Optimization of Ni (II) biosorption from aqueous solution on modified lemon peel

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Abstract

The valorization of agricultural waste peels as a low-cost biosorbent is a promising approach to water treatment. In this work, the improvement of the adsorption capacity of lemon peel to remove Ni (II) from aqueous effluents was explored using several chemical modifiers: HNO_3, HCl, H_3PO_4, $CaCl_2$, NH_3 and NaOH. The surface pretreatment using NaOH was selected as the best option because of the improvement of the maximum adsorption capacity. The maximum adsorption capacity was of 36.74 mg g^{-1} according to the Langmuir model at optimum conditions (pH=5, S/L=5 g L^{-1}, 25ºC). The pseudo-first order model of biosorption kinetics provides the best fit for experimental data. From thermodynamic studies, it was concluded that Ni (II) biosorption by modified lemon peel was endothermic and spontaneous. After five consecutives adsorption-desorption cycles using 0.1 M of HNO_3 and H_2SO_4, a recovery of 90 % of Ni (II) was obtained. Regarding characterization of the biosorbent, the surface morphology was studied by Scanning Electron Microscopy while the functional groups responsible for Ni (II) adsorption were evaluated by Fourier transform infrared spectroscopy.

Keywords:

Biosorption, Agricultural Wastes, Surface Modification, Industrial Effluent Treatment, Lemon Peel, Ni (II) ions.

Highlights

- Biosorption as an alternative method of Ni (II) removal from industrial effluents.

- The maximum adsorption capacity was obtained using NaOH as surface modifier.
- High removal rates of Ni (II) were obtained under optimized conditions.

1. Introduction

Metal pollution is a major environmental issue worldwide due to the important increase in the use of heavy metals in various industries, such as mining, metal finishing, electroplating, leather tanning, metallurgy, electronic, battery industries, chemical manufacturing, and petroleum industries (Lesmana et al., 2009). Heavy metals are non-degradable and tent to accumulate in photosynthetic organism transferring these pollutants to humans (Duruibe et al., 2007; Abdullah et al., 2019). Therefore, it is widely accepted that heavy metals disposal into natural waters entails serious problems for both human health and the environment.

Conventional technologies, such as chemical precipitation, ion-exchange and electro-dialysis, have been widely used to remove heavy metals from industrial wastewater (Fu and Wang, 2011; Purkayastha et al., 2014). However, some important limitations, including low removal efficiency, high operational cost, high energy consumption, sensitive operating conditions, incomplete metal removal, and production of secondary sludge which requires an additional treatment (Gavrilescu, 2004; Raval et al., 2016), have been found. These limitations together with the development of stricter environmental regulations for the content of heavy metal in effluents promote the development of alternative techniques. Biosorption is an effective, low-cost and eco-friendly technology for the removal of heavy metals using a passive binding process with biomass capable of collecting heavy metals (Veglio' and Beolchini, 1997; Lesmana et al., 2009). The binding of heavy metal ions has been associated with the constituent of biomaterials: carbohydrates, protein and phenolic compounds containing functional groups such as carboxyl, hydroxyl and amines (Choi and Yun, 2006). Biosorbent could be mainly derived from (Fu and Wang, 2011): 1) non-living biomass such as lignin, bark and agricultural wastes (Sud et al., 2008), 2) algal biomass (Hansen et al., 2006; Romera et al., 2007; Benaisa et al., 2019; Filote et al., 2019) and 3) microbial biomass, i.e. bacteria, fungi and yeast (Beolchini et al., 2003; Ahluwalia and Goyal, 2007).

The ideal adsorbent should be economic, eco-friendly, highly efficient, abundant and renewable. The agricultural waste materials, mainly composed of lignin and cellulose, meet these requirements representing a viable option for remediation of wastewater containing heavy metals. Waste peels from fruits and vegetables have been proposed as an emerging biosorbent presenting promising results in the treatment of water polluted with heavy metals (Sud et al., 2008).

