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Modelling of the Ni(II) removal from aqueous solutions onto grape stalk wastes in fixed-bed column

César Valderrama*, Jaime A. Arévalo, Ignasi Casas, María Martínez, Nuria Miralles, Antonio Florido

Departament d'Enginyeria Química, ETSEIB, Universitat Politècnica de Catalunya, 08028 Barcelona, Spain

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1. Introduction

Heavy metals are still being used in various industries due to their technological importance. Yet, imperfect treatment of waste products from these industries may lead to both human health and environmental issues [1]. Considering the harmful effects of heavy metals, it becomes then necessary to remove them from liquid wastes at least to the limit accepted by the regulations. For instance, nickel (II) ions have been proved to cause dermatitis or chronic asthma [2,3]. Several methods are employed to remove heavy metal ions from wastewater, which include precipitation, flotation, ion exchange, membrane-related process, electrochemical technique and biological process [1]. In regards of its simplicity and high-efficiency characteristics, the sorption process is one of the few alternatives available for the removal of heavy metals at low concentrations from industrial effluents [4]. Activated carbon, activated alumina or polymer resins which are non-regenerable and expensive materials, are the sorbents usually used for this purpose [5].

A low-cost sorbent is here defined as one which is abundant in nature, or is a by-product or waste material from another industry. Such materials could be an alternative to the conventional sorbents [6]. One of these sorbents is grape stalks wastes generated in the

ABSTRACT

Grape stalk wastes generated in the wine production process were used for the removal of nickel (II) from aqueous solution. The experimental breakthrough curves were obtained in fixed-bed columns. Experiments we carry out in order to evaluate the influence of inlet metal concentration (30 and 70 mg L^{-1}) and the regeneration process in a double sorption cycle.

The CXTFIT code was used to fit the experimental data and to determine the transport and sorption parameters of the convective–dispersive equation (CDE) and the two-site deterministic non-equilibrium (TSM/CDE) model by adjusting the models to the experimental breakthrough curves (BTC). The results showed that bed capacity as well as transport and sorption parameters were affected by the initial metal concentration, at the highest Ni(II) concentration the grape stalks column saturated quickly leading to earlier breakthrough. The sorption capacity of the sorbent was slightly reduced in a double sorption cycle, while the recovery of the metal in the desorption step was ranging between 80% and 85% in both cycles. © 2009 Elsevier B.V. All rights reserved.

wine production process, which has been satisfactorily applied in batch experiments for lead and cadmium removal [6]; copper and nickel [7,8]; and chromium [9]. In these works, sorption of nickel on grape stalks showed the release of an equivalent amount of alkaline and alkaline earth metals (K⁺, Mg²⁺, Ca²⁺) as well as protons, indicating that ionic exchange is predominantly responsible for metal ion uptake. Both batch and kinetic experiments performed at different pH, showed sorption uptake to have a pH-dependent profile, with a maximum metal sorption recovery at around pH 5.5–6.0 [7].

Batch experiments are basically used to obtain equilibrium sorption isotherms and to evaluate the sorption capacity of sorbents for given metals present in fluid phases [10]. However, in the practical operation of full-scale biosorption processes, continuous-flow fixed-bed columns are required in order to predict the transport and sorption parameters. In such systems, the concentration profiles in the liquid and sorbent phases vary in both space and time [11]. As a result, it is difficult to carry out a priori design and optimization of fixed-bed columns without a quantitative approach. From the perspective of process modelling, the dynamic behaviour of a fixed-bed column is described in terms of breakthrough curve [12].

The aim of this study is the evaluation of the grape stalk wastes as sorbent to remove Ni(II) from aqueous solutions in a fixed-bed column. For this purpose, the CXTFIT code [13] was used to estimate the transport and sorption parameters of the convective–dispersive equation (CDE) and the two-site deterministic non-equilibrium (TSM/CDE) models by adjusting the models to the experimental breakthrough curves (BTC). Additionally, sorption zone height and the breakthrough capacity were determined by the column

^{*} Corresponding author at: Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, Av. Diagonal 647, Edifici H Planta 4^{*a*}, 08028 Barcelona, Spain. Tel.: +34 93 401 65 70; fax: +34 93 401 58 14.

E-mail address: cesar.alberto.valderrama@upc.edu (C. Valderrama).

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Table 1

Physical and chemical properties of grape stalk wastes.

