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Analysis and modeling of multicomponent sorption of heavy metals on chicken feathers using Taguchi's experimental designs and artificial neural networks

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ABSTRACT

In this study, we have used an integrated approach based on Taguchi's experimental designs and artificial neural networks (ANNs) for the analysis and modeling of the simultaneous removal of cadmium (Cd^{2+}), nickel (Ni^{2+}), and lead (Pb^{2+}) ions from ternary aqueous solutions using chicken feathers. Our results indicated that the multicomponent sorption of these heavy metals on chicken feathers is a complex antagonistic process. Specifically, chicken feathers showed a strong preference for the removal of Pb^{2+} ions in multicomponent solutions and the presence of these ions affected significantly the multicomponent removal of Cd^{2+} and Ni^{2+}. This antagonistic sorption effect is more significant at pH 5 and the sorption preference of chicken feathers during heavy metal removal depends on the solution pH. Results of X-ray absorption near edge structure suggested that sulfide and carboxylic groups of chicken feathers appear to play a relevant role for the removal of heavy metal ions using this biomass. On the other hand, the desorption process using diluted acidic solutions is effective for the recovery of both Pb^{2+} and Cd^{2+} from metal-loaded chicken feathers indicating the feasibility of sorbent regeneration. Finally, ANNs model offers a better performance and more advantages for modeling the sorption of heavy metals in multicomponent solutions than those obtained using Langmuir- and Sips-type multicomponent isotherm equations. This ANNs model is capable of modeling and predicting the sorbent performance at different conditions of pH. In summary, the application of Taguchi's experimental designs and ANNs models is promising for data analysis and modeling of multicomponent pollutant removal for wastewater and water treatment.

Keywords: Multicomponent sorption modeling; Heavy metals; Chicken feathers; Artificial neural networks; Taguchi's experimental designs

1. Introduction

Sorption process is considered as one of the most used and effective techniques for treatment and purification of wastewaters polluted by inorganic and organic toxic compounds including heavy metal ions [1–3]. Until now, several studies on the sorption of heavy metal ions have mainly focused on the uptake of single metals (i.e. monocomponent solutions) using

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a great variety of sorbents [4–8]. However, industrial effluents usually contain several metallic species and it is necessary to study the simultaneous removal of different metal ions to identify and quantify the interactive influence of these pollutants on the sorbent performance [9]. Therefore, the equilibrium and kinetics sorption studies in multicomponent solutions are necessary for this purpose because they allow characterizing the capabilities and limitations of available sorbents for the treatment of wastewaters containing several pollutants. In particular, kinetic experiments are performed to establish the equilibrium time, to study the rate of solute uptake, and to deduce the rate-controlling step; while equilibrium sorption studies are necessary to provide the maximum sorption capacities of the sorbent to calculate physicochemical parameters of sorption process and to determine competitive/synergistic/no-interaction effects in multicomponent solutions [10].

The multicomponent sorption studies are generally performed using the one-factor-at-a-time experiments and factorial experiment designs to determine the effect of operating conditions on the process performance [11–14]. However, the use of these experimental approaches for studying the removal of heavy metals under competitive conditions is very time and effort consuming because the experimental work increases significantly with each additional pollutant present in the solution. Therefore, it is convenient to use experimental strategies that can reduce the number of experiments as well as effective statistical tools to identify and quantify the interactions among different process parameters that affect the sorption performance in multicomponent solutions. In particular, Taguchi's experimental designs are useful to minimize the number of experiments to be conducted because only a fraction of the combination of independent variables is considered. These experimental designs can be used to evaluate the statistical effects of several factors and operating parameters for achieving the optimum conditions of the studied process [15–17]. Taguchi methodology employs several orthogonal arrays such as L_4, L_9, L_{12}, and L_{18}, which focus on the main effects of independent variables and increase the efficacy and reproducibility of small-scale experiments. To date, Taguchi orthogonal arrays have been successfully applied in several science and engineering fields, including the removal of heavy metal ions from water [15,17,18]. For example, Taguchi methodology has been used to identify the effect of several operating parameters on the removal of heavy metals using rice husk ash [17], to optimize the operating conditions for the simultaneous removal of metal ions using bagasse fly ash [15], and to improve the sorption properties of commercial activated carbons for heavy metal removal from water [18], among other applications. In summary, this type of experimental designs is promising and reliable for the analysis of sorption data.

Herein, it is convenient to remark that the data collection in the study of sorption process is normally followed by regression of the experimental information using theoretical or empirical models with the aim of developing mathematical equations that describe satisfactorily the system under analysis. These models can be used for interpolation or extrapolation of sorption behavior, to investigate removal mechanisms, and to calculate parameters useful for the design, optimization, and control of water treatment processes. The modeling of multicomponent equilibrium sorption has been a research topic during several years. The modeling of multisolute sorption is usually approached using classical multicomponent isotherm equations, e.g. Langmuir-, Freundlich- and Sips-type equations [10,19]. However, the modeling of multicomponent sorption data is complex in nature and difficult to face even using traditional sorption equations because the multicomponent systems may show a diversity of sorption effects (i.e. synergistic, antagonistic, and not interaction) that may occur simultaneously depending on the quantity and type of pollutants present in solution. Thus, it is necessary to develop/apply alternative strategies for the reliable modeling and prediction of multicomponent sorption processes. In particular, the complex relationships between the sorbent and the sorbates in multicomponent solutions can be modeled using artificial neural networks (ANNs). ANNs are black-box models useful to establish and analyze non-linear relationships in systems where traditional modeling tools may fail [20]. Consequently, these models are promising for correlating and predicting the complex performance of heavy metal removal in multicomponent solutions.

Based on this fact, in this study, we have used an integrated approach based on Taguchi's experimental designs and ANNs for the analysis and modeling of multicomponent sorption data. Specifically, we have studied the simultaneous removal of cadmium (Cd^{2+}), nickel (Ni^{2+}), and lead (Pb^{2+}) ions from ternary aqueous solutions using chicken feathers as sorbent. Literature indicates that Pb^{2+}, Cd^{2+}, and Ni^{2+} are among the most commonly found metals in industrial effluents. The toxicity of these metallic species on living beings and their impact on the environment have been discussed in several publications, e.g. [8]. Until now, a limited number of studies have been reported on the simultaneous removal of these heavy metal ions in multicomponent systems. On the other hand, chicken feathers are keratin-rich waste residues from the poultry industry, which can be considered as an interesting and promising sorbent for heavy metal removal [7,21–26]. To the best of our knowledge, sorption studies involving chicken feathers and these heavy metals in ternary aqueous solutions have not been reported. Therefore, multicomponent experimental data of heavy metal removal on chicken feathers and ternary systems at different pH conditions have been obtained, using Taguchi orthogonal arrays and ANNs, and have been used for data processing. Our results indicated that the application of both Taguchi's experimental designs and ANNs offers several advantages for the analysis and modeling of the multicomponent sorption of heavy metal ions from aqueous solution.

2. Methodology

2.1. Chicken feathers used as sorbents of heavy metals

Chicken feathers were obtained from the local poultry company Sabropollo (Aguascalientes, Mexico). These feathers were washed with detergent and treated with an aqueous solution of ethanol (20% v/v). Finally, this biomass was rinsed with deionized water several times and dried for 24 h. The rachis of chicken feathers was discarded and the barbs of chicken feathers (0.5 cm length) were used in the sorption experiments.

