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Valorization of lemon peel waste as biosorbent for the simultaneous removal of nickel and cadmium from industrial effluents

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ABSTRACT

The valorization of agricultural waste as biosorbent requires studies dealing with aqueous systems containing coexisting heavy metals. Batch adsorption experiments were carried out to study the competitive biosorption of Ni(II) and Cd(II) on alkali-modified lemon peel. The biosorption kinetic analysis indicated that the uptake of Ni(II) on lemon peel was better described by pseudo first-order model whereas for Cd(II) results were no conclusive. A rapid uptake of both metals on alkali-modified lemon peel was detected during the first 10 min obtaining more than 90% of the maximum sorption. The maximum adsorption capacity of Ni(II) and Cd(II) for single metal systems at optimum conditions ($pH = 5$, $S/L = 5$ g L^{-1}, 25 °C), which were obtained from Langmuir model, reached as high as about 0.626 and 0.726 mmol g^{-1}, respectively. These values were reduced 30 and 20 % in the presence of 100 mg L^{-1} of Cd and Ni, respectively. Regarding the reusability of the biosorbent, after five consecutive adsorption–desorption cycles using HNO_3 and H_2SO_4 as desorption reagents percentages of 90 and 70 % were recovered for Ni and Cd. The promising results obtained through this work are expected to promote the use of lemon peel as an efficient biosorbent for industrial applications.

1. Introduction

As a result of many industrial activities, metal pollution increases which entails risks not only for the human health but also for the environment. Currently, the removal of these contaminants from water receives an increasing attention (Abdullah et al., 2019). Biosorption is an emerging and low-cost technology, which involves sorption of dissolved solutes on a biomaterial. This technique overcomes some important limitations of conventional techniques (*i.e.* chemical precipitation, ion-exchange and electrodialysis) such as limited uptake efficiency, high energetic and operational costs, sensitive operating conditions and generation of secondary sludge which requires additional treatments (Fu and Wang, 2011; Raval et al., 2016).

Recently, agricultural waste materials, mainly composed of lignin and cellulose, has been proposed as an ideal adsorbent for the removal of heavy metals from water effluents. Among several agricultural waste, peels from fruit and vegetables have received an important attention because of the promising results presented in the treatment of

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water polluted with heavy metals (Basu et al., 2017; Bhatnagar et al., 2010; Mahindrakar and Rathod, 2018; Ranasinghe et al., 2018; Sud et al., 2008; ul Haq et al., 2020; Veglio' and Beolchini, 1997). However, some shortcomings, such as, low adsorption capacity and release of soluble organic compound should be overcome. The application of chemical methods involving the biosorbent exposition to acids, alkali, organic solvent and other reagents, has been proposed (Bhatnagar et al., 2010; Ranasinghe et al., 2018; Rosales et al., 2016; Segovia-Sandoval et al., 2018). The use of NaOH as surface modifier has been reported as one of the most effective reagents to improve the metal adsorption on agricultural waste (Qin et al., 2020; Ranasinghe et al., 2018; Noli et al., 2019).

As wastewater effluents usually contain not one but a combination of contaminants, studying the effects of binary systems is more representative of the current environmental issues (Wang et al., 2020). Liang et al. evaluated the competitive adsorption of binary mixture of heavy metals (Pb^{2+}/Cu^{2+} and Pb^{2+}/Ni^{2+}) on garlic peel concluding that the presence of several metal ions reduced the adsorption capacity as compared with individual adsorption (Liang et al., 2013). In industrial wastewaters such as, battery manufacturing (Pietrelli et al., 2005), mine drainage (Simate and Ndlovu, 2014), electroplating (Kanani, 2004), and electronics manufacturing (Wu et al., 2018), nickel (Ni) and cadmium (Cd) ions are usually encountered. Although previous studies have evaluated the single-metal biosorption using different agricultural waste (Kalak et al., 2020; Singh and Shukla, 2017; Villen-Guzman et al., 2019), limited research about the biosorption behaviour and mechanisms of cadmium and nickel sorption in binary-metal systems have been conducted to provide useful information for real applications. Torab-Mostaedi et al. evaluated the biosorption of Ni and Cd onto grapefruit peel concluding that this biosorbent can be used for the treatment of wastewater (Torab-Mostaedi et al., 2013). However, as far as we are aware, there is no data in literature about the use of alkali-modified fruit peel for the recovery of Ni and Cd from water effluents. In this work, lemon peel has been selected due to the large production of this waste reported by Food and Agriculture Organization of the United Nations (FAO) (Food and Agriculture Organization of the United Nations (FAO), 2016).

The aim of this study was to evaluate the removal of Ni and Cd encountered in industrial wastewaters using as biosorbent modified lemon peel as an abundant and inexpensive agricultural waste. This research is based on the use of synthetic solutions simulating industrial wastewater contaminated with Ni and Cd for a better understanding of adsorption processes at different experimental conditions. Characterization of biosorbent surface was carried out by Attenuated Total Reflection Fourier-Transform Infrared Spectroscopy (FTIR-ATR) and the study of surface morphology by Scanning Electron Microscopy (SEM). To obtain high efficiency of ion metal removal, the most influential parameters in the sorption performance (*i.e.* contact time, *pH*, particle size and adsorbent dosage) were optimized. Kinetics models were studied to describe Ni(II) and Cd(II) sorption on alkali-modified lemon peel. Biosorption of Ni and Cd cations as single and binary systems was evaluated applying several isotherm models.

