heavy metal retained in column (g)
 m_o Total mass of the adsorbate (g)
 u_o Superficial velocity of fluid (cm/min)
 H Bed length (cm)
 H_{UNB} Length of unused bed (cm)
 H_{sat} Longitude of saturated bed (cm)
 N Overall number of transfer units
 W_{sat} Adsorbate amount in equilibrium with the fluid (mg/g)
 K_{ca} Overall volumetric mass transfer coefficient (min^{-1})

✉ M. Calero de Hoces
 mcalero@ugr.es

I. L. Rodríguez Rico
 ivanl@uclv.edu.cu

R. J. Cabrera Carrazana
 rjcabrera@nauta.cu

N. Kumar Karna
 n.karna@udt.cl

I. Iáñez-Rodríguez
 ireneir@ugr.es

¹ Central University “Marta Abreu” of Las Villas, Carretera a Camajuani Km 5 1/2, Santa Clara, Villa Clara, Cuba

² Central University “Marta Abreu” of Las Villas, Calle Danielito entre Central y San Miguel, Santa Clara, Villa Clara, Cuba

³ Technological Development Unit, University of Concepción, Concepción, Chile

⁴ Department of Chemical Engineering, University of Granada, 18071 Granada, Spain

Greek letters

τ Dimensionless time
 ϵ Bed porosity
 ρ_s Bulk density (g/L)
 ρ_p Particle density (g/L)

Introduction

Nowadays, pollution of wastewaters by heavy metals caused by anthropogenic activities is a problem to be solved (Martín-Lara et al. 2017). Chromium and nickel are heavy metals that are considered as very dangerous pollutants in wastewaters because they are persistent as they do not degrade to harmless compounds. They are toxic substances known to cause multiple organ damage, even at low concentrations. Moreover, they are human carcinogens and they cause long-term health problems in human population (Iqbal 2016; Tchounwou et al. 2012).

Different technologies have been tested for heavy metal removal from wastewater such as chemical precipitation, ion exchange, reverse osmosis, electro-flotation and bioremediation among others. These methodologies present some drawbacks like the production of toxic sludge, high energy and chemical requirements and low efficiency (Mushtaq et al. 2016; Rashid et al. 2016).

Biosorption is an interesting alternative for metal removal which overcomes the disadvantages of the aforementioned methods. It is low cost and it has a high efficiency and selectivity for particular contaminants. Moreover, the use of chemicals is minimum and no sludge is generated. Furthermore, regeneration of the biosorbents and metal recovery are possible (Bhatti et al. 2016). Many agricultural and forestry waste materials have been tested for biosorption such as rice husk, pine bark, sawdust, peanut and orange peels among others (Nadeem et al. 2016; Tahir et al. 2017).

Use of adsorption systems for industrial and municipal wastewater treatment has become more prevalent during the recent years (Babu and Gupta 2004). An adsorption process is often used at the end of a treatment sequence for pollution control as high degree of purification can be achieved. Adsorption is an important step in industrial downstream processing. It is important to stop the adsorption stage before the adsorbent is saturated which requires a thorough understanding of adsorption characteristics (Bautista et al. 2003). At industrial scale, the breakthrough time of the operation must be determined through an economic and, eventually, environmental evaluation of the process.

The adsorption kinetics can be described by various models depending upon the mechanism of transport (pore diffusion, solid diffusion, and both mechanisms in parallel) assumed inside the particles or in the external film (Bajpai et al. 2004, 2007; Dizge et al. 2009; Gupta and Babu 2009; Plazinski and Rudzinski 2010).

In the present study, the effect of various operating variables (bed height and inlet adsorbate concentration) on the process of fixed-bed biosorption was studied. Furthermore,

the adsorption kinetics were studied through a mathematical model that takes into account both the external and internal mass transfer resistances, nonideal plug flow along the column, and the variation of fluid velocity along the column.