Physicochemical characterization of this sorbent was performed and results were used in data analysis. First, the point of zero charge (i.e. pH_{pzc}) of chicken feathers was determined using a sorbent-electrolyte ratio of 4 g/L, NaCl solutions and pH from 2 to 8 at 25˚C. The acidic and basic sites of chicken feathers were determined using the procedure reported by Faria et al. [27]. Specifically, 0.2 g of chicken feathers was used with 25 mL of 0.025 M HCl, which were stirred for 3 days at 25˚C. Later, the remaining solution was titrated with 0.025 M NaOH to determine the basic sites. The estimation of acidic sites was performed with a similar procedure, but using 25 mL of 0.025 M NaOH and 0.025 M HCl as titration agent. On the other hand, micrographs of chicken feathers were recorded to observe their morphology using a JEOL JSM-5900LV SEM equipment. FTIR spectra of this biomass were also recorded at a wavelength from 4,000 to 400 cm^{-1} with a resolution of 4 cm^{-1} using a Thermo Scientific Nicolet IS10 FTIR spectrometer with the Smart iTR accessory. Finally, X-ray absorption near edge structure (XANES) analysis was performed on metal-loaded chicken feathers. XANES spectra of the biomass and model compounds were collected at the Stanford Synchrotron Radiation Lightsource (SSRL, Palo Alto, CA) following the procedure reported in previous studies [28] and the data analysis was performed using WinXAS® software.

2.2. Multicomponent sorption studies of Pb^{2+}, Ni^{2+}, and Cd^{2+} in ternay aqueous solutions

The simultaneous sorption of Pb^{2+}, Ni^{2+}, and Cd^{2+} ions on chicken feathers from ternary aqueous solutions were studied at different operating conditions. Specifically, ternary solutions of Pb^{2+}-Ni^{2+}-Cd^{2+} were prepared using reactive-grade nitrate salts and deionized water. Different initial metal concentrations for the ternary systems were used in sorption experiments according to an orthogonal array L_{25}. In particular, we have considered five initial concentrations for each heavy metal ion in the ternary solution, see Table 1. This Taguchi's experimental design was employed to study the effects on sorbent performance caused by the presence of co-ions in the ternary solution using a total of 25 experiments for each pH condition. Note that sorption experiments using monometallic solutions were performed with the same initial concentrations reported in the Taguchi's experimental design. These experiments were employed to identify the antagonistic sorption effects caused by the presence of other metals in the multicomponent system. All experiments were performed randomly at all pH conditions. It is important to remark that the concentrations used in sorption experiments allowed the saturation of the chicken feathers (i.e. maximum sorption capacity) and, consequently, the results obtained are useful to identify the maximum competitive effects caused by the co-ions in the ternary solution. Metal concentrations of ternary systems include: 0.1–1.0 mmol/L for Pb^{2+}, 0.1–3.0 mmol/L for Ni^{2+}, and 0.1–1.78 mmol/L for Cd^{2+}, respectively. The pH of metal solutions was adjusted using HNO_3 and NaOH. Multicomponent sorption experiments were performed using 15 mL of ternary solution and 0.06 g of chicken feathers at 30˚C and given pH (i.e. from 3 to 5). Batch reactors were used for these experiments and the equilibrium time was determined as 24 h using 200 rpm of stirring. Metal uptakes were calculated using initial and equilibrium concentrations via a mass balance

$$q_{\text{mix,i}} = \frac{\left([M^{2+}]_0 - [M^{2+}]_e\right)V}{m} \quad (1)$$

where $[M^{2+}]_0$ and $[M^{2+}]_e$ are the initial and final concentration of metal i in the multicomponent solution,

Table 1
Taguchi orthogonal array L_{25} used for the analysis of multicomponent removal of Pb^{2+}, Cd^{2+}, and Ni^{2+} in ternary aqueous solutions using chicken feathers. Ternary solutions used in sorption experiments were prepared using the initial concentrations reported in this table

Experiment no.	Initial concentration of ternary aqueous solutions		
	Pb^{2+}	Ni^{2+}	Cd^{2+}
1	0.10	0.10	0.11
2	0.10	0.85	0.49
3	0.10	1.53	0.98
4	0.10	2.21	1.51
5	0.10	2.98	1.78
6	0.24	0.10	0.49
7	0.24	0.85	0.98
8	0.24	1.53	1.51
9	0.24	2.21	1.78
10	0.24	2.98	0.11
11	0.48	0.10	0.98
12	0.48	0.85	1.51
13	0.48	1.53	1.78
14	0.48	2.21	0.11
15	0.48	2.98	0.49
16	0.75	0.10	1.51
17	0.75	0.85	1.78
18	0.75	1.53	0.11
19	0.75	2.21	0.49
20	0.75	2.98	0.98
21	1.01	0.10	1.78
22	1.01	0.85	0.11
23	1.01	1.53	0.49
24	1.01	2.21	0.98
25	1.01	2.98	1.51

V is the volume of ternary mixture used for sorption experiments, and m is the amount of chicken feathers employed in the removal of heavy metals, respectively. Metal concentrations in sorption experiments were determined using a Perkin Elmer Analyst 100 atomic absorption spectrometer.

Data analysis of the L_{25} design was performed using the signal-to-noise (S/N) ratio applied on the ratio of sorption capacities (R_{qi})

$$R_{qi} = \frac{q_{\text{mix,i}}}{q_{0,i}}\bigg|_{[\text{Metal i}]_0} \quad (2)$$

where $q_{\text{mix},i}$ is the uptake of metal ion i in the ternary mixture with a given initial concentration and $q_{0,i}$ is the metal uptake for the same metal in a monocomponent solution with the same initial concentration used in the ternary mixture, respectively. Note that $R_{qi} < 1$ for tested metal ions because these metals showed an antagonistic (i.e. competitive) sorption in ternary systems using chicken feathers.

The S/N analysis for R_{qi} was performed to identify the magnitude of the effect of co-ion concentrations on the removal performance of chicken feathers. We have used the following equations for the statistical analysis of our experimental data

$$S/N = -10\log\left(\frac{1}{n_{\text{rep}}}\sum_{i=1}^{n_{\text{rep}}}\left[\frac{1}{x_i^2}\right]\right) \quad (3)$$

$$SS_T = \left[\sum_{i=1}^{n_{\text{dat}}} y_i^2\right] - \frac{T_t^2}{n_{\text{dat}}} \quad (4)$$

$$SS_F = \left[\sum_{i=1}^{k_F}\left(\frac{F_i^2}{n_{F_i}}\right)\right] - \frac{T_t^2}{n_{\text{dat}}} \quad (5)$$

$$\sigma_F = \frac{SS_F}{v_F} \quad (6)$$

where Eq. (2) is used for the calculation of S/N ratio involving the quality characteristic ($x_i = R_{qi}$) obtained from the experimental design, n_{dat} is the number of experimental data used for the statistical analysis, and $n_{\text{rep}} = 3$ is the number of replicates of experiments performed for the orthogonal array. Eqs. (4)–(6) have been used for the variance analysis, where n_{Fi} is the number of observations under the level i; F_i is obtained from the sum of observations under the level i; T_t is the sum of all observations; y_i is the value of the S/N ratio; SS_T is the total sum of squares; k_F is the number of levels of factor F; v_F is the degrees of freedom of factor F (i.e. $k_F - 1$); σ_F is the variance for factor F; and SS_F is the sum of squares for factor F, respectively. For this statistical analysis, the initial concentrations of each co-ion are considered as the independent variables. Plots of the mean S/N ratios were used for identifying the effect and magnitude of co-ion concentrations on the multicomponent removal of chicken feathers.

Finally, we have performed desorption experiments using metal-loaded chicken feathers obtained from sorption experiments at pH 5 and 30°C. In particular, different diluted acidic solutions were used in these experiments: 0.1 M HCl and CH_3COOH. For these experiments, the metal-loaded samples obtained from sorption experiments with different initial metal concentrations were used. Thus, these samples were prepared according to an orthogonal array L_9 (see

Table 2) and the desorption process was performed using 0.06 g of metal-loaded chicken feathers and 15 mL of desorbing solution at 30˚C during 24 h, which was established as the equilibrium time. The final concentration of metal ions in the solution was determined and the metal recovery ratio was calculated.