2. Material and methods

2.1. Preparation of biosorbent and chemicals

The lemon peel was washed with distilled water and dried in an oven at 60 °C until steady weight. Then, dried peels were cut into small pieces with a grinder and separated into particles of different size, (0.04 mm $< d <$ 0.150 mm; 0.150 mm $<$ d $<$ 0.710 mm; 0.710 mm $< d <$ 0.8 mm; 0.8 mm $< d <$ 1.25 mm;1.25 mm $< d <$ 2 mm; $d >2$ mm), using a set of sieves. With the aim of pretreating the lemon peel surface, samples of 4 g were treated with 100 mL of 0.1 M NaOH (Sigma Aldrich, Germany) during 6 h at 30 °C. To remove alkali solution, samples were washed with distilled water until neutral *pH*. Then, the treated peels were again dried in an oven at 60 °C until steady weight.

Standard aqueous solutions containing Ni(II) and Cd(II) ions were prepared adding 1 g L^{-1} of single metal solutions in deionized water to the desired concentration. Stock solutions were obtained by dissolving $NiCl_2 \cdot 6H_2O$ and $CdSO_4$ 8/3 H_2O (Panreac, Spain), analytical grade, in deionized water. Solution *pH* values were adjusted by appropriate addition of HNO_3 or NaOH (Panreac, Spain) solutions.

2.2. Biosorption of Ni(II) and Cd(II) on lemon peel

Batch experiments were carried out to evaluate the biosorption of Ni(II) and Cd(II) on lemon peel. A known mass of raw or pre-treated lemon peel was mixed with 25 mL of metal ion solution at 25 °C with continuous stirring on a rotatory shaker at 200 rpm. Preliminary experiments were carried out using raw lemon peel to optimize some relevant parameters, such as: contact time, size particle and *pH* value of the metal-aqueous solutions. With the aim to evaluate the effect of contact time, single metal ion solution of 100 mg L^{-1} with a biosorbent dosage of 10 g L^{-1} was added to raw lemon peel at *pH* of 5. A total of 22 batch extraction experiments for each metal were prepared at the same experimental conditions to be withdrawn at different times. Five *pH* values (from 2 to 6) were evaluated using an initial metal concentration of 100 mg L^{-1}. Samples with different size particle (0.04 mm $< d <$ 0.150 mm; 0.150 mm $< d <$ 0.710 mm; 0.710 mm $< d <$ 0.8 mm; 0.8 mm $< d <$ 1.25 mm; 1.25 mm $< d <$ 2 mm; $d >$ 2 mm) were also submitted to batch essays to evaluate the effect of this operating conditions on the metal adsorption. Once the optimal contact time was selected, size particle and *pH* value were optimized, the surface modification was carried out as described previously. The NaOH-modified lemon peel samples were used to carry out the experiments described below. The optimization of biosorbent dosage was carried out by varying it from 1 to 20 g L^{-1}.

The biosorbent uptake capacity and the removal percentage of metal ions could be computed as:

$$q = \frac{C_0 - C_f}{m} V \tag{1}$$

$$\%Removal = \frac{C_0 - C_f}{C_0} \cdot 100 \tag{2}$$

where q (mg g^{-1}) is the amount of adsorbed metal ions, C_0 (mg L^{-1}) is the metal concentration at the beginning, C_f (mg L^{-1}) is the metal concentration at the end, V (L) is volume of the metal solution and m (g) is the mass of the biosorbent.

The concentration of Ni(II) and Cd(II) in initial and final biosorption solution was determined by AAs Varian SpectrAA-110. The experiments described were carried out by duplicated to assure the reproducibility. The error bars for graphical figures correspond to two times the standard deviation of the duplicated experiments.

2.3. Adsorption models

2.3.1. Kinetics of biosorption

Kinetic experiments for single metal systems were carried out using initial Ni(II) and Cd(II) concentration in the range from 25 to 100 mg L^{-1} at optimum conditions of *pH*, *S/L* and size particle. The pseudo-first and pseudo-second order models were examined to analyse the kinetics of Ni(II) and Cd(II).

Pseudo-first order equation:

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{3}$$

Pseudo-second order equation:

$$q_t = \frac{q_e^2 k_2\, t}{1 + (q_e k_2\, t)} \tag{4}$$

where q_e and q_t are the amount of metal adsorbed (mmol g^{-1}) at equilibrium and at time t (min), respectively. k_1 is the first order rate constant (L min^{-1}) and k_2 is the second order rate constant (g $mmol^{-1}min^{-1}$).

2.3.2. Adsorption isotherm

Single biosorption thermodynamic studies of Ni(II) and Cd(II) were obtained by increasing the initial concentrations of Ni and Cd from 5 to 500 and 2000 mg L^{-1}, respectively, at optimized conditions. Binary studies were obtained in two series, one of them by varying the initial concentration of Ni(II) from 5 to 350 mg L^{-1} while the initial Cd(II) concentration was held constant at 25, 50, 100 and 150 mg L^{-1}, and another by increasing concentration of Cd(II) from 25 to 500 mg L^{-1} while the initial Ni(II) concentration was held constant at 25, 50, 100 and 150 mg L^{-1}. Based on the experimental data, the isotherm models presented in Table A.1. were examined.