Property	Grape stalks
Net amount of cation released (meq g ⁻¹) due to Ni(!	II) sorption
Ca ²⁺	0.382
Mg ²⁺	0.126
K ⁺	0.107
Na ⁺	0.001
CEC ^a (mmol g ⁻¹)	0.36
BET ^b Surface area (m ² g ⁻¹)	0.42
Total porosity (%)	72.3
Bulk density (g dm ⁻³)	304
Apparent density (g dm ⁻³)	1101
Particle size (mm)	0.8–1.0

^a Cation exchange capacity (CEC) [7].

^b BET (Brunauer, Emmet, Teller) method.

experimental data. The influence of the inlet Ni(II) concentration and the desorption process in a consecutive double sorption cycle were evaluated.

2. Materials and methods

2.1. Materials

Grape stalks wastes generated in the wine production process (supplied by a wine manufacturer of the Empordà-Costa Brava region, Girona, Spain), were rinsed three times with deionised water, dried in an oven at 110 °C until constant weight, and finally cut and sieved for a particle size of 0.8-1.0 mm. The properties of the sorbents are listed in Table 1. Metal solutions were prepared by dissolving appropriate amounts of NiCl₂·2H₂O(s) in deionised water (MilliQ system). All reagents were analytical grade and were purchased from Panreac (Barcelona, Spain). Metal standard solutions of 1000 mg L^{-1} purchased from Carlo Erba (Milano, Italy) were used for flame atomic absorption spectroscopy (FAAS).

2.2. Characterization of the sorbent

Fourier transform infrared analysis (FTIR) was performed in order to give a qualitative and preliminary analysis of the main functional groups that might be involved in metal uptake. The FTIR analysis in solid phase was performed using a Fourier transform infrared spectrometer (Galaxy Series FTIR 5000, Mattson). Spectra of the sorbent before and after nickel sorption process were carried out. For FTIR analysis, 300 mg KBr disks containing 3 mg of finely grounded grape stalks were prepared. The surface structure of the grape stalks before and after nickel sorption process was also analysed by scanning electronic microscopy (SEM, Jeol JSM-6400) coupled with energy dispersive X-ray analysis (EDX).

2.3. Sorption column experiments

For nonreactive tracers, like the NO_3^- used to characterize the hydraulic conditions in this study, the convective–dispersive equation can be reduced to [10,14]:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x}$$
(1)

The flow regime can then be characterized by applying the tracer at the same flow rate as the solute influent. Nitrate tracer solutions were prepared by dissolving appropriate amounts of NaNO₃(s). Nitrate anion (100 mg L⁻¹) was used as a tracer previously to each column experiment in order to determine the transport parameters of the column. The tracer was pumped trough the column at the same flow rate to be used in the successive metal uptake determinations and was quantified by high performance liquid chromatography coupled with UV-diode array detector (Waters 2695).

All column experiments were conducted in duplicate in glass columns of 72 mm length and 10 mm internal diameter (Omnifit) and uniformly packed with 1.7–1.8 g of grape stalks treated as explained above. During the column sorption operation, the aqueous metal solution containing either 30 or 70 mg L⁻¹ of the metal under study was pumped upwards through the column at a constant flow rate (11 mL h^{-1}) . The initial pH of the solutions was adjusted to 6. Samples were collected from the outlet of the column by a fraction collector (Gilson FC204) at pre-set time intervals. The pH of the solution was monitored by using a glass electrode and the metal concentration in solution was determined by flame atomic absorption spectrometry using a Varian absorption spectrometer (Model 1275).

2.4. Column regeneration

For any sorption process, one of the most important factors is the recovery of the sorbate material and regeneration capacity of the sorbent. Although, in the present work the recovery of the sorbate it is clearly not an issue because of its nature, the knowledge of this process can give an important insight on the understanding of the overall mechanism of sorption. Consequently, experiments were carried out in which a grape stalks sample was loaded with sorbate and subjected to elution of metal ions with 0.1 M HClO₄ at a flow rate of 11 mL h⁻¹, as in the previous experiments. Samples were collected as described above, and metal concentration was determined by FAAS. The behaviour of sorbent was also evaluated in a double cycle sorption process. The sorbent used after the first cycle (loaded and eluted) was previously washed with deionised water until constant pH before starting the second cycle.