Some studies have evaluated fruit peels for their capacity to remove heavy metal ion through interactions (complexation, physical and chemical adsorption, precipitation and ion exchange) between the metal ion and functional groups on the surface of the peel. Literature review shows the use of banana, orange and cucumber peel for the removal of lead ions from wastewater (Liang et al., 2009; Massocatto et al., 2013; Basu et al., 2017). An important cadmium sorption from aqueous solutions using peels of peas, broad bean and medlar has been also reported (Benaïssa, 2006). Bhatnagar et al. (2010) evaluated the feasibility of lemon peel waste as biosorbent for the removal of cobalt from aqueous solution obtaining promising results. The adsorption capacities of lemon peel for other contaminants, such as dyes, has been widely studied (Bhatnagar et al., 2009). Among waste from fruits, a special attention should be paid to the large production of citrus fruits. According to the Food and Agricultural Organization of the United Nations (FAO-STAT), the total citrus production was more than 120 million tons in 2016. Spain was the 9th producer in the world of this agricultural raw material which entails a large quantity of wastes (FAO, 2016). As most of the peels are discarded as waste without application, their use as a low-cost and eco-friendly adsorbent is a promising alternative.

There are some limitations in the use of fruit peel as biosorbent, such as low adsorption capacity and release of soluble organic compounds. With the aim of overcoming these limitations, some modification methods, such as physical and chemical treatments, have been proposed. Chemical methods go not only after the increasing of metal biosorption efficiency and the removal of soluble organic compounds but also after the elimination of coloration from aqueous solutions. These methods have been mainly associated with the modification of selective functional groups which entails, among other improvements, the enhancement of binding groups and the elimination of inhibiting groups from the biosorbent (Ramrakhiani et al., 2016). Various chemical methods, such as, exposing the biosorbent to dissolutions of acids, alkali, organic solvent and other reagents, can be found in literature (Kapoor and Viraraghavan, 1998; Bhatnagar et al., 2010; Ranasinghe et al., 2018; Segovia-Sandoval et al., 2018). However, to the best of our knowledge, there are no data in literature related to the used of modified lemon peel as biosorbent for the removal of nickel from aqueous solutions.

In this work, the surface modification of lemon peel for the removal of Ni (II) from aqueous effluents is proposed. With this aim, different modifiers (HNO_3, HCl, H_3PO_4, NH_3, $CaCl_2$ and NaOH) were evaluated. The most influential parameters in the sorption performance, such as contact time, pH and adsorbent dosage, were optimized. Thermodynamic and kinetic studies were carried out to evaluate the performance of modified lemon peel as biosorbent. With the aim of evaluating the reuse of biosorbent, regeneration studies using different reagents were conducted. The identification of chemical groups in the 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).

2. Material and methods

2.1. Preparation of biosorbent and nickel solutions

The lemon peel used in this study was collected from the local fruit market. These were first washed with distilled water and dried in an oven at 60 ºC until steady weight. The dried adsorbent was ground in a coffee mill and separated into different size fractions using a set of sieves. Samples of particle size between 1.25 to 2 mm were used in further experiments. With the aim of enhancing the surface, samples of 4 g of lemon peel were gently stirred with 100 mL of different solutions of 0.1 M of HNO_3, HCl, H_3PO_4, NH_3, $CaCl_2$, (Panreac, Spain) and NaOH (Sigma Aldrich, Germany) during 6 h at 30 ºC and then were washed with distilled water until neutral pH. The lemon peel modified was again dried in an oven at 60 ºC until steady weight.

Standard aqueous solutions of Ni (II) were prepared using $NiCl_2 \cdot 6H_2O$ (Panreac, Spain), analytical grade, in deionized water. Solution pH values were adjusted by appropriate addition of 0.1 M HNO_3 or NaOH solutions.

2.2. Batch biosorption experiments

Adsorption of Ni (II) on lemon peel was studied by batch experiments. The experiments were carried out by immersing a known mass of raw lemon peel in 25 mL of aqueous metal ion solution for different contact times at 25 ºC with continuous stirring on a rotary shaker at 200 rpm. The effect of contact time was evaluated using a metal ion solution of concentration 100 mg L^{-1} and at pH of 5. By varying the pH of initial solution from 2 to 6 with an initial Ni (II) concentration of 100 mg L^{-1}, the effect of solution pH was evaluated. The use of different modifiers to pretreat the lemon peel surface was also evaluated. Once the most appropriate reagent was selected, further experiments were carried out with modified lemon peel. The effect of biosorbent dosage was studied by varying the solid to liquid ratio (S/L) from 1 to 20 g L^{-1}, under optimized conditions. Kinetic experiments were carried out using initial Ni (II) concentration in the range from 25 to 100 mg L^{-1}. Results for isotherms studies were obtained by varying the initial Ni (II) concentration from 5 to 500 mg L^{-1} at constant temperature (25 ºC). The effect of temperature on the adsorption processes has been also evaluated conducting experiments at different temperatures ranged from 20 to 45 ºC.