2.3.3. Evaluation of models performance

The non-linear form of isotherm and kinetics models were used to fit the experimental data by modifying the model parameters and, simultaneously, minimizing the error between experimental and simulated values. The non-linear method, based on a trial-and-error procedure, was applied using the solver add-in with Microsoft Excel. The root mean square error (RSME) parameter was obtained as:

$$RMSE = \sqrt{\frac{\sum_1^m (q_{exp} - q_{model})^2}{m}} \tag{5}$$

where m is the number of data points, q_{exp} (mmol g^{-1}) is the average value of experimental adsorption capacity and q_{model} (mmol g^{-1}) is the adsorption capacity predicted by the model.

With the aim of assessing the accuracy of models, the correlation coefficient (R^2) of parity plots (a scatter plot comparing experimental data against model prediction values) was evaluated.

2.4. Biosorbent characterization

The lemon peel was characterized before and after biosorption experiments. The specific surface area (BET surface) of biosorbent before and after modification was measured by N_2 adsorption with a surface area analyser (ASAP 2420). The study of surface functional groups was carried out using a FTIR spectrometer (Bruker. Model Vertex70) with the Golden Gate Single Reflection Diamond ATR System. The spectra were recorded by 64 scans in absorbance mode from 4000 to 500 cm^{-1} range with a resolution of 4 cm^{-1}. Scanning Electron Microscopy (JEOL JSM-6490LV with Energy dispersive X-ray (EDX) analyzer) was used to study the surface morphology of lemon peel before and after exposure to the metallic ions. Presence of metals sorbed on the biosorbent surface was determined using Energy dispersive X-ray spectroscopy

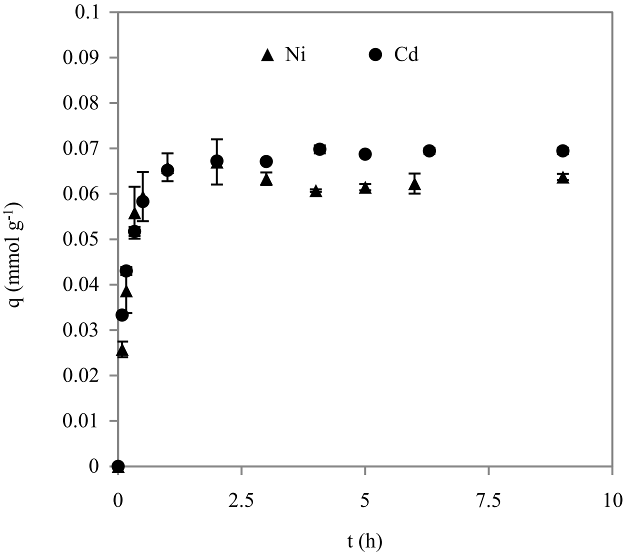

Fig. 1. Effect of contact time on single adsorption of Ni(II) and Cd(II) on raw lemon peel ($pH = 5$; $C_0 = 100$ mg L^{-1}, $S/L = 10$ g L^{-1}).

(EDX). XPS spectra were obtained with a Physical Electronics PHI 5701 spectrometer with a multi-channel hemispherical electron analyser. The photoelectron lines Cu 2p3/2, Ag 3d5/2 and Au 4f7/2 at 932.7, 368.3 and 84.0 eV were selected to calibrate the spectrometer energy scale. The spectra were linearly shifted to C1s line to correspond to the binding energy of 284.8 eV.

3. Results and discussion

3.1. Preliminary experiments: Effect of contact time, particle size and pH

With the aim of determining the equilibrium time, batch experiments were carried out using raw lemon peel as biosorbent. As can be observed (Fig. 1), the Ni and Cd uptake increased rapidly within the first hour maintaining constant for higher experimental times. No important differences were obtained for Ni and Cd expressing results in mmol g^{-1} which could be associated with a predominant ion exchange mechanism. The adsorption capacity within the first 10 min represents almost 60% of equilibrium capacity for Ni(II) and Cd(II). These results have been previously justified by the interaction of metal ions with carboxylic groups (Meseldzija et al., 2019). The equilibrium contact time selected was 3 h to assure the maximum adsorption of Ni(II) and Cd(II).

The effect of particle size on Ni(II) and Cd(II) biosorption was examined using six different particle size (Figure A.1). For both metal ions, no important variations were observed at different particle size. However, the largest particles resulted in slightly worse biosorption performance in particular for Cd(II). Based on results and considering that the use of large particles are preferable to be used in sorption column processes (Vijayaraghavan et al., 2006), particles of 1.25 to 2 mm were selected to be used in subsequent experiments.

The *pH* of the metal solution plays an important role in the efficiency of biosorption processes. The experimental results for Ni(II) and Cd(II) uptake on lemon peel for initial *pH* values in the range of 2 to 6 are shown in Fig. 2. According to Pourbaix diagram for metal-H_2O system, Ni and Cd are mainly presents as Ni(II) and Cd(II) at *pH* values lower than 7 (Anoop Krishnan et al., 2011; Pap et al., 2016). As can be observed, nickel and cadmium removal experimentally obtained was significantly lower for a *pH* value of 2. Previous works associated this fact with the competition between cations and hydrogen ions for active sites (Chojnacka et al., 2005; Ngabura et al., 2018). The protonation of the surface hinders the access of cations due to repulsive forces. The increasing cation removal with increasing *pH* from 2 to 3 may be related to the increase of negative charge of the biosorbent surface. For *pH* values from 3 to 6, no important differences were reported. Therefore, the selected *pH* value as optimum was 5 since the *p*H value of the aqueous Ni(II) and Cd(II) solutions without adjustment were 5.4 and 5.2, respectively.