Tan and Spinner (1994), developed a more complete model for ionic exchange that includes the limitation of total transference. This model can predict the breakthrough curves for any species removed by the biosorbent and elution curves obtained during regeneration. However, the solution of the model is extremely complex and the values of the mass transfer coefficients for all ionic species present in the system is required.

The values of these coefficients can be estimated or determined by fitting the model to experimental data (Yang and Volesky 1996; Hatzikioseyan et al. 2001; Borba et al. 2006; Escudero et al. 2013; Gu et al. 2013; Sulaymon et al. 2014). The main advantage of the model is that it can simulate and predict the performance of a column under various conditions including different flow rates, feed compositions, column size, bed porosities and ionic forms of the biosorbent.

Materials and methods

Biosorbent

Sugar cane bagasse samples were collected from the Sugar Power Station located in the Central University “Marta Abreu” of Las Villas, in Santa Clara, Cuba. The bagasse was sieved in a sieve machine Model MLW with a group of sieves (Tyler Series). The fraction between 0.5 and 1 mm was selected.

Preparation of standards and reagents

Preparations of Cr (VI) and Ni (II) solutions was carried out using analytical grade reagents. Potassium dichromate ($K_2Cr_2O_7$) and nickel sulfate (II) hexahydrate ($NiSO_4 \cdot 6H_2O$) ACS 99% supplied by J. T. Baker were used for preparing the synthetic wastewater.

Solutions were prepared by diluting the analytical reagents with distilled water to desired concentrations. The solutions of nickel were prepared at concentrations of 15 and 25 mg/L. Chromium solutions were prepared at a concentration of 10 and 15 mg/L.

The pH of the solution is a key parameter for the evaluation of biosorption performance, specifically in the metal speciation (Guzman et al. 2003). In the case of heavy metals, biosorption studied in this work, the speciation of the metals is not changed with the pH (constant in the process), therefore, the main effect will be explained by the impact of this parameter on the functional groups of the biomass. It was

studied that the most reactive groups (carboxylic groups) on the biomass are generally found under charge point zero (pH 6). (Vicente 2011; Bermúdez et al. 2011).

Castro et al. 2004, reported that the pKa of carboxylic groups on alginate fraction in the biomass is generally found between 2 and 4.

Then, the pH of the solution was adjusted by adding the appropriate quantity of 0.1 M hydrochloric acid (HCl). The initial pH of solutions was fixed at 2 and 5 for dichromate solutions and nickel sulfate, respectively.

Hydraulic tests and selection of the operation parameters

The column (diameter: 1 cm, height: 20 cm) was filled with natural sugar cane bagasse and water was circulated with the purpose of determining the most appropriate flows for the established operation conditions.

Ko et al. (2001) suggested for the processes on the macroscopic level, that if the flow rate increases, the residence time of the fluid in the bed decreases, resulting in a low use of the biosorption capacity of the bed. On the other hand, for the processes on the microscopic level, the change of the volumetric flow rate affects only the diffusion of the ions in the liquid film, but not the one in the bioadsorbent. According to this author, high volumetric flow rates result in small resistances in the liquid film and high values of the external mass transfer coefficient. Based on these considerations, the best flow allows a non-fragmenting stable bed and no draining occurrence at the end of the operation. Besides, an appropriate flow gives a proper drop pressure. As a result, the selected feed flow was of 2 mL/min. The selected bed height was six times the internal diameter of the column (Khalid et al. 1998; Treybal 1993).

Once studied, the biosorption of Cr (VI) and Ni (II) using one fixed bed column, several models were applied to the experimental data of the breakthrough curves for carrying out the fitting and the determination of the mass transfer parameters. The samples were collected every 5 min for the first 100 min and then each 10 min, until the biosorbent was saturated.

The chromium and nickel concentrations were determined by atomic absorption spectrophotometry using Pye Unicam SP9 PHILIPS Atomic Absorption Spectrophotometer, Chromium Analytical Line: 357.9 nm and Nickel Analytical Line: 232.0 nm to calculate the metal removal percent in a column.