In a previous work [7] the release of cations (K⁺, Mg²⁺, Ca²⁺, H⁺) from grape stalks due to the uptake of Ni(II) indicates that ion exchange as the most important mechanism that take place in sorption process. In a consecutive double cycle sorption process ion exchange between cations and Ni(II) ions take place in the first cycle; therefore protons and Ni(II) ions are exchanged in a second cycle, since the sorbent is eluted with acid prior to the second cycle.

2.5. Breakthrough capacity

The breakthrough point is chosen arbitrarily at some low value, $C_b (mgL^{-1})$, for the effluent concentration, $C_x (mgL^{-1})$, closely approaching to 90% of C_0 (initial concentration of sorbate, mgL⁻¹) then the sorbent is considered to be essentially exhausted [15–17].

The sorption zone computations are defined by the time of exhaustion t_x (h) and the time of passage of through the sorption zone t_{δ} (h):

$$t_{\rm X} = \frac{V_{\rm X}}{Q} \tag{2}$$

$$t_{\sigma} = \frac{(V_{\rm x} - V_{\rm b})}{Q} \tag{3}$$

where V_x and V_b (L) are the volumes of liquid passed through column at exhaustion and breakthrough (90% and 2% of C₀) respectively and Q (Lh⁻¹) is the flow rate. The velocity at which the sorption zone moves through the column is constant except during its formation. This velocity defines the sorption zone height σ (cm).

$$\sigma = \frac{L}{(t_{\rm x} - t_{\rm f})} t_{\sigma} \tag{4}$$

where *L* is the column height (cm) and t_{f} (h) the zone formation time.

The capacity at exhaustion q_{column} (g kg⁻¹) is determined by calculating the total area below the breakthrough curve. This area represents the amounts of solute sorbed by mass of solid in the sorption zone from the breakpoint to exhaustion [16–18].

$$q_{\rm column} = \frac{\int_{V_{\rm b}}^{V_{\rm x}} (C_0 - C) dV}{m_{\rm s}}$$
(5)

where *C* is the outlet metal concentration $(mg L^{-1})$ and m_s is the mass of the sorbent (g).

2.6. Two-site non-equilibrium model

The conceptual model of chemical (two-site) non-equilibrium transport [19] regards the sorption mechanism in two steps, occurring either in series or in parallel. The two-site non-equilibrium concept assumes that sorption sites in soils can be classified into two fractions. In the first fraction, sorption is instantaneous and is described by an equilibrium sorption isotherm (Type 1, equilibrium). In the second fraction, sorption is time-dependent and follows first-order kinetics (Type 2, kinetic).

A model incorporating more than two types of sorption would be more realistic, but difficult to use in the sense of practical application. Thus, the two-site model appears to be a good balance between the degree of accuracy and field applicability. For nonlinear sorption, which is assumed for both sorption domains, the governing equations for the two-site model are [20]:

$$\frac{\partial C}{\partial t} + \left(\frac{\rho}{\theta}\right) \left(\frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t}\right) = D \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x}$$
(6)

$$\frac{\partial S_2}{\partial t} = \alpha[(1 - F)f(C) - S_2]$$
(7)

where *C* is the flux average or resident concentration (mg L⁻¹), ρ is the sorbent bulk density (kg m⁻³), θ is the volumetric water content (m³ m⁻³), *t* is time (h), *S*₁ is the solid phase concentration on equilibrium sites (mg kg⁻¹), *S*₂ is the solid phase concentration on kinetic non-equilibrium sites (mg kg⁻¹), *D* is the dispersion coefficient (cm² h⁻¹), *x* is distance (cm), ν is the average pore water velocity (cm h⁻¹), *F* represents the fraction of the sites available for instantaneous sorption and α is a first-order rate coefficient (h⁻¹).

CXTFIT [13] is a program presenting a number of analytical solutions for one-dimensional transport models based on the convection–dispersion equation (CDE). Assuming steady-state flow in a homogeneous sorbent and first-order transformation kinetics. Both transport and sorption parameters were estimated by using the CXTFIT code under flux-type boundary conditions [10]. In this case, the rate-limiting step for Type 2 sites would be either chemical (chemisorption), or diffusive intra-particle or intrasorbent diffusive mass transfer [13].

At equilibrium, sorption on both types of sorption sites is described by the following linear equations [21–23]:

$$S_1 = Ff(C)$$

$$S_2 = (1 - F)f(C)$$
 (9)

where the subscripts 1 and 2 refer to Type-1 and Type-2 sites, respectively; thus, total sorption, *S*, is given by $S = S_1 + S_2$.