2.3. Modeling of multicomponent sorption of heavy metals on chicken feathers using ANNs

An ANN-based model was used for data fitting of multicomponent sorption of heavy metals on chicken feathers. ANNs model consists of input, hidden, and output layers, which are constituted by an interconnected group of processing units called artificial neurons [20]. These neurons are interconnected to each other via connection weights, which represent the relative strength of an input neuron in contribution to the

Table 2
Taguchi orthogonal array L_9 used for the metal desorption experiments. Samples of metal-loaded chicken feathers were prepared using the metal concentrations given in this experimental design

	Ternary aqueous solution used for the preparation of sorbent samples, mmol/L		
Sample no.	Pb^{2+}	Ni^{2+}	Cd^{2+}
1	0.1	0.1	0.1
2	0.1	1.53	0.98
3	0.1	3.07	1.78
4	0.48	0.1	0.98
5	0.48	1.53	1.78
6	0.48	3.07	0.1
7	1	0.1	1.78
8	1	1.53	0.1
9	1	3.07	0.98

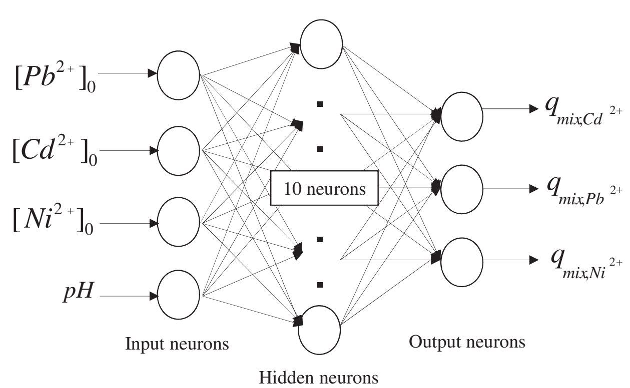

Fig. 1. ANN architecture used for modeling the multicomponent sorption of Pb^{2+}, Ni^{2+}, and Cd^{2+} on chicken feathers.

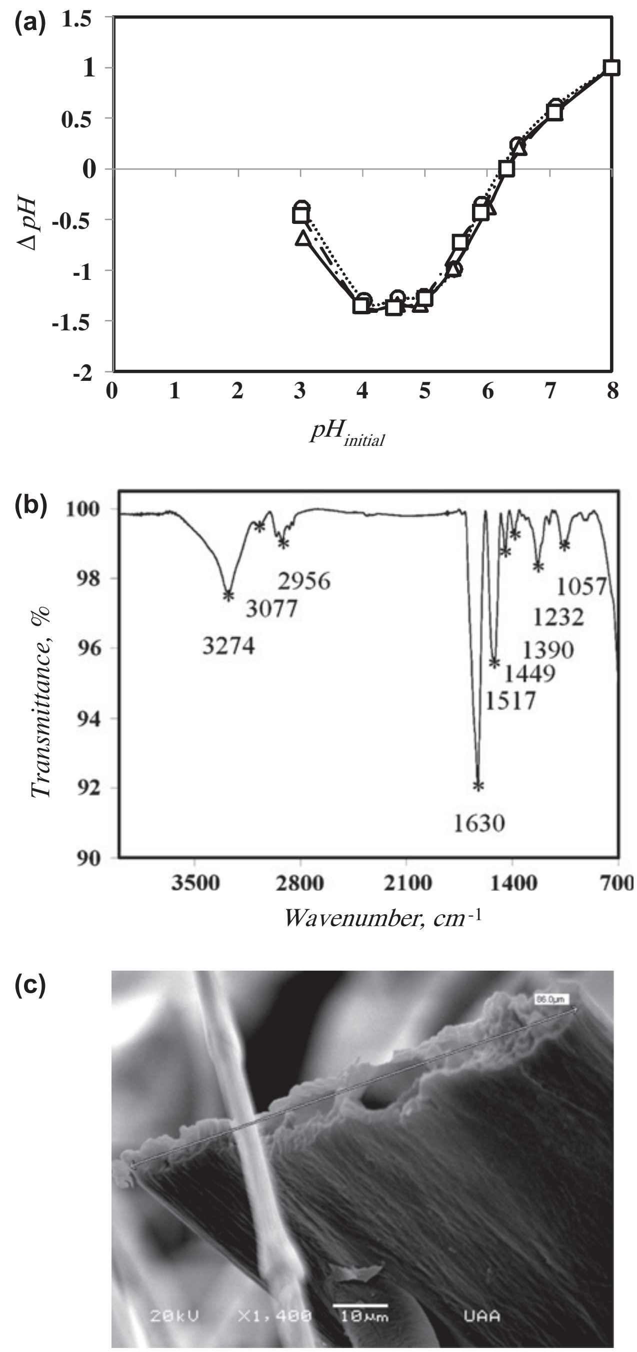

Fig. 2. Results of physicochemical characterization of chicken feathers used for heavy metal removal. (a) pH of zero charge (pH_{pzc}), (b) FTIR spectrum, and (c) SEM image.

output neuron. Mathematically, the net input Y_{ij} of the neuron j in the layer i is given by

$$Y_{ij} = \sum_{k=1}^{n_{i-1}} w_{ijk} V_{i-1,k} + \theta_{ij} \quad (7)$$

$$V_{ij} = g(Y_{ij}) \quad (8)$$

where w_{ijk} is the connection weight, V_{ik} is the neuron input, and θ_{ij} is the bias of the neuron. An activation function $g(Y_{ij})$ is applied to calculate the neuron output V_{ij}. A training process is used to determine suitable values of w and θ for each neuron of the ANNs model where input data and target output values obtained from the system under study are employed. In this study, we have proposed the network topology given in Fig. 1 for modeling the simultaneous sorption of Pb^{2+}, Ni^{2+}, and Cd^{2+} on chicken feathers. In this ANNs model, the input data include the initial concentration of metal ions $[M^{2+}]_0$ in the ternary mixture and pH, while the target values were the sorption capacities ($q_{\mathrm{mix},i}$) of the three metal ions. It is convenient to note that the multilayer perceptron is the common and standard ANNs model. This ANNs approach can model complex non-linear problems and it is considered as a universal approximator due to its flexibility and reliability for data modeling [29,30]. Literature indicates that the multilayer perceptron is capable of modeling complex systems if the proper number of hidden neurons is identified [29]. Based on this fact, data modeling was performed using the neural network toolbox of Matlab® where the backpropagation algorithm with one hidden layer, with 10 neurons, was employed. The architecture of ANNs model was determined via trial-and-error calculations where the number of neurons were changed until finding a proper ANNs performance. Note that these conditions for ANNs model were used to avoid overfitting. The ratios of experimental data used for training, testing, and validation of ANNs model were 70, 15, and 15%, respectively. Overall, 225 experimental data were used in the ANNs modeling. The weights w and biases θ of the ANNs model were iteratively

Table 3
Results of the multicomponent sorption of Pb^{2+}, Cd^{2+}, and Ni^{2+} on chicken feathers in ternary aqueous solutions at 30°C and pH 3