Data analysis

To analyze the dynamic Cr (VI) and Ni (II) removal in up-flow fixed bed column, breakthrough curves were drawn and the data were evaluated with the following equations.

- Effluent volume, V_{ef} (mL), can be calculated using Eq. (1):

$$V_{ef} = F * t_b \quad (1)$$

where F is the volumetric flow rate circulating through the column expressed in mL/min and t_b represents the total flow time in min.

- Total amount of metal which entered in the column, m_{total} in mg, can be calculated as follows:

$$m_{total} = \frac{C_o \times F \times t_b}{1000} \quad (2)$$

where C_o represents the metal inlet concentration in mL/min.

- Total amount or metal retained by the column, m_{ads} in mg, is represented by the area under the breakthrough curve. It can be calculated by the following expression:

$$m_{ads} = \frac{F}{1000} \int_{t=0}^{t=t_b} C_R dt \quad (3)$$

where C_R denoted the concentration of metal removal in mg/L.

Estimation of mass transfer parameters

The concentration in the fluid and the solid phase change with time as well as with position in a fixed bed. The transfer process is described by the overall volumetric mass transfer coefficient ($K_c a$) obtained from a solute material balance in the column considering irreversible isotherms (McCabe et al. 1993).

$$K_c a = \frac{u_o N}{H} \quad (4)$$

N is defined as:

$$N(\tau - 1) = 1 + \ln \left(\frac{C}{C_o} \right) \quad (5)$$

The parameter τ is defined as:

$$\tau = \frac{u_o C_o \left(t - H \frac{\epsilon}{u_o} \right)}{\rho_s (1 - \epsilon) H W_{sat}} \quad (6)$$

where $H \frac{\epsilon}{u_o}$ is the time to displace fluid from the bed voids (normally negligible); $u_o C_o t$ is the total solute fed to a unit cross-section of bed up to time t ; and $\rho_s (1 - \epsilon) H W_{sat}$ is the capacity of the bed, or the amount of the solute exchanged if the entire bed came to equilibrium with the feed.

The solid line in Fig. 1 represents the predicted breakthrough curve (McCabe et al. 1993). The slope increased with time and C/C_o becomes 1 for $N(\tau - 1) = 1$.

Fig. 1 Breakthrough curves for irreversible adsorption

If the diffusion in the pores control the rate of adsorption, the breakthrough curve has an opposed form to that of the corresponding to the control of the external film. The breakthrough curve is S-shaped when both internal and external resistance are significant, as shown in dashed line.

Calculation of the unused bed surface

Calculation of the unused bed surface is a method to evaluate the adsorption capacity of biosorbents in continuous flow-packed columns.

Hence, for a full bed length (H), the length of unused bed (H_{UNB}) is:

$$H_{UNB} = \left(1 - \frac{t_b}{t_s}\right) \quad (7)$$

where t_s represents the saturation time of the biosorbent in min. Small values of this parameter mean that the breakthrough curve is close to an ideal step with negligible mass-transfer resistance. Then, minimum H_{UNB} quantities are desirable in optimized operational conditions.

It is important to set the breakthrough point considering the concentration according to the limit fixed by environmental standards that sets discharge concentration limits for heavy metal ions, or other process conditions.

Breakthrough curve simulation

Simulation is a modern technique that uses mathematical models to predict the behavior of a system.

To predict the breakthrough point in biosorption systems, Eq. (8) can be applied (McCabe et al. 1993).

$$\ln \frac{C}{C_0} = \frac{-K_c a (H - H_{sat})}{u_0} \quad (8)$$

The longitude of saturated bed (H_{sat}) it is the product of the speed of the mass transfer section for the time since the area begins to move and it can be calculated using Eq. (9)

$$H_{sat} = \frac{u_0 C_0}{\rho_p (1 - \epsilon) W_{sat}} \left[t - \frac{\rho_p (1 - \epsilon) W_{sat}}{K_c a C_0} \right] \quad (9)$$