The CXTFIT code adjusts the following dimensionless form of the two-site non-equilibrium model to the breakthrough curves in order to estimate the transport and sorption parameters. If the dimensionless parameters are used the two-site non-equilibrium model reduces to the following dimensionless form:

$$\beta R \frac{\partial C_1}{\partial T} = \left(\frac{1}{P}\right) \left(\frac{\partial^2 C_1}{\partial X^2}\right) - \frac{\partial C_1}{\partial X} - \omega(C_1 - C_2)$$
(10)

$$(1-\beta)R\frac{\partial^2 C_2}{\partial T} = \omega(C_1 - C_2) \tag{11}$$

where the subscripts 1 and 2 refer to equilibrium and nonequilibrium sites, respectively; the dimensionless parameters are defined as follows [13,23]:

$$C_1 = \frac{C}{C_0} \tag{12}$$

$$C_2 = \frac{S_2}{[(1-F)k_L C_0]}$$
(13)

In the above equations C_1 and C_2 (mg L⁻¹) are the relative concentration of metal in equilibrium and kinetic sites, respectively, with respect to the input concentration C_0 (mg L⁻¹);

$$T = \frac{vt}{L} \tag{14}$$

where *T* is the dimensionless time and *L* is column length;

$$X = \frac{x}{L} \tag{15}$$

where X is the dimensionless distance;

$$R = 1 + \frac{\rho k_{\rm L}}{\theta} \tag{16}$$

where *R* is the retardation factor;

$$P = \frac{\nu L}{D} \tag{17}$$

where *P* is the Peclet number;

$$\beta = \frac{(\theta + F\rho k_{\rm L})}{(\theta + \rho k_{\rm L})} \tag{18}$$

where β is the fraction of instantaneous metal retardation and k_{L} (m³ kg⁻¹) is the linear isotherm sorption coefficient;

$$\omega = \frac{\alpha(1-\beta)RL}{\nu} \tag{19}$$

where ω is a dimensionless mass transfer coefficient.

3. Results and discussion

(8)

3.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of grape stalks and grape stalks loaded with nickel are presented in Fig. 1. As shown in the figure, the spectra display a number of absorption peaks, indicating the complex nature of the material examined. The broad absorption peaks around 3424 cm⁻¹ are indicative of the existence of bonded hydroxyl groups (3340–3380 \mbox{cm}^{-1}). The peaks observed at 2921 \mbox{cm}^{-1} can be assigned to the C-H group. The peaks observed at 2925 and 2860 cm⁻¹ can be assigned to the C–H groups of aliphatic acids. The peaks around 1750 cm^{-1} can be attributed to $\hat{C}=0$ stretching vibrations. The peaks around 1623 cm⁻¹ correspond to the C=C stretching that may be attributed to the lignin aromatic C-C bond. The strong C-O band at 1058 cm⁻¹ also confirms the lignin structure of the grape stalks. This C-O band absorption peak is observed to shift to 1032-1034 cm⁻¹ when grape stalks are loaded with nickel, respectively. Thus, it seems that this type of functional group is likely to participate in metal binding.



Fig. 1. FTIR spectra in solid phase of grape stalk wastes in KBr disk.

3.2. Analysis of grape stalks by SEM-EDX

Scanning electron micrographs and spectra of grape stalks before and after sorption are shown in Fig. 2. The pellets observed in SEM were also characterized by energy dispersive X-ray spectrometry (EDX). The EDX analysis shown in Fig. 2b reveal Ni(II) signals, on the surface of the grape stalks after metal sorption. The presence of gold peaks in all spectra is due to the gold purposely settled to make the samples conductive.

3.3. Tracer experiments

The breakthrough curve obtained for the nonreactive tracer (NO_3^-) was fitted by using Eq. (1), using the CXTFIT code. The

Fixed-bed calculations and breakthrough capacity for $\operatorname{Ni}(\operatorname{II})$ sorption onto grape stalks.

C_0	C _x	C _b	$V_{\rm x}$	$V_{\rm b}$	$t_{\rm x}$	t_{f}	$q_{\rm column}$	δ
70	63	1.4	0.59	0.20	54	0.23	14	3.98
30	27	0.6	0.99	0.25	90	0.33	12	4.50
		4.						