3.2. Surface modification: Biosorbent characterization

The influence of surface modification on the adsorption capacity of lemon peel for Ni and Cd is presented in Figure A.2. In a previous work, NaOH was selected as an efficient chemical modifier of lemon peel reporting an important improvement in the efficiency of the biosorption processes (Villen-Guzman et al., 2019). The Ni and Cd adsorption capacity

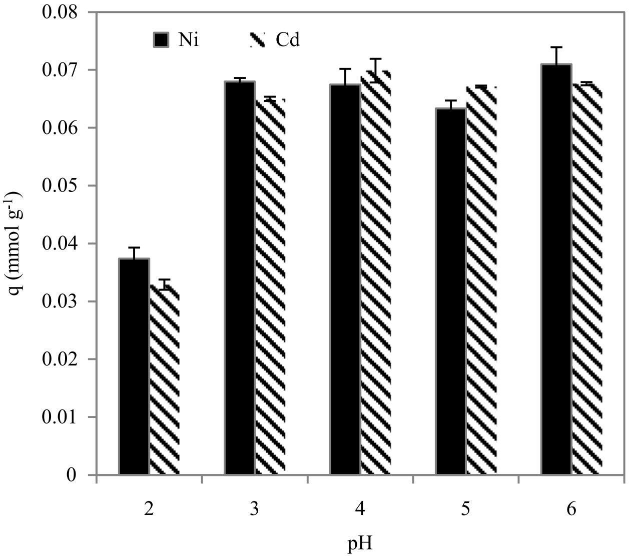

Fig. 2. Effect of pH on biosorption of Ni(II) and Cd(II) by raw lemon peel. ($C_0 = 100$ mg L^{-1}, S/L = 10).

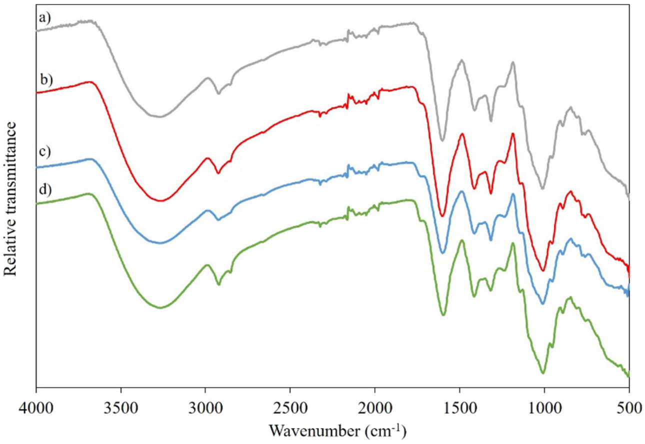

Fig. 3. FTIR-AR spectra for: a) NaOH-modified lemon peel, b) NaOH-modified lemon peel + Ni(II), c) NaOH-modified lemon peel + Cd(II), d) NaOH-modified lemon peel + Ni(II)+Cd(II).

for alkali-modified lemon peel represent, respectively, about 2.6 and 1.4 times than the raw peel under the experimental conditions studied. These results have been previously associated not only with the conversion of lignin structure into negative surfaces charges but also with the superficial precipitation of metal hydroxides (Min et al., 2004). As initial mass concentration was the same for Ni(II) and Cd(II) solutions, the differences in the adsorption behaviour of metals ions could be partially attributed to the higher molar concentration of Ni(II) for the initial solutions. An accurate comparison of maximum adsorption capacity based on model predictions is presented in Section 3.5.

The specific surface area, determined by BET method, was 0.4090 ± 0.0058 and 0.5367 ± 0.0048 m^2 g^{-1} for raw and NaOH-modified lemon peel, respectively, which is in agreement with results previously reported for fruit peels (Oyekanmi et al., 2019; Pathak et al., 2015). The low surface area of modified lemon peel is a characteristic of carbonaceous materials (Castro et al., 2011). The average pore diameter of the modified adsorbent was found 31.6 Å, which is in line with other studies (Thirumavalavan et al., 2011).

FTIR-ATR spectra of modified lemon peel biosorbent before and after Ni(II) and Cd(II) loaded are presented in Fig. 3. The presence of functional groups contained in protein, pectin, cellulose and pigments, as the most relevant component of peels, has been previously identified from these peaks (Thirumavalavan et al., 2011). The carboxyl and hydroxyl functional groups are characterized by a broad peak around 3200–3400 cm^{-1}. These well-resolved peaks indicate the presence of the aforementioned functional groups which plays an important role in the metal binding. The presence of alkyl groups ($-CH_n$) was detected with the peak around 2900 cm^{-1} which could have been altered after surface modification. After