And W_{sat} , which is adsorbate amount in equilibrium with the fluid (mg/g) can be calculated as:

$$W_{sat} = \frac{m_{ads}}{m_0} \quad (10)$$

To check the validity of the obtained results, the $K_c a$ values determined from the experimental data were used to simulate the breakthrough curves using Matlab2010a software. Simulations were limited to $C/C_0 \approx 0.5$, as the considered margin is enough to contain the breakthrough point under all the experimental conditions. The disposal limits of Ni (II) and Cr (VI) according to Cuban Norm NC 27-12 are 2.0 and 0.5 mg/L, respectively.

Statistical analysis of the data

A statistical analysis was performed using the software Statgraphics Centurion-X_v15.2.06 to compare the simulated and experimental data. R squared coefficient, standard deviation and F tests were calculated to determine the reliability of the data calculated by mathematical models compared to experimental data.

Results and discussion

The breakthrough curves for adsorption of Cr (VI) and Ni (II) were determined experimentally in a packed column with sugarcane bagasse. All the experiments were performed at 25 °C.

Figure 2 shows the plot of the mean data from three experiments for each operation conditions.

Table 1 shows characteristic parameters of the removal of Cr (VI) and Ni (II). It is observed that the best operating conditions for the removal of Cr (VI) are $C_0 = 15$ mg/L and $m = 1.5$ g, while for the Ni (II) are $C_0 = 25$ mg/L and $m = 1.5$ g, with a removal percentage of 94.70 and 97.90%, respectively. The maximum retention capacities of natural sugarcane bagasse were similar to that reported by Karna

(2013). However, Mishra et al. (2016), who studied biosorption process of Ni and Cr with *Hydrilla verticillata*, found a higher removal percentage for chromium than for nickel (96 and 92%, respectively) which is in contrast with the obtained results.

Sharma and Singh (2013) observed that the percentage Ni absorbed by rice straw increased with increasing inlet concentration, which is in accordance with the results found in

this work. They found that a higher adsorbate concentration gave a higher driving force for biosorption process.

On the other hand, Manikandan et al. (2016) studied Cr (VI) adsorption by waste litchi peels. They found that when inlet concentration increased, the breakthrough time decreased which is in accordance with the results obtained in this work.

Fig. 2 Breakthrough curves of Cr (VI) and Ni (II) on natural sugar cane bagasse at different experimental conditions: **a** Co (Cr)= 10 mg/L and $m=1.5$ g; **b** Co (Cr)= 15 mg/L and $m=1.5$ g; **c** Co (Ni)= 15 mg/L and $m=1.5$ g; **d** Co (Ni)= 25 mg/L and $m=1.5$ g.

(filled circle) represents the breakpoint in each case. The data plotted represent the mean of three experimental runs for each operating condition

Table 1 Characteristic parameters of the removal of Cr (VI) and Ni (II) in fixed bed columns filled with sugarcane bagasse

Metal	C_o (mg/L)	m (g)	t_b (min)	V_{ef} (ml)	m_{total} (g)	m_{ads} (g)	% removal
Cr(VI)	10	1.5	5	10	0.1	0.096	96.00
	15	1.5	35	70	1.05	1.020	97.50
Ni (II)	15	1.5	130	260	3.90	3.750	96.20
	25	1.5	70	140	3.50	3.430	97.90

Table 2 Mass transfer parameters for the dynamic runs

Metal	C_o (mg/L)	H (cm)	$K_c a$ (min^{-1})	N	H_{UNB} (cm)	W_{sat} (mg/g)
Cr(VI)	10	20	0.302	2.10	19.44	1.07
	15	20	0.437	3.62	17.62	1.99
Ni (II)	15	20	0.587	2.65	11.61	3.43
	25	20	0.644	4.46	12.22	3.58

The mass transfer parameters were estimated from the breakthrough data of Cr (VI) and Ni (II) in solutions and are enlisted in Table 2. It is observed that the Cr (VI) and Ni (II) increase significantly the parameters with increasing initial concentration of the solution, indicating that the biosorption process was fast and very favorable.