	$[M^{2+}]_0$, mmol/L			$q_{\mathrm{mix},i}$, mmol/g			$R_{qi} = q_{\mathrm{mix},i}/q_{0,i}$		
No.	Pb^{2+}	Ni^{2+}	Cd^{2+}	Pb^{2+}	Ni^{2+}	Cd^{2+}	Pb^{2+}	Ni^{2+}	Cd^{2+}
1	0.10	0.10	0.11	0.0017	0.0020	0.0014	1.02	0.97	1.14
2	0.10	0.85	0.49	0.0015	0.0073	0.0076	1.17	0.92	0.63
3	0.10	1.53	0.98	0.0014	0.0156	0.0113	1.10	1.12	0.47
4	0.10	2.21	1.51	0.0015	0.0171	0.0178	1.16	0.92	0.66
5	0.10	2.98	1.78	0.0012	0.0206	0.0195	0.94	1.00	0.72
6	0.24	0.10	0.49	0.0026	0.0018	0.0074	0.80	0.88	0.61
7	0.24	0.85	0.98	0.0025	0.0084	0.0169	0.77	1.06	0.70
8	0.24	1.53	1.51	0.0037	0.0137	0.0204	1.14	0.98	0.76
9	0.24	2.21	1.78	0.0030	0.0167	0.0169	0.92	0.91	0.62
10	0.24	2.98	0.11	0.0033	0.0167	0.0016	1.02	0.81	1.16
11	0.48	0.10	0.98	0.0056	0.0017	0.0148	0.86	0.84	0.62
12	0.48	0.85	1.51	0.0062	0.0077	0.0185	0.96	0.98	0.69
13	0.48	1.53	1.78	0.0064	0.0124	0.0136	0.98	0.88	0.50
14	0.48	2.21	0.11	0.0048	0.0190	0.0014	0.73	1.03	1.23
15	0.48	2.98	0.49	0.0040	0.0147	0.0068	0.73	0.72	0.56
16	0.75	0.10	1.51	0.0067	0.0024	0.0167	0.90	1.14	0.62
17	0.75	0.85	1.78	0.0064	0.0071	0.0118	0.86	0.90	0.43
18	0.75	1.53	0.11	0.0060	0.0150	0.0012	0.81	1.07	1.04
19	0.75	2.21	0.49	0.0074	0.0116	0.0033	0.99	0.63	0.28
20	0.75	2.98	0.98	0.0077	0.0133	0.0128	1.03	0.65	0.53
21	1.01	0.10	1.78	0.0073	0.0023	0.0103	0.98	1.13	0.38
22	1.01	0.85	0.11	0.0073	0.0053	0.0008	0.97	0.67	0.80
23	1.01	1.53	0.49	0.0070	0.0100	0.0041	0.94	0.84	0.34
24	1.01	2.21	0.98	0.0064	0.0137	0.0171	0.86	0.74	0.71
25	1.01	2.98	1.51	0.0059	0.0134	0.0131	0.79	0.65	0.49

adjusted to minimize the following performance function

$$\mathrm{MSE} = \frac{1}{n_{\mathrm{dat}}}\sum_{j=1}\left[\left(q^{\exp}_{\mathrm{mix,Pb,j}} - q^{\mathrm{ANNs}}_{\mathrm{mix,Pb,j}}\right)^2 + \left(q^{\exp}_{\mathrm{mix,Ni,j}} - q^{\mathrm{ANNs}}_{\mathrm{mix,Ni,j}}\right)^2 + \left(q^{\exp}_{\mathrm{mix,Cd,j}} - q^{\mathrm{ANNs}}_{\mathrm{mix,Cd,j}}\right)^2\right] \quad (9)$$

where $q^{\exp}_{\mathrm{mix,ij}}$ and $q^{\mathrm{ANNs}}_{\mathrm{mix,ij}}$ are the experimental and ANNs-calculated multicomponent sorption capacities of metal ions for chicken feathers and n_{dat} is the number of experimental used for ANNs training, respectively.

Finally, we have performed a comparison of the results obtained with ANNs model and those obtained with the non-modified Langmuir, extended Langmuir and non-modified Sips multicomponent isotherms. These isotherm equations are given by

$$q_{\mathrm{mix,i}} = \frac{q_{m,i}K_{L,i}[M^{2+}]_{e,i}}{1 + \sum_{j=1}^{N} K_{L,j}[M^{2+}]_{e,j}} \quad (10)$$

$$q_{\mathrm{mix,i}} = \frac{q_{\max}K_{L,i}[M^{2+}]_{e,i}}{1 + \sum_{j=1}^{N} K_{L,j}[M^{2+}]_{e,j}} \quad (11)$$

$$q_{\mathrm{mix,i}} = \frac{a_{si}[M^{2+}]_{e,i}^{1/n_{si}}}{1 + \sum_{j=1}^{N} b_{si}[M^{2+}]_{e,i}^{1/n_{si}}} \quad (12)$$

where q_{max}, $q_{m,i}$, and $K_{L,i}$ are the parameters of Langmuir-based models; a_{si}, b_{si}, and n_{si} are the adjustable parameters of Sips model for each competitive pollutant; and N is the number of pollutants in the solution [31,32]. A non-linear regression procedure was used for determining the adjustable parameters of multicomponent isotherm equations using the Simulated Annealing optimization method [33].

Table 4
Results of the multicomponent sorption of Pb^{2+}, Cd^{2+}, and Ni^{2+} on chicken feathers in ternary aqueous solutions at 30°C and pH 4

	$[M^{2+}]_0$, mmol/L			$q_{\mathrm{mix},i}$, mmol/g			$R_{qi} = q_{\mathrm{mix},i}/q_{0,i}$		
No.	Pb^{2+}	Ni^{2+}	Cd^{2+}	Pb^{2+}	Ni^{2+}	Cd^{2+}	Pb^{2+}	Ni^{2+}	Cd^{2+}
1	0.10	0.10	0.11	0.0058	0.0024	0.0039	0.97	1.13	1.12
2	0.10	0.85	0.49	0.0066	0.0140	0.0096	1.11	0.96	0.71
3	0.10	1.53	0.98	0.0065	0.0236	0.0165	1.08	0.73	0.60
4	0.10	2.21	1.51	0.0064	0.0312	0.0153	1.08	0.74	0.49
5	0.10	2.98	1.78	0.0054	0.0321	0.0161	0.91	0.66	0.51
6	0.24	0.10	0.49	0.0105	0.0024	0.0093	1.04	1.11	0.69
7	0.24	0.85	0.98	0.0109	0.0134	0.0149	1.08	0.92	0.53
8	0.24	1.53	1.51	0.0099	0.0237	0.0174	0.98	0.74	0.55
9	0.24	2.21	1.78	0.0100	0.0239	0.0192	0.99	0.57	0.61
10	0.24	2.98	0.11	0.0090	0.0267	0.0031	0.89	0.55	0.97
11	0.48	0.10	0.98	0.0169	0.0018	0.0141	0.97	0.81	0.51
12	0.48	0.85	1.51	0.0178	0.0110	0.0154	1.03	0.76	0.49
13	0.48	1.53	1.78	0.0176	0.0180	0.0138	1.02	0.56	0.44
14	0.48	2.21	0.11	0.0155	0.0251	0.0023	0.89	0.60	0.71
15	0.48	2.98	0.49	0.0143	0.0291	0.0060	0.82	0.60	0.45
16	0.75	0.10	1.51	0.0203	0.0021	0.0140	0.93	0.98	0.44
17	0.75	0.85	1.78	0.0183	0.0106	0.0118	0.83	0.73	0.37
18	0.75	1.53	0.11	0.0189	0.0194	0.0018	0.86	0.60	0.56
19	0.75	2.21	0.49	0.0209	0.0177	0.0059	0.95	0.42	0.44
20	0.75	2.98	0.98	0.0211	0.0201	0.0073	0.96	0.42	0.26
21	1.01	0.10	1.78	0.0219	0.0014	0.0105	1.01	0.63	0.33
22	1.01	0.85	0.11	0.0218	0.0084	0.0019	1.00	0.58	0.60
23	1.01	1.53	0.49	0.0203	0.0135	0.0054	0.93	0.42	0.40
24	1.01	2.21	0.98	0.0182	0.0158	0.0087	0.84	0.38	0.31
25	1.01	2.98	1.51	0.0211	0.0156	0.0089	0.97	0.32	0.28