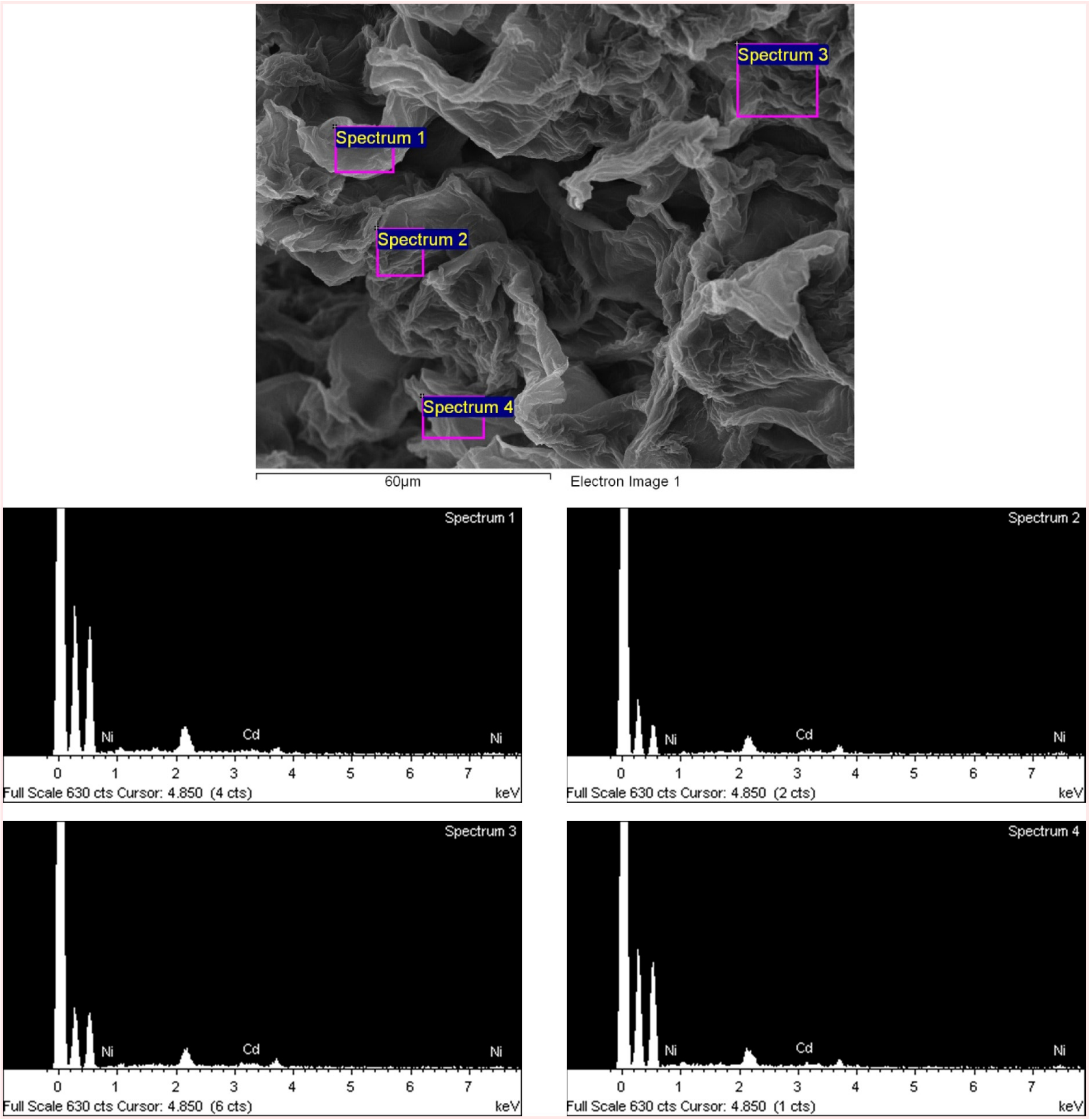

Fig. 4. SEM micrograph of modified lemon peel after Cd and Ni adsorption ($C_0(\mathrm{Ni}) = 50\ \mathrm{mg\ L^{-1}} C_0(\mathrm{Cd}) = 50\ \mathrm{mg\ L^{-1}}$) and X-ray spectra.

surface modification with NaOH, the complex split of stretching vibration of CH_3 was detected. Peaks around wavenumber 1020–1300 cm^{-1} are associated with C–O group. Previous studies concluded that the absence of peaks related to bond of carboxyl groups (1640–1750 cm^{-1}) could be due to the hydrolysis of this group after surface modification (Singh and Shukla, 2016). After the adsorption of Ni(II) and Cd(II) on treated lemon peel, some changes were observed. The intensity of peaks associated with C–O groups was reduced, probably, as a consequence of the adsorption of metal cations. The peak at wavenumber around 2900 cm^{-1} was slightly reduced after metal adsorption, which is probably due to metal–carbon bond formation (Thirumavalavan et al., 2011). Shifts in wavenumber were also found which has been mainly associated with changes in energy of the functional groups after metal adsorption. These results indicate the importance of the functional groups mentioned in the mechanisms of Ni(II) and Cd(II) uptake (Iqbal et al., 2009).

The surface morphology of modified lemon peel before and after metal biosorption is presented in Figure A.3. In a previous work (Villen-Guzman et al., 2019), no significant differences in the superficial structure of lemon peel after modification with NaOH were found. The particle lemon peel was characterized by a honeycomb-like structure with porous of 10-20 µm. After metal binding, no important differences were observed in the surface structure. SEM-EDX analysis of modified lemon peel after Cd(II)+Ni(II) adsorption are presented in Fig. 4. As can be observed, the characteristics peaks of Cd and Ni were identified after metal adsorption. The results of mass ratio of Cd/Ni (Table A.2) were in agreement with experimental results for batch experiments carried out using aqueous solutions with initial concentrations of Ni(II) and Cd(II) of 50 mg L^{-1}.