This process was considered as irreversible adsorption because the mass transfer rate was proportional to the initial concentration of the fluid. As a result, it could be concluded that initial metal concentration influenced significantly the driving force that governs all process of mass transfer.

In the biosorption of Cr (VI), the height of unused bed (H_{UNB}) varied with operating conditions in the column. However, this behavior is less marked in the removal of Ni (II).

The plot of $N(\tau-1)$ versus C/C_0 for the biosorption of Cr (VI) and Ni (II) on natural sugar cane bagasse showed that the rate-controlling step of the process was the external film, which proved that the biosorption of these metals were irreversible. Figure 3 shows the behavior described above and explained in Sect. “Calculation of the unused bed surface” corresponding to different operation conditions.

Figure 4 shows the simulated curves using the model that include the calculated values of K_{ca} .

A statistical analysis was carried out using the software Statgraphics Centurion-X_v15.2.06 to check the reliability

of the results obtained in the simulation compared to the experimental ones. Table 3 shows the obtained results.

It is clear that the breakthrough curves presented good agreement with the experimental data (R^2 is always above 0.94). In addition, the F tests demonstrated that in all the cases there was no significant difference between the simulated data and the experimental data because the significance level was always bigger than 0.05.

Other authors like Chao et al. (2014) and Chen et al. (2012) applied other mathematical models like Thomas model and Yoon–Nelson models, obtaining good agreement between experimental and predicted results (R^2 values above 0.90). In future works, different models could be applied to experimental data obtained for sugarcane bagasse to determine which of the models give the best fitting.

Conclusions

It can be concluded that the use of sugarcane bagasse for Cr (VI) and Ni (II) removal from wastewater is suitable as the metal retention values obtained in this work were high. Hence, it can be considered as a low-cost and efficient alternative for the removal of those metals. Results showed that metal retention was higher when inlet metal concentrations were 15 and 25 mg/L for chromium and nickel, respectively.

Fig. 3 Breakthrough curves for irreversible adsorption of Cr (VI) and Ni (II) natural sugar cane bagasse at different experimental conditions: **a** C_0 (Cr) = 10 mg/L and $m = 1.5$ g; **b** C_0 (Cr) = 15 mg/L and $m = 1.5$ g; **c** C_0 (Ni) = 15 mg/L and $m = 1.5$ g; **d** C_0 (Ni) = 25 mg/L and $m = 1.5$ g

Fig. 4 Breakthrough curves of Cr (VI) and Ni (II) on natural sugar cane bagasse experimental (o) and simulates (-) at different experimental conditions: **a** Co (Cr)=10 mg/L and $m=1.5$ g; **b** Co

(Cr)=15 mg/L and $m=1.5$ g; **c** Co (Ni)=15 mg/L and $m=1.5$ g; **d** Co (Ni)=25 mg/L and $m=1.5$ g. Filled circle represents the break-point in each case

Table 3 Statistical analysis carried out to check the reliability of the results obtained in the simulation

Metal	C_0 (mg/L)	R^2	Standard deviation	F tests
Cr(VI)	10	0.98	0.157	0.985
	15	0.94	0.150	0.427
Ni (II)	15	0.99	0.127	0.826
	25	0.98	0.145	0.782

Values of mass transfer coefficients were reported for the removal of Cr (VI) and Ni (II) with sugarcane bagasse as biosorbent. Through the estimation of the mass transfer parameters, it was possible to establish that the biosorption of Cr (VI) and Ni (II) by sugarcane bagasse was fast and irreversible. The controlling stage was mainly governed by the resistance in the external film. The $K_c a$ values determined from the experimental data were used to simulate the breakthrough curves. The statistical analysis of experimental and theoretical data showed no significant differences between both data.

Future work will focus on the study of the use of sugarcane bagasse for the removal from wastewater of other heavy metals or other kind of contaminants such as emergent pollutants.