 $C_0, C_x, C_b \text{ (mg } L^{-1}\text{)}; V_x, V_b \text{ (L)}; t_x, t_f \text{ (h)}; \delta \text{ (cm)}; q_{\text{column}} \text{ (g } \text{kg}^{-1}\text{)}.$

dispersion coefficient (D) and the average pore water velocity (ν) obtained are presented in the following sections as the physical parameters (R=1). Those two parameters were kept constant for the fitting of the sorption breakthrough curves.

The pore velocity for both columns used in the dynamic test at different inlet concentrations was 3.8 cm h^{-1} . It was expected, since the columns experiments at different inlet concentration were performed at the same flow rate. In the case of dispersion coefficients, the values obtained were $2.88 \text{ and } 2.52 \text{ cm}^2 \text{ h}^{-1}$ for inlet concentrations of $30 \text{ and } 70 \text{ mg L}^{-1}$, respectively. This slightly deviation can be related to the heterogeneity of the sorbent material inside of each column.

3.4. Effect of initial Ni(II) concentration

The increase of the initial Ni(II) concentration, while keeping the other experimental conditions constant, significantly affected the sorption column performance. Fig. 3 shows the experimental breakthrough data and the theoretical model for Ni(II) sorption on grape stalks, while Table 2 reports the breakthrough capacities obtained at both initial concentrations.

When the initial Ni(II) concentration is increased from 30 to 70 mg L⁻¹, the corresponding sorption bed capacity (q_{column}) appears to be no significant differences, a slight increase from 11.83



Fig. 2. (a) (Bar 20 μm) SEM micrograph and EDX spectra of grape stalks before loading and (b) (Bar 20 μm) SEM micrograph and EDX spectra of grape stalks after loading with Ni(II) (1000 mg L⁻¹).



Fig. 3. The measured and modelled breakthrough curves for the sorption of Ni(II) onto grape stalks at different initial concentration.

Table 3

Comparison of the removal capacity obtained for Ni(II) removal onto grape stalks and other types of sorbents in fixed-bed column system.

Sorbent	$q ({ m mg}{ m g}^{-1})$	Reference
Waste of tea factory	11.1	[11]
Sphagnum peat moss	5.41	[25]
Mollusk shells	0.33	[25]
Calcium-treated anaerobic biomass	15	[26]
Marine green alga Ulva reticulata	41.7	[27]
Crab shell particles	24.7	[28]
Grape stalk wastes	14	This work

to 14.36 g kg⁻¹ was observed. A decreased inlet nickel (II) concentrations gave delayed breakthrough curves and the treated volume was also higher, since the lower concentration gradient caused slower transport due to decreased diffusion coefficient [11,24]. At the highest Ni(II) concentration (70 mg L⁻¹) the grape stalks column saturated quickly leading to earlier breakthrough and shorter exhaustion time.

Table 3 shows a comparison between the results of this work and others found in the literature for different types of sorbents in a fixed-bed sorption system [11,25–28]. The values of nickel (II) sorption uptake found in this work in a fixed-bed column configuration were competitive to those reported in literature for different types of sorbents and different experimental conditions.

The simulation of the breakthrough curves at different initial concentration was performed by the CXTFIT code as it has been mentioned in Section 2.6. The transport and sorption parameters are reported in Table 4. Fig. 3 shows the experimental break-through and the theoretical model obtained by the two sites non-equilibrium sorption mechanism. As can be observed, a good fit was obtained for both initial concentrations, denoting that this model describes adequately the transport and the sorption processes. As was expected from the breakthrough calculations the nickel transport was more retarded (large *R* values) at lower inlet concentration [20]. This behaviour was also observed (Table 4) for the parameter β , a partition coefficient which indirectly represents the fraction of the sites available for instantaneous sorption. The



Fig. 4. Breakthrough curves in a first and second cycle (SC) consecutive sorption/desorption experiments at different Ni(II) initial concentration. The continuous line represents the theoretical breakthrough curve for the first cycle and dashed line the second cycle.

linear isotherm sorption coefficients as well as the first-order rate coefficient α were in the same order of magnitude for both inlet Ni(II) concentrations.

The maximum sorbent capacity was also determined in previous batch experiments by the Langmuir isotherm model. The value reported for nickel (II) onto grape stalks waste was 10.5 g kg^{-1} [7]. A comparison of this value to those obtained in the column experiments (Table 2) indicates that batch parameters underestimate the values obtained in the column operation.