3. Results

3.1. Multicomponent sorption of Pb^{2+}, Ni^{2+}, and Cd^{2+} on chicken feathers from ternary aqueous solutions

Fig. 2 shows the results of physicochemical characterization of chicken feathers used as sorbents for heavy metal removal. Overall, chicken feathers showed a slight acidic character with a $pH_{pzc} = 6.25 \pm 0.1$, see Fig. 2(a). In particular, the concentrations of acidic and basic sites of this sorbent are 0.52 and 0.42 mmol/g, respectively. FTIR spectrum confirmed that absorption bands, identified in chicken feathers, are characteristic of keratin, see Fig. 2(b). The vibrations in the amide group of the peptide bonds correspond to bands at 1,232, 1,517, 1,630, and 3,274 cm^{-1}. The signals observed in the region 2,700–3,100 cm^{-1} correspond to the C–H vibrations of aliphatic structures. The amide I band is originated mainly by C=O stretching vibration; while the amide II band results from N–H bending and C–N stretching vibrations; finally, the amide III is a very complex band deriving from in-phase combination of C–N stretching and N–H in-plane bending with contributions of C–C stretching and C=O bending [34–36]. FTIR analysis also confirmed the presence of ionizable-functional groups as carboxylic, carbonyl, and amine, which are able to interact with heavy metal ions [37,38]. SEM micrographs of chicken feathers (Fig. 2(c)) showed a fibrous surface where the main elements of this biomass are carbon, oxygen, nitrogen, hydrogen, and sulfur, which are also associated to the keratin content of the sorbent.

Tables 3–5 show the results of multicomponent removal of heavy metals Pb^{2+}, Ni^{2+}, and Cd^{2+} on chicken feathers from ternary solutions at 30˚C and pH from 3 to 5. In particular, these tables provide the equilibrium sorption capacities ($q_{mix,i}$) for each metal ion and the corresponding values of $q_{mix,i}/q_{0,i}$ for the experimental conditions given by the ortogonal array L_{25}. Overall, there is a reduction in the uptakes of all heavy

Table 5
Results of the multicomponent sorption of Pb^{2+}, Cd^{2+}, and Ni^{2+} on chicken feathers in ternary aqueous solutions at 30˚C and pH 5

	$[M^{2+}]_0$, mmol/L			$q_{mix,i}$, mmol/g			$R_{qi} = q_{mix,i}/q_{0,i}$		
No.	Pb^{2+}	Ni^{2+}	Cd^{2+}	Pb^{2+}	Ni^{2+}	Cd^{2+}	Pb^{2+}	Ni^{2+}	Cd^{2+}
1	0.10	0.10	0.11	0.0132	0.0025	0.0050	0.95	0.87	0.83
2	0.10	0.85	0.49	0.0129	0.0193	0.0139	0.93	0.98	0.80
3	0.10	1.53	0.98	0.0125	0.0294	0.0190	0.90	0.71	0.61
4	0.10	2.21	1.51	0.0121	0.0400	0.0293	0.87	0.67	0.75
5	0.10	2.98	1.78	0.0126	0.0410	0.0284	0.91	0.64	0.72
6	0.24	0.10	0.49	0.0206	0.0027	0.0141	0.97	0.91	0.81
7	0.24	0.85	0.98	0.0208	0.0171	0.0221	0.98	0.87	0.71
8	0.24	1.53	1.51	0.0209	0.0265	0.0274	0.99	0.64	0.70
9	0.24	2.21	1.78	0.0214	0.0371	0.0266	1.01	0.62	0.68
10	0.24	2.98	0.11	0.0202	0.0382	0.0030	0.95	0.59	0.50
11	0.48	0.10	0.98	0.0299	0.0028	0.0240	0.92	0.95	0.78
12	0.48	0.85	1.51	0.0307	0.0140	0.0265	0.95	0.71	0.68
13	0.48	1.53	1.78	0.0301	0.0279	0.0256	0.93	0.67	0.65
14	0.48	2.21	0.11	0.0306	0.0360	0.0023	0.94	0.60	0.39
15	0.48	2.98	0.49	0.0312	0.0315	0.0089	0.96	0.49	0.51
16	0.75	0.10	1.51	0.0359	0.0033	0.0326	0.89	1.14	0.84
17	0.75	0.85	1.78	0.0360	0.0133	0.0203	0.89	0.67	0.52
18	0.75	1.53	0.11	0.0356	0.0208	0.0024	0.88	0.50	0.40
19	0.75	2.21	0.49	0.0360	0.0331	0.0079	0.89	0.56	0.45
20	0.75	2.98	0.98	0.0362	0.0340	0.0160	0.90	0.53	0.52
21	1.01	0.10	1.78	0.0375	0.0027	0.0196	0.92	0.92	0.50
22	1.01	0.85	0.11	0.0401	0.0160	0.0025	0.98	0.82	0.41
23	1.01	1.53	0.49	0.0421	0.0245	0.0079	1.03	0.59	0.45
24	1.01	2.21	0.98	0.0388	0.0273	0.0190	0.95	0.46	0.61
25	1.01	2.98	1.51	0.0410	0.0298	0.0177	1.00	0.46	0.45

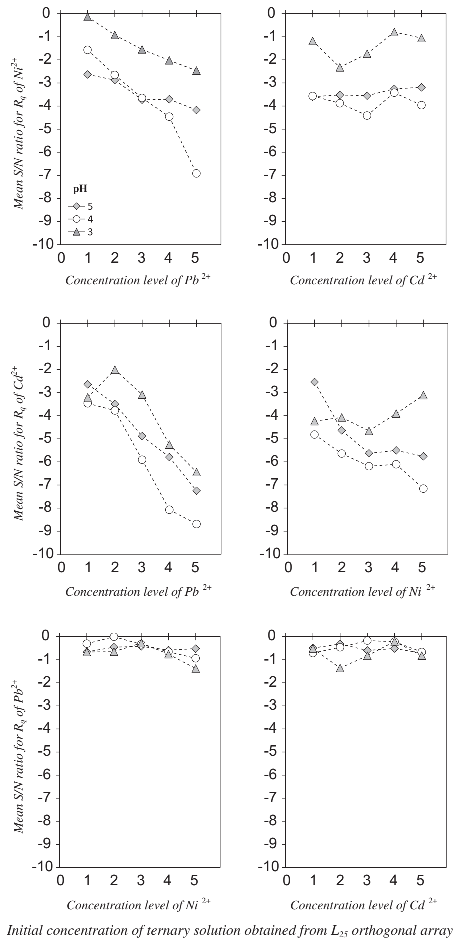

Fig. 3. Mean S/N ratios calculated for $R_{q,i}$ in the multicomponent sorption of heavy metals in ternary aqueous solutions using chicken feathers. Metal concentration level: (a) Pb^{2+}: 1 = 0.1, 2 = 0.24, 3 = 0.48, 4 = 0.75, and 5 = 1.0; (b) Ni^{2+}: 1 = 0.1, 2 = 0.85, 3 = 1.53, 4 = 2.21, and 5 = 2.98; and (c) Cd^{2+}: 1 = 0.1, 2 = 0.49, 3 = 0.98, 4 = 1.51, and 5 = 1.78 mmol/L, respectively.

metals in ternary mixtures with respect to the results obtained with monometallic solutions (i.e. $R_{qi} < 1$). These results confirmed that the simultaneous presence of Pb^{2+}, Cd^{2+}, and Ni^{2+} in the ternary mixture caused an antagonistic effect (i.e. competitive sorption) during heavy metal removal using chicken feathers. It is convenient to remark that the removal of Pb^{2+} is less affected by the presence of other metal co-ions in ternary systems independent of the solution pH. In addition, the multicomponent sorption of Ni^{2+} is mainly inhibited by the presence of Pb^{2+}, while the removal of Cd^{+2} is more sensitive to the presence of both Pb^{2+} and Ni^{2+} ions. These trends can be clearly observed in the plots of mean S/N ratios given in Fig. 3. Overall, the removal performance of chicken feathers (i.e. R_{qi}) decreased with increments of the initial concentrations of the heavy metals in the ternary system and the antagonistic sorption is more significant when the concentration of the target metal is low and the co-ion concentrations are high. This unfavorable effect on the uptakes of chicken feathers is caused by the competition of metal ions for the binding sites of the sorbent. Similar findings have been reported by Mahamadi and Nharingo [38] using *Eichhornia crassipes* for the