XPS results (Figure A.4) showed that the biosorbent consists of two major elements: carbon and oxygen as was concluded from FTIR results. The presence of Ni and Cd was detected on the adsorbent after batch experiments through the analysis of peaks associated with Ni2p and Cd3d, respectively. Regarding mass concentration of Ni and Cd in the biosorbent surface after adsorption, an uptake capacity of 10.2 and 7.6 mg kg^{-1} was obtained. These results are in agreement with those obtained from batch experiments (10.1 and 9.4 mg kg^{-1}, for Ni and Cd respectively) for the same experimental conditions.

3.3. Effect of biosorbent dosage

Experimental results of the effect of biosorbent dosage on the adsorption capacity of Ni(II) and Cd(II) by alkali-modified lemon peel are presented in Figure A.5. As can be observed, the error bars were imperceptible due to the small relative error for each sample. The increase of biosorbent dosage entailed the increase of the percentage of metal removed which has been associated with a larger availability of actives sites for adsorption of metal cations. As can be observed, the percentage of Ni(II) and Cd(II) removed was close to 100% for a biosorbent dosage equal or greater than 5 and 2.5 g L^{-1}, respectively. The adsorption capacity, as expected, decreased with increasing biosorbent dosage. The adsorbent dosage selected for further experiments was 5 g L^{-1} since higher biosorbent dosage can involve agglomeration of biosorbent particles which is related to the reduction of active surface area.

3.4. Kinetic study

The experimental data from kinetic studies was assessed using the pseudo-first and pseudo-second order model equations. The kinetic parameters obtained from the nonlinear regression analysis of average values of experimental data for different initial concentration of Ni(II) and Cd(II) are presented in Table A.3. Concerning the time evolution of the biosorption of metals, the same trend was observed for both metals at different concentrations: more than 90% of sorption took place in the first 10 min followed by a progressive rate decrease. As can be concluded from high values of R^2 coefficient ($>$ 0.991) and low values of RMSE, the sorption of both metals on lemon peel could be described as pseudo-first-order process. However, for Cd(II) biosorption a slightly higher value was obtained from the fitting of experimental data to the pseudo-second order kinetic model. Therefore, the sorption of Ni(II) on lemon peel could be described as a pseudo-first order reaction while results are not conclusive for the Cd(II). The amount of metal adsorbed at equilibrium (q_e) increased linearly with the initial metal ions concentrations for Ni and Cd. The maximum adsorption capacity for Ni and Cd, 0.626 and 0.726 mmol g^{-1}, would be achieved for initial metal ion concentration of about 3.2 and 3.5 mmol L^{-1}, respectively, which is in agreement with the adsorption isotherm results presented in the next section. Regarding values of the rate constant for both metals, it has been observed an inverse dependence of this parameter with metal concentration which is in agreement with previous studies (Boyd et al., 1947).

3.5. Adsorption isotherms

Experimental biosorption equilibrium of Ni and Cd was described by various isotherm models: Freundlich, Langmuir and Dubinin–Radushkevich whose fitting results are given in Table 1. According to these results, Langmuir model fits better the experimental data for Ni and Cd than the others, obtaining values of R^2 of 0.992 and 0.984, respectively. Therefore, the biosorption of Ni(II) and Cd(II) on the modified lemon peel surface could be considered a monolayer adsorption which has been previously associated with the homogeneity of the physical structure and chemicals properties of fruit peels (Beni and Esmaeili, 2020). These results are in agreement with other reported in literature (Basu et al., 2017; Ngabura et al., 2018). According to Langmuir model, the complete monolayer coverage, *i.e.* the maximum adsorption capacity (q_{max_L}), was 0.626 mmol g^{-1} and 0.726 mmol g^{-1} for Ni and Cd, respectively. Comparing experimental results with those obtained with alternative materials (Table A.4), it could be concluded that modified lemon peel has higher uptake capacity for Ni and Cd than other promising materials. Thus, modified lemon peel could be considered as an inexpensive and effective biosorbent for Ni and Cd adsorption from aqueous effluents.

The equilibrium adsorption constant (k_L) obtained for single metal ions indicated a high affinity of the lemon peel for Cd(II). These results could be explained comparing the effective diameter of the hydrated ion (5 and 6 Å for Cd(II) and Ni(II), respectively, Kielland, 1937), *i.e.* the mean distance between the solvated cation and anion of an electrolyte. In other words, the lower affinity of the modified lemon peel for the Ni(II) could be associated with its bigger ion size in comparison with Cd(II). However, other additional aspects, such the metal-binding mechanisms involved, should be considered to evaluate sorption affinity. On the other hand, the Dubinin–Radushkevich parameters can offer valuable information about the biosorption process nature. According to the experimental value of mean free energy of adsorption, E, lower than 8 kJ mol^{-1}, the biosorption of Ni(II) and Cd(II) on the modified lemon peel could be considered of physical nature (Hu and Zhang, 2019).

Table 1
Equilibrium isotherm parameters for biosorption of single systems Ni(II) and Cd(II) on NaOH-modified lemon peel. ($pH = 5$, $S/L = 5$ g L^{-1}).