3.5. Desorption experiments

Desorption flow experiments were conducted after column saturation with Ni(II) under the conditions mentioned in Section 2.4. The amount of contaminant desorbed was calculated as the area under the breakthrough curve [29]. Fig. 4 shows the results of double consecutive sorption–desorption curves for nickel at two influent metal concentrations. It is observed that the use of the same amount of sorbent after a first cycle reduces the capacity and the efficiency of the breakthrough curve. This effect is slightly more noticeable at higher concentration. For instance, the 30% of the initial concentration (70 mg L⁻¹) was reached at 0.28 and 0.13 L for first and second cycle, respectively. For the 30 mg L⁻¹ column the volumes reported were 0.40 and 0.30 L for first and second cycle, respectively.

From the point of view of the sorption parameters, the sorption capacity in the second cycle decreases to 9.1 and 10.3 mg g⁻¹ for 70 and 30 mg L⁻¹, respectively. The retardation factor (*R*) reported a significant decrease after the first cycle, thus, the values obtained for the second cycle were 21% and 31% the values reported in first cycle for 70 and 30 mg L⁻¹, respectively. These results were in concordance with other studies which observed a significant fall in the sorption capacity of the columns after subsequent cycles [15,30].

Fig. 5 shows the recovery of Ni(II) after the first and second cycle for both initial loaded concentrations. The desorption of grape stalks was completed after 0.033 and 0.045 L of elution solution for

Table 4

Physical parameters obtained by fitting the equilibrium CDE to the breakthrough of NO_3^- tracer (R=1), and model parameters obtained by fitting Ni(II) experimental breakthrough data to the non-equilibrium sorption model.

	Physical parameters $(R=1)$				Two-site sorption model parameters				Langmuir	Pseudo-first-order	
<i>C</i> ₀	D	ν	r ²	SSE	R	β	ω	r^2	SSE	$k_{\rm L}$	α
70	2.52	3.8	0.991	70.2	29.9	0.71	0.035	0.993	56.4	0.02	0.003
30	2.88	3.8	0.995	10.6	36.3	0.88	0.01	0.995	9.2	0.03	0.001

 $SSE = \sum_{i=1}^{N} (q_{cal} - q_{exp})^{2}; C_{0} (mg L^{-1}); D (cm^{2} h^{-1}); \nu (cm h^{-1}); k_{L} (m^{3} kg^{-1}); \alpha (h^{-1}); N = number of experimental points.$



Fig. 5. Recovery of Ni(II) at different initial concentration in a first and second cycle consecutive sorption/desorption experiments.

30 and 70 mg L^{-1} , respectively, and no significant differences were observed in a second cycle desorption. The desorption was ranging between 80% and 85% in both cycles and for both inlet metal concentrations.

The pH was monitoring as a function of time. In the fists cycle the values measured were ranging between 6.3 at starting point of the experiment and 6 when the column was exhausted. In the second cycle the measured pH decreased to values ranging between 2.9 and 3.8 as a consequence of protons release and confirms the ion exchange as a most important mechanism in the metal sorption on the grape stalk wastes. In previous work, batch experiments reported maximum metal removal at pH 6 [7] indicating that the second cycle was performed at no better conditions. Therefore the decrease in the sorption capacity after the first cycle can be explained by decreased in pH as consequence of the ion exchange between protons and metal ions in the second cycle; and can be also related to the possible loss of active sites due to the regeneration process and to the 80% total recovery in the desorption process after first cycle.

4. Conclusions

The results show that the grape stalks wastes can be employed for the removal of nickel (II) from aqueous solutions in column experiments. The breakthrough curve of a nonreactive tracer (NO_3^-) added in the feed solutions enables us to estimate the hydrodynamic dispersion coefficient and mean pore velocity, previous to each column experiment.

The experimental breakthrough curves can be properly described by the convective–dispersive equation (CDE) and the two-site deterministic non-equilibrium (TSM/CDE) model by using the CXTFIT code, a good agreement between the predicted and experimental breakthrough vales were observed. The sorption parameters obtained by the two-site non-equilibrium model were influenced by the inlet nickel (II) ion concentration. At the highest Ni(II) concentration the grape stalks column saturated quickly leading to earlier breakthrough and exhaustion time.

In a consecutive double sorption cycle, a significant decrease in the sorption capacity was observed for nickel (II) sorption at two inlet concentrations, it can be explained by the possible loss of the active sites and the incomplete regeneration of the sorbent after the first cycle was completed; additionally the pH during the second cycle was under the optimal value reported in the batch experiments. The metal desorption was ranging between 80% and 85% in both cycles and for both inlet metal concentrations.

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