Table 7
Results of data modeling of multicomponent sorption of Pb^{2+}, Cd^{2+}, and Ni^{2+} on chicken feathers using traditional multicomponent isotherm equations and ANNs model

Model	R^2
Non-modified Langmuir	0.92
Extended Langmuir	0.88
Non-modified Sips	0.95
ANNs model	0.97

Table 6
Statistical analysis of Taguchi's experimental designs used for the multicomponent sorption of heavy metals on chicken feathers

		S/N ratio for					
		R_q of Pb^{2+}		R_q of Ni^{2+}		R_q of Cd^{2+}	
pH	Factor: $[M^{2+}]_0$	SS_F	σ_F	SS_F	σ_F	SS_F	σ_F
5	Pb^{2+}	2.09	0.52	8.30	2.08	66.72	16.68
	Ni^{2+}	0.18	0.04	78.15	19.54	36.11	9.03
	Cd^{2+}	0.42	0.11	0.69	0.17	30.28	7.57
4	Pb^{2+}	2.87	0.72	82.25	20.56	114.46	28.61
	Ni^{2+}	2.57	0.64	98.41	24.60	14.57	3.64
	Cd^{2+}	1.23	0.31	2.96	0.74	75.02	18.75
3	Pb^{2+}	18.28	4.57	16.76	4.19	64.80	16.20
	Ni^{2+}	3.17	0.79	18.09	4.52	6.49	1.62
	Cd^{2+}	3.65	0.91	7.48	1.87	253.20	63.20

removal of Pb^{2+}, Cd^{2+}, and Zn^{2+} in binary and ternary solutions, where an antagonistic sorption effect was observed for all metal ions.

In fact, we can conclude that chicken feathers have a more affinity for the removal of Pb^{2+} ion in multicomponent solutions. The sorption preference of chicken feathers for Pb^{2+} may due to this metal that showed the major electronegativity and the lowest ionic radius. According to literature, this removal behavior of Pb^{2+} ions appears to prevail for different sorbents. For example, Qin et al. [39] have reported the removal of Pb^{2+}, Cd^{2+}, and Cu^{2+} using peat in ternary systems. These authors observed decrements in the removal performance of peat from 30 to 91%. In particular, this study showed that the presence of Pb^{2+} inhibited the removal of both Cu^{2+} and Cd^{2+}. In other study, Seker et al. [40] used *Spirulina platensis* for the removal of Pb^{2+}, Cd^{2+}, and Ni^{2+} in ternary systems and they reported that the presence of both Cd^{2+} and Ni^{2+} did not affect the removal of Pb^{2+}, where Cd^{2+} and Ni^{2+} showed $q_{\mathrm{mix},i}/q_{0,i}$ values of 0.28 and 0.61, respectively. Finally, Romera et al. [41] reported the multicomponent removal of Cd^{2+}, Cu^{2+}, and Ni^{2+} using *Fucus spiralis* in ternary mixtures. These authors showed that the removal of Cu^{2+} was higher than those obtained for both Cd^{2+} and Ni^{2+} in multicomponent systems. In fact, it appears that Ni^{2+} did not affect the removal of Cd^{2+}, nevertheless Cd^{2+} affected the removal of Ni^{2+} for low concentrations of Cu^{2+}. This study concluded that the sorption of Cu^{2+} was slightly affected by Ni^{2+}, while Cd^{2+} did not show a significant effect on the removal of this heavy metal.

On the other hand, pH is a relevant parameter for the multicomponent sorption of metal ions using chicken feathers and the metal uptake decreased with the solution acidity. In particular, the sorption capacities of Ni^{2+} and Cd^{2+} are significantly affected by changes in solution pH, see results reported in Tables 3–5 and Fig. 3. For the case of Pb^{2+}, the metal uptakes showed a reduction of 37, 18, and 13% for pH 3, 4, and 5, respectively. The multicomponent sorption of Ni^{2+} decreased from 37 to 68% for the same pH conditions, while the Cd^{2+} uptakes of chicken feathers were reduced by 61–74% at these operating conditions. This removal performance suggests that the deprotonation of functional groups may contribute significantly to the mechanism of metal binding by chicken feathers. The analysis of mean S/N ratios for R_q confirmed that the selectivity of chicken feathers for the sorption of tested heavy metals was reduced significantly at pH 3. As stated in previous studies [7,25,26], the sorption capacities of chicken feathers are pH dependent and the removal performance is reduced with decrements on solution pH due to the competition of protons for the binding sites of the sorbent. Therefore, it is expected that the concentration of H^+ is higher if the solution acidity increases and, consequently, the competition between these protons and heavy metal ions

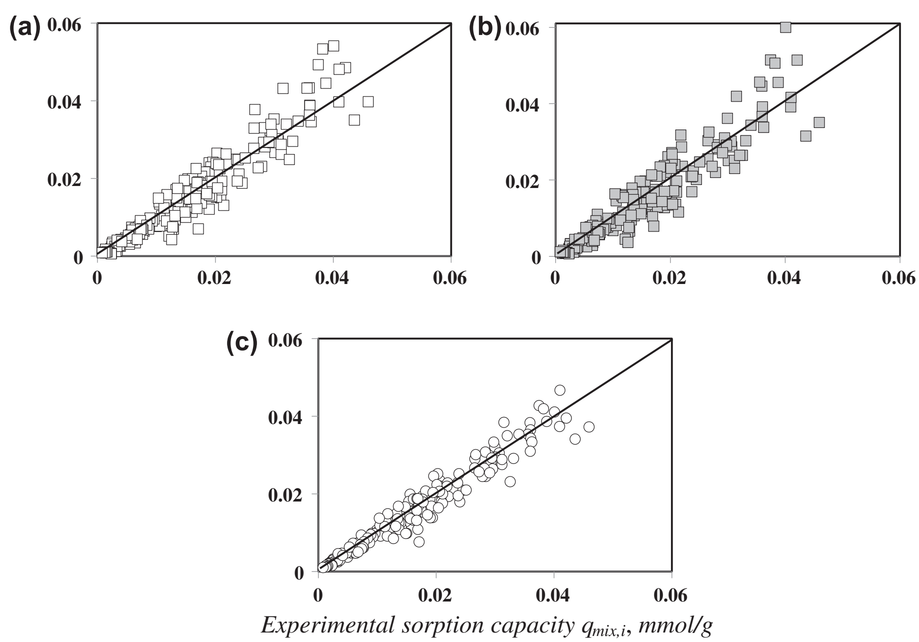

Fig. 4. Comparison of experimental and calculated multicomponent sorption capacities of heavy metals on chicken feathers using (a) Non-modified Langmuir, (b) Extended Langmuir and (c) Non-modified Sips isotherm model.