Model	Parameters	Ni	Cd
Freundlich	k_f	0.518	0.558
	n	4.9	6.9
	$RMSE$	$7.46 \cdot 10^{-2}$	$6.7 \cdot 10^{-2}$
	R^2	0.913	0.917
Langmuir	k_L (L mmol^{-1})	33.14	110.11
	q_{max_L} (mmol g^{-1})	0.626	0.726
	$RMSE$	$2.55 \cdot 10^{-2}$	$4.30 \cdot 10^{-2}$
	R^2	0.992	0.984
Dubinin–Radushkevich	q_{max_DR} (mmol g^{-1})	0.587	0.644
	β (mol^2 kJ^{-2})	0.34	0.11
	E (kJ mol^{-1})	1.21	2.16
	$RMSE$	$5.92 \cdot 10^{-2}$	0.110
	R^2	0.960	0.803

Table 2
Equilibrium isotherm parameters for biosorption of binary system Ni(II)–Cd(II) on NaOH-modified lemon peel. ($pH = 5$, $S/L = 5$ g L^{-1}).

		Cd concentration (for i = 1, 2 where Ni = 1, Cd = 2)			
Model	**Parameters**	25 mg L^{-1}	50 mg L^{-1}	100 mg L^{-1}	150 mg L^{-1}
Competitive Langmuir	$k_{CL,1}$ (L mmol^{-1})	15.49	17.96	18.86	10.13
	$k_{CL,2}$ (L mmol^{-1})	0	26.81	1.20	1.58
	$q_{max\_CL,1}$ (mmol g^{-1})	0.584	0.557	0.431	0.416
	$RMSE$	$4.6 \cdot 10^{-2}$	$3.4 \cdot 10^{-2}$	$5.74 \cdot 10^{-3}$	$1.2 \cdot 10^{-2}$
	R^2	0.979			
Uncompetitive Langmuir	$K_{UL,1}$ (L mmol^{-1})	15.47	15.51	19.64	119.91
	$K_{UL,2}$ (L mmol^{-1})	0	34.68	35.30	1062.48
	$K_{UL1,2}$ (L mmol^{-1})	18.37	26.31	359.22	5280.25
	q_{max_LU1} (mmol g^{-1})	0.582	0.581	0.445	0.430
	$RMSE$	$4.6 \cdot 10^{-2}$	$3.5 \cdot 10^{-2}$	$5.1 \cdot 10^{-3}$	$8.1 \cdot 10^{-3}$
	R^2	0.979			
Extended Freundlich	x_1	1.596	0.461	0.534	0.198
	y_1	$1.52 \cdot 10^{-4}$	0.142	0.246	0.524
	z_1	0	0.199	0.192	0
	$RMSE$	$4.7 \cdot 10^{-2}$	$3.5 \cdot 10^{-2}$	$3.2 \cdot 10^{-2}$	$2.9 \cdot 10^{-2}$
	R^2	0.9626			
		Ni concentration (for i = 1, 2 where Cd = 1, Ni = 2)			
Model	**Parameters**	25 mg L^{-1}	50 mg L^{-1}	100 mg L^{-1}	150 mg L^{-1}
Competitive Langmuir	$k_{CL,1}$ (L mmol^{-1})	163.94	500.16	71.19	3.42
	$k_{CL,2}$ (L mmol^{-1})	162.14	336.71	25.77	0
	$q_{max\_CL,1}$ (mmol g^{-1})	0.654	0.573	0.515	0.447
	$RMSE$	$2.0 \cdot 10^{-2}$	$2.2 \cdot 10^{-2}$	$1.8 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$
	R^2	0.9885			
Uncompetitive Langmuir	K_{UL1} (L mmol^{-1})	180.46	494.80	117.02	3.53
	K_{UL2} (L mmol^{-1})	179.64	329.15	46.68	0
	$K_{UL1,2}$ (L mmol^{-1})	459.89	47.84	49.00	0.454
	q_{max_LU1} (mmol g^{-1})	0.625	0.568	0.493	0.436
	$RMSE$	$2.0 \cdot 10^{-2}$	$2.2 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$
	R^2	0.9887			
Extended Freundlich	x_1	1.659	2.107	0.559	0.551
	y_1	1.49·10–2	7.67	0.428	0.628
	z_1	1.06	3.54	0.435	0
	$RMSE$	$1.8 \cdot 10^{-2}$	$2.4 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$	$1.8 \cdot 10^{-2}$
	R^2	0.9882			

The competitive biosorption of Ni(II) and Cd(II) on treated lemon peel has been studied using binary mixtures of metal ions (Figure A.6). The error bars correspond to two time the standard deviation of duplicated experiments. As can be observed, the error bars were imperceptible due to the small relative error for each sample. The parameters of non-linearized adsorption isotherm of Cd(II) in the presence of increasing concentration of Ni(II) and those associated with the adsorption isotherm of Ni(II) in the presence of increasing concentration of Cd(II) are presented in Table 2.