Acknowledgement The authors thank the Central University “Marta Abreu” of Las Villas, Cuba, for providing the means to carry out this work.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- Babu BV, Gupta S (2004) Modeling and Simulation for Dynamics of Packed Bed Adsorption. In: Proceedings of International Symposium and 57th Annual Session of IChE in association with AIChE (CHEMCON-2004), Mumbai
- Bajpai J, Shrivastava R, Bajpai AK (2004) Dynamic and equilibrium studies on adsorption of Cr (VI) ions onto binary bio-polymeric beads of cross linked alginate and gelatin. Colloid Surf A 236:81–90
- Bajpai J, Shrivastava R, Bajpai AK (2007) Binary biopolymeric beads of alginate and gelatin as potential adsorbent for removal of toxic

- Ni²⁺ ions: a dynamic and equilibrium study. *J Appl Polym Sci* 103:2581–2590
- Bautista L, Martínez M, Aracil J (2003) Adsorption of ALPHA-amylase in a fixed bed: operating efficiency and kinetic modeling. *AIChE J* 49:2631–2641
- Bermúdez YG, Rico ILR, Bermúdez OG, Guibal E (2011) Nickel biosorption using *Gracilaria caudata* and *Sargassum muticum*. *Chem Eng J* 166:122–131
- Bhatti HN, Zaman Q, Kausar A, Noreen S, Iqbal M (2016) Efficient remediation of Zr (IV) using citrus peel waste biomass: kinetic, equilibrium and thermodynamic studies. *Ecol Eng* 95:216–228
- Borba CE, Guirardello R, Silva EA, Veit MT, Tavares CRG (2006) Removal of Ni (II) ions from aqueous solution by biosorption in a fixed bed column: experimental and theoretical breakthrough curves. *Biochem Eng J* 30:184–191
- Castro C, Herrero R, Vicente MES (2004) Gibbs–Donnan and specific-ion interaction theory descriptions of the effect of ionic strength on proton dissociation of alginic acid. *J Electroanal Chem* 564:223–230
- Chao H-P, Chang C-C, Nieva A (2014) Biosorption of heavy metals on Citrus maxima peel, passion fruit shell, and sugarcane bagasse in a fixed-bed column. *J Ind Eng Chem* 20:3408–3414
- Chen S, Yue Q, Gao B, Li Q, Xu X, Fu K (2012) Adsorption of hexavalent chromium from aqueous solution by modified corn stalk: a fixed-bed column study. *Bioresour Technol* 113:114–120
- Dizge N, Keskinler B, Barlas H (2009) Sorption of Ni(II) ions from aqueous solution by Lewatit cation-exchange resin. *J Hazard Mater* 167:915–926
- Escudero C, Poch J, Villaescusa I (2013) Modelling of breakthrough curves of single and binary mixtures of Cu (II), Cd (II), Ni (II) and Pb (II) sorption onto grape stalks waste. *Chem Eng J* 217:129–138
- Gu T, Iyer G, Cheng KSC (2013) Parameter estimation and rate model simulation of partial breakthrough of bovine serum albumin on a column packed with large Q Sepharose anion-exchange particles. *Sep Purif Technol* 116:319–326
- Gupta S, Babu BV (2009) Modeling, simulation, and experimental validation for continuous Cr (VI) removal from aqueous solutions using sawdust as an adsorbent. *Bioresour Technol* 100:5633–5640
- Guzman J, Saucedo J, Revilla J, Navarro R, Guibal E (2003) Copper sorption by chitosan in the presence of citrate ions: influence of metal speciation on sorption mechanism and uptake capacities. *Int J Biol Macromol* 33:57–65
- Hatzikioseyan A, Tsezos M, Mavituna F (2001) Application of simplified rapid equilibrium models in simulating experimental breakthrough curves from fixed bed biosorption reactors. *Hydrometallurgy* 59:395–406