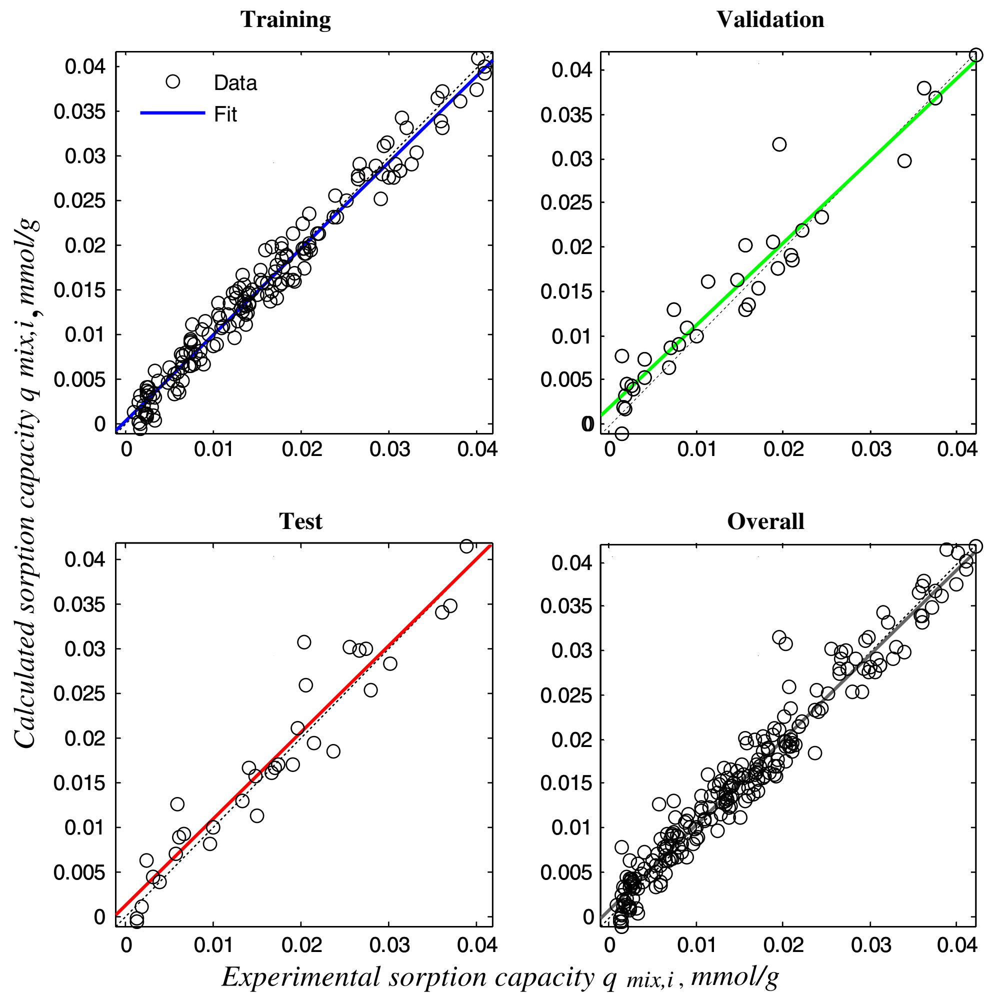

Fig. 5. Results of multicomponent sorption modeling of heavy metals on chicken feathers using ANNs model.

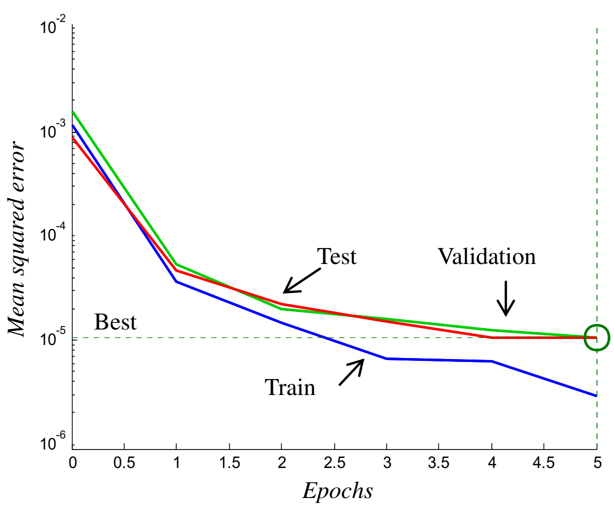

Fig. 6. Convergence profile of ANNs model for data correlation of multicomponent sorption of heavy metals on chicken feathers.

is more intensive, causing a reduction of the antagonistic effect of co-ion concentrations on the sorbent performance (i.e. there is a reduction on the competitive sorption of these metal ions). Note that a strong acidic pH may affect the removal mechanisms involved in the sorption of heavy metal ions [42], which may include a combination of different mechanisms such as ion exchange, quelation, electrostatic interactions, among others [10]. On the other hand, the Pb^{2+} removal was less affected by solution pH, see Fig. 3. This result suggests that there may be more effective interactions between the sorbent and Pb^{2+} ions than those of other co-ions.

Results of the statistical analysis of experimental data using the S/N ratios are reported in Table 6. We confirmed that both the co-ion concentrations and solution pH have a significant impact on the multicomponent sorption performance of chicken feathers for the removal of heavy metal ions. In general, the

Table 8
Results of desorption experiments using multicomponent metal-loaded chicken feathers and diluted acidic solutions

No	$[M^{2+}]$[a], mmol/L			Desorption (%) for HCl			Desorption (%) for CH_3COOH		
	Pb^{2+}	Ni^{2+}	Cd^{2+}	Pb^{2+}	Ni^{2+}	Cd^{2+}	Pb^{2+}	Ni^{2+}	Cd^{2+}
1	0.1	0.1	0.1	88.94	10.67	62.14	86.78	8.60	64.70
2	0.1	1.53	0.98	85.52	8.51	45.90	82.38	6.20	41.93
3	0.1	3.07	1.78	83.79	5.03	34.31	80.07	4.02	34.47
4	0.48	0.1	0.98	65.05	0.00	25.91	61.06	0.00	24.78
5	0.48	1.53	1.78	66.06	0.00	23.77	63.41	0.00	22.31
6	0.48	3.07	0.1	73.38	0.00	43.95	65.72	0.00	36.51
7	1	0.1	1.78	59.40	0.00	20.03	55.60	0.00	21.58
8	1	1.53	0.1	66.20	0.00	36.50	63.93	0.00	35.99
9	1	3.07	0.98	60.59	0.00	17.86	64.14	0.00	20.02

[a]Initial concentration of the ternary aqueous solutions used for the preparation of metal-loaded chicken feathers. These metal-loaded samples were used in the desorption experiments.

removal of Cd^{2+} ions is more sensitive to co-ion concentrations and solution pH in ternary metallic mixtures.

Table 7 and Figs. 4 and 5 show the results of data modeling using ANNs and the multicomponent isotherm models. It is clear that the ANNs model is capable of modeling and predicting the complex behavior of the multicomponent removal of heavy metals using chicken feathers. Results for training, validation, and test of ANNs model are reported in Fig. 5, while the convergence performance of ANNs model is given in Fig. 6. For this black-box model, it is feasible to obtain a high determination coefficient ($R^2 > 0.97$) and the mean error of experimental and calculated values for metal uptakes is lower than 5%. ANNs model outperformed the results obtained with traditional multicomponent isotherm equations, see results reported in Table 7. In fact, these multicomponent models showed mean errors from 10 to 22% in the modeling of multicomponent sorption capacities of tested heavy metals. In particular, the non-modified Sips isotherm model offers the best performance for modeling the multicomponent sorption of heavy metals on chicken feathers in ternary solutions. However, ANNs model outperformed the non-modified Sips multicomponent equation. Overall, ANNs model is capable of modeling the complex behavior of heavy metal removal using chicken feathers in multicomponent systems at different pH conditions. Results of a sensitivy analysis indicated that pH is the most influencial input variable in the ANNs model. As stated, the solution pH is a relevant parameter for the sorption of heavy metal ions using biomasses because this operating parameter affects the degree of protonation of functional groups involved in metal uptake. It is important to remark that this ANNs model can be used to predict the multicomponent sorption capacities of chicken feathers at other process operating conditions. Therefore, this ANNs model can be used for the design of multicomponent sorption processes for heavy metal removal. In contrast to traditional sorption equations, ANNs model offers several advantages such as flexibility, reliability, and the possibility to predict the antagonistic sorption performance of chicken feathers at a wide range of operating conditions.