As can be concluded from the values of the maximum adsorption capacity (q_{max}), the equilibrium uptake of Ni(II) decreased linearly with the increasing concentration of Cd(II) ions. The effect of Cd(II) on the Ni(II) equilibrium could be associated with the limited number of surface binding sites. The presence of high concentration of Cd(II) entails a competition for the available sites on the biosorbent surface. A similar biosorption trend was observed for the adsorption isotherm of Cd(II) in the presence of increasing concentration of Ni(II). The presence of 100 mg L^{-1} of Cd(II) (corresponding to a molar concentration of 0.88 mmol L^{-1}) caused a 30% reduction in the maximum adsorption capacity of Ni(II) whereas the presence of the same initial Ni(II) mass concentration (corresponding to a molar concentration of 1.70 mmol L^{-1}) only entailed a 20% reduction in the maximum adsorption capacity of Cd(II). These results indicated the preferential uptake of Cd(II) on the biosorbent comparing with Ni(II) as co-ion which agrees with results obtained from isotherm for single systems. The isotherm parameters were estimated by fitting the average values of experimental data to non-linear equations as described in Section 2.3.3. For the evaluation of model performance of binary systems, parity plots included experimental results of adsorption capacity of Ni or Cd in presence of different Cd or Ni concentration values, respectively. For this reason, only one value of the correlation coefficient was obtained for each model. Regarding the non-linear regression of experimental equilibrium data of binary biosorption, the models based on Langmuir isotherm fitted slightly better the experimental results in view of the correlation coefficient (R^2) of parity plots, especially for Ni adsorption in presence of different Cd concentration, which is also in agreement with results obtained from single systems. Regarding competitive and uncompetitive adsorption described by Langmuir models, from the comparison of the correlation coefficient (R^2) and RMSE values no important differences were found.

3.6. Desorption studies

The recovery efficiency of Ni(II) and Cd(II) from loaded-biosorbent using HNO_3 and H_2SO_4 as desorbing agent within 5 consecutive cycles is presented in Fig. 5. The desorption percentage of Ni and Cd after 5 cycles was close to 90 % and 70 %, respectively, by both nitric and sulphuric acids. No significant losses in the desorption capacity of lemon peel were experimentally detected. Therefore, both acids could be proposed as desorbing agent for industrial applications.

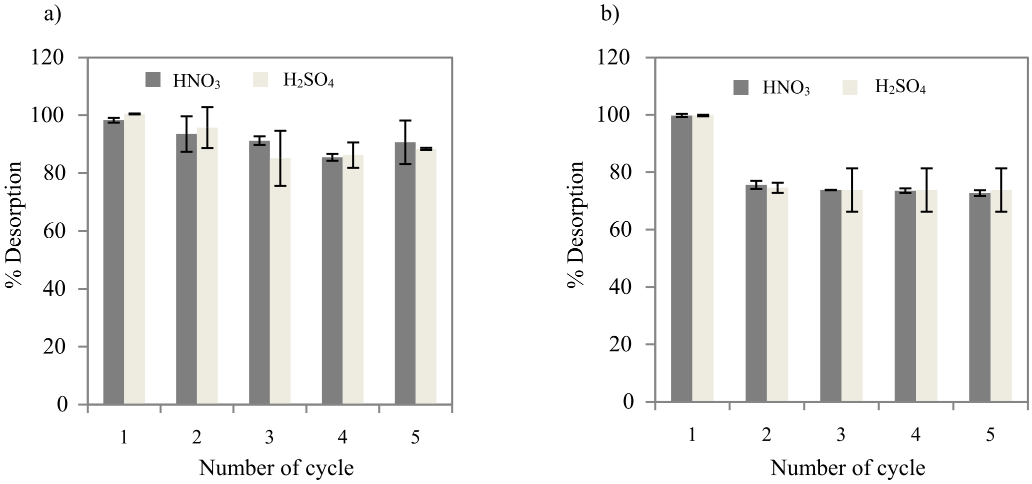

Fig. 5. Desorption studies of (a) Ni(II) and (b) Cd(II) using 0.1 M of HNO_3 and H_2SO_4 as desorbing agents.

4. Conclusions

The use of NaOH as a modifier surface of lemon peel has been proved to be an efficient approach to improve the adsorption capacity of this waste. The uptake of Ni and Cd on alkali-modified lemon peel was enough rapid (90% of the maximum sorption in the first 10 min) to propose the valorization of lemon peel as an efficient biosorbent for batch and column industrial applications. Langmuir isotherm was the most suitable model to describe biosorption equilibrium for both metals under optimum conditions ($pH = 5$, $S/L = 5$ g L^{-1}, 25 °C, particle size: 1.25 mm $<$ d $<$ 2 mm). The maximum adsorption capacity for single systems (0.626 and 0.726 mmol g^{-1} for Ni(II) and Cd(II), respectively) decreased linearly with the initial concentration of the other metal in binary systems. This reduction was more relevant for Ni(II) uptake in presence of Cd which has been associated with the higher affinity of alkali-modified lemon peel for Cd(II) ions. These promising results will allow the development of a circular economy strategy where an agricultural waste is applied for the treatment of industrial wastewater containing several contaminants.

CRediT authorship contribution statement

M. Villen-Guzman: Conceptualization, Methodology, Data acquisition, Software, Writing - original draft, Writing - review & editing. **M.M. Cerrillo-Gonzalez:** Data acquisition, Validation, Writing - review & editing. **J.M. Paz-Garcia:** Software, Validation, Writing - review & editing. **J.M. Rodriguez-Maroto:** Conceptualization, Software, Writing - original draft, Writing - review & editing, Supervision. **B. Arhoun:** Conceptualization, Methodology, Data acquisition, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.eti.2021.101380.

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