- Iqbal M (2016) Vicia faba bioassay for environmental toxicity monitoring: a review. *Chemosphere* 144:785–802
- Karna NK (2013) Modelación matemática del proceso de biosorción de Cr⁺⁶ y Ni⁺²: estudios en serie en columnas de lecho fijo con Bagazo de Caña de Azúcar. Trabajo de Diploma, Universidad Central “Marta Abreu” de Las Villas, Santa Clara
- Khalid NRA, Ahmad S, Kiani SN, Ahmed J (1998) Adsorption of cadmium from aqueous solutions on rice husk. *Radiochim Acta* 83:157–162
- Ko DCK, Poter JF, McKay G (2001) Film-pore diffusion model for the fixed bed sorption of copper and cadmium onto bone char. *Water Res* 36:3786–3886
- Manikandan NA, Alemu AK, Goswami L, Pakshirajan K, Pugazhenth G (2016) Waste litchi peels for Cr (VI) removal from synthetic wastewater in batch and continuous systems: sorben characterization, regeneration and reuse study. *J Environ Eng* 142(9):C4016001
- Martín-Lara MA, Iáñez-Rodríguez I, Blázquez G, Quesada L, Pérez A, Calero M (2017) Kinetics of thermal decomposition of some biomasses in an inert environment. An investigation of the effect of lead loaded by biosorption. *Waste Manag*. <https://doi.org/10.1016/j.wasman.2017.09.021>
- McCabe WL, Smith JC, Harriott P (1993) Unit operations of chemical engineering, 5th edn. McGraw-Hill, New Delhi
- Mishra A, Tripathi BD, Rai AK (2016) Packed-bed column biosorption of Cr (VI) and Ni (II) onto fenton modified *Hydrilla verticillata* dried biomass. *Ecotoxicol Environ Saf* 132:420–428
- Mushtaq M, Bhatti N, Iqbal M, Noreen S (2016) Eriobotrya japonica seed biocomposite efficiency for copper adsorption: isotherms, kinetics, thermodynamic and desorption studies. *J Environ Manag* 176:21–33
- Nadeem R, Manzoor Q, Iqbal M, Nisar J (2016) Biosorption of Pb (II) onto immobilized and native *Mangifera indica* waste biomass. *J Ind Eng Chem* 35:185–194
- Plazinski W, Rudzinski W (2010) A novel two-resistance model for description of the adsorption kinetics onto porous particles. *Langmuir* 26:802–808
- Rashid A, Bhatti HN, Iqbal M, Noreen S (2016) Fungal biomass composite with bentonite efficiency for nickel and zinc adsorption: a mechanistic study. *Ecol Eng* 91:459–471
- Sharma R, Singh B (2013) Removal of Ni (II) ions from aqueous solutions using modified rice straw in a fixed bed column. *Bioresour Technol* 146:519–524
- Sulaymon AH, Yousif SA, Al-Faize MM (2014) Competitive biosorption of lead mercury chromium and arsenic ions onto activated sludge in fixed bed adsorber. *J Taiwan Inst Chem E* 45:325–337
- Tahir N, Bhatti HN, Iqbal M, Noreen S (2017) Biopolymers composites with peanut hull waste biomass and application for crystal violet adsorption. *Int J Biol Macromol* 94:210–220
- Tan HKS, Spinner IH (1994) Multicomponent ion exchange column dynamics. *Can J Chem Eng* 72:330–341
- Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ (2012) Heavy metals toxicity and the environment. *EXS* 101:133–164
- Treybal RE (1993) Mass transfer operations, 2nd edn. McGraw-Hill, New Delhi
- Vicente IA (2011) Tecnología sostenible para la obtención de un biosorbente de metales pesados a partir del bagazo de caña de azúcar. PhD Thesis, Universidad Central “Marta Abreu” de Las Villas, Santa Clara
- Yang J, Volesky B (1996) Intraparticle diffusivity of Cd ions in a new biosorbent material. *J Chem Technol Biotechnol* 66:355–364

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.