Table 8 shows the results of desorption studies using metal-loaded chicken feathers. Statistical analysis indicated that both desorbing agents showed the same performance for the recovery of heavy metal ions from chicken feathers (p-level > 0.05). However, it appears that the metal recovery decreased with respect to the content of heavy metal loaded on chicken feathers especially for Pb^{2+} and Cd^{2+} ions. Similar trends have been reported by Balasubramanian et al. [43]. These results indicated that, for low contents of metal loaded on the sorbent, the process of metal desorbing is easier because the metal sorption appears to occurr in the external surface of the biomass. Overall, the recovery ratios for Pb^{2+} are higher than those obtained for other co-ions and it appears that the content of Pb^{2+} loaded on the chicken feathers affected the desorption efficiencies of Cd^{2+} and Ni^{2+} ions. In particular, the desorption of Ni^{2+} is low and depends on the quantity of other co-ions loaded in the sorbent. These results indicate that the sorption process of both Pb^{2+} and Cd^{2+} is reversible and the sorbent regeneration is feasible using diluted acidic solutions.

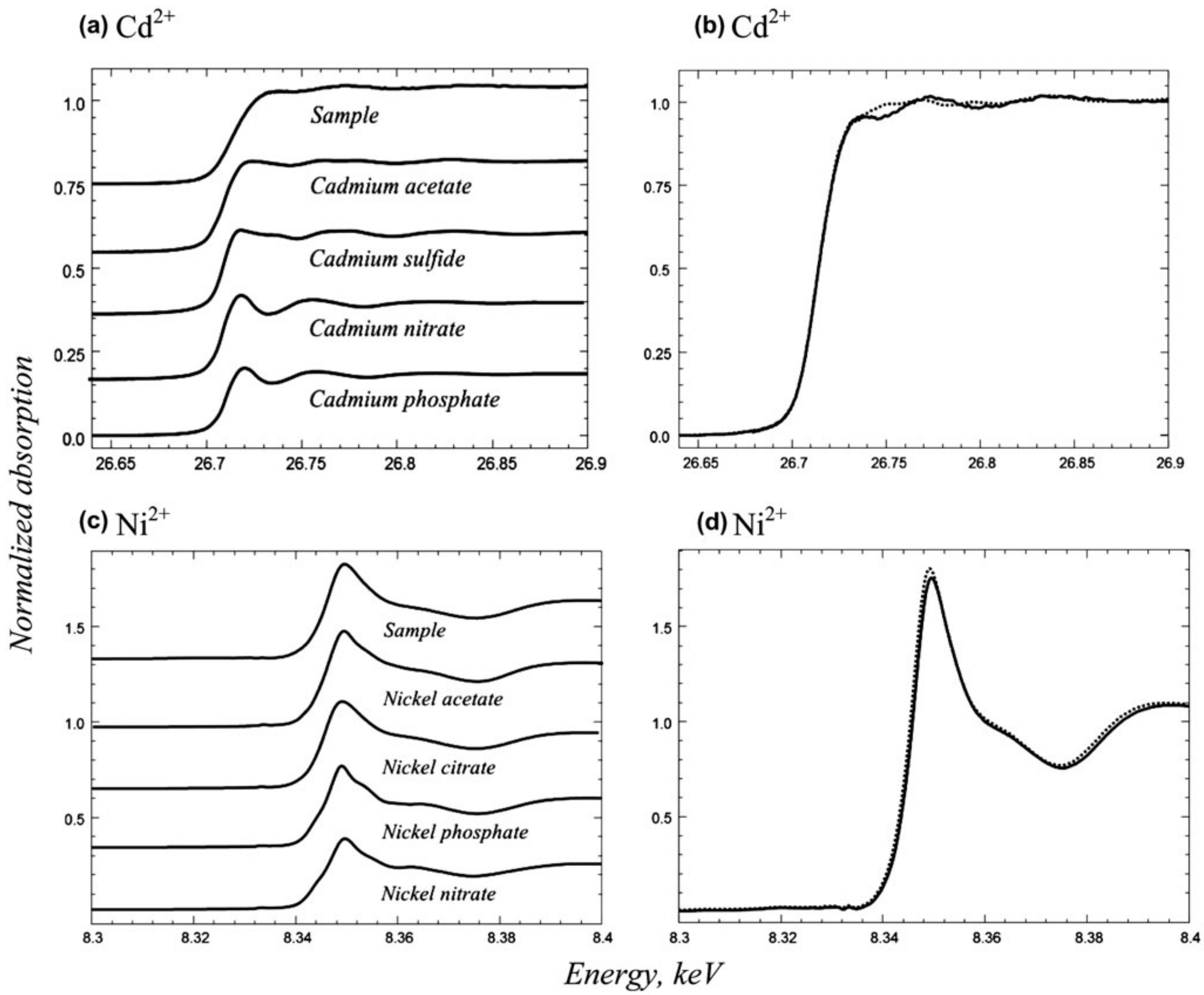

Fig. 7. (a), (c) XANES spectra of metal-loaded chicken feathers (sample) and Cd^{2+} and Ni^{2+} model compounds and (b), (d) results of LC-XANES fitting.

Finally, the linear combination analysis of XANES (LC-XANES) is a useful tool to determine the possible bonds between the sorbate and the different functional groups of the sorbent. For illustration, Fig. 7 and Table 9 show the LC-XANES results obtained with metal-loaded chicken feathers (i.e. sample) and the following model compounds: (a) Cd^{2+}: nitrate, sulfide, acetate, and phosphate; (b) Ni^{2+}: nitrate, acetate, phosphate, and citrate. These results suggest that Cd^{2+} ions may bind to sulfide and carboxylic groups, while Ni^{2+} appears to be predominantly bound to carboxylic groups. These results could explain the increments on the metal sorption capacities with solution pH since the metal removal is enhanced with the deprotonation of these functional groups.

Table 9
Results of LC-XANES fitting for metal-loaded chicken feathers

Model compound	Cd^{2+}, %	Ni^{2+}, %
Acetate	35.7	100
Phosphate	10.9	<0
Nitrate	<0	<0
Sulfide	52.2	NA
Citrate	NA	<0

NA: Not analyzed.

4. Conclusions

The application of Taguchi's experimental designs and *S*/*N* ratios is a robust approach for analyzing the removal performance of chicken feathers in multimetallic solutions. Our results indicated that the multicomponent sorption of heavy metals Pb^{2+}, Ni^{2+}, and Cd^{2+} on chicken feathers is a complex antagonistic process. In particular, chicken feathers showed a strong preference for the removal of Pb^{2+} ions in multicomponent systems. The presence of Pb^{2+} ions affected significantly the multicomponent removal of Cd^{2+} and Ni^{2+}. This antagonistic sorption effect is more significant at pH 5 and the sorption preference of chicken feathers decreased at pH 3 due to the competition of heavy metal ions and protons for the binding sites of chicken feathers. LC-XANES results indicated that sulfide and carboxylic groups of chicken feathers appear to play a relevant role for the removal of heavy metal ions using this biomass. On the other hand, the desorption process using diluted acidic solutions is more effective for the recovery of both Pb^{2+} and Cd^{2+} from metal-loaded chicken feathers indicating the feasibility of sorbent regeneration. Finally, ANNs model offers a better performance and more advantages for modeling the sorption of heavy metals on chicken feathers in multicomponent systems. In fact, this black-box model is capable of providing high determination coefficients and is robust for modeling the complex removal behavior of heavy metals in multicomponent solutions at different pH conditions. In summary, the application of Taguchi's experimental designs and ANNs models are promising for data analysis and for the modeling of multicomponent pollutant removal for wastewater and water treatment.

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