The capacity of adsorbed metal ions and the percent removal of metal ions were obtained as:

$$q = \frac{C_0 - C_f}{m} V \qquad \text{Eq (1)}$$

$$\% \, Removal = \frac{C_0 - C_f}{C_0} \cdot 100 \qquad \text{Eq (2)}$$

where q (mg g^{-1}) is the amount of adsorbed metal ions, C_0 (mg L^{-1}) is the initial concentration of metal ions, C_f (mg L^{-1}) is the final metal concentration, V (L) is the volume of the used metal solution and m (g) is the weight of the sorbent.

For desorption studies, the capacity of regeneration for the lemon peel loaded with Ni (II) was studied using 0.1 M HNO_3 and H_2SO_4 (Panreac, Spain). With the aim of determining the potential reusability of the biosorbent under study, consecutive adsorption-desorption cycles were repeated 5 times. A mass of 0.25 g of modified-lemon peel was contacted with 50 mL of Ni (II) solution of 100 mg L^{-1} at 200 rpm for 3 hours. Then, the Ni (II) loaded was desorbed with the addition of 50 mL of the aforementioned acid solutions at 200 rpm for 3 hours at 25 ºC. After each adsorption and desorption step, the biosorbent was washed with distilled water and dried in an oven at 60 ºC until steady weight.

The desorption percentage was obtained as:

$$\% \, Desorption = \frac{Amount\ of\ metal\ ions\ desorbed}{Amount\ of\ metal\ ions\ adsorbed} \cdot 100 \qquad \text{Eq (3)}$$

Concentration of Ni (II) solutions was determined by AAS Varian SpectrAA-110. Each essay was carried out by duplicated at the same controlled conditions to assure the reproducibility.

2.3. Adsorption models

2.3.1. Adsorption Isotherm

Based on the experimental data, the isotherm models: Freundlich (Freundlich, 1906), Langmuir (Langmuir, 1916) and Dubinin-Radushkevich (Dubinin, 1960) were examined. Although these classical isotherm models consider sorption by free binding sites rather than ion exchange, the use of these models is widely accepted for evaluating the biosorption equilibrium because of their ease of interpretation (Liu and Liu, 2008; Schiewer and Patil, 2008).

The Freundlich model can be expressed as:

$$q_e = \mathrm{k_f}\, \mathrm{C_e^{1/n}} \qquad \text{Eq (4)}$$

where q_e (mg g^{-1}) is the amount of metal adsorbed per unit mass of adsorbent at equilibrium, k_f (mg$^{(n-1)/n}$ L$^{1/n}$ g^{-1}) is the adsorption capacity, n is a dimensionless parameter associated with the adsorption intensity and C_e (mg L^{-1}) is the metal equilibrium concentration.

The Langmuir equation is given by:

$$q_e = \frac{q_{\max\_L}(\mathrm{k_L}\,\mathrm{C_e})}{1 + (\mathrm{k_L}\,\mathrm{C_e})} \qquad \text{Eq (5)}$$

where q_{max_L} (mg g^{-1}) theoretically represents the maximum amount of metal ions bound per unit mass of biosorbent when all binding sites are occupied and k_L (L mg^{-1}) is the equilibrium adsorption constant.

The Dubinin-Radushkevich isotherm model was developed to consider the effect of the porous structure of an adsorbent. This model can be expressed as:

$$q_e = q_{\max\_DB}\, exp\,(-\beta\varepsilon^2) \qquad \text{Eq (6)}$$

where q_{max_DB} (mg g^{-1}) is the maximum adsorption capacity, β (mol^2 J^{-2}) is a constant related to the adsorption energy and ε (J mol^{-1}) is Polanyi potential obtained as:

$$\varepsilon = RT\ ln\left(1 + \frac{1}{C_e}\right) \qquad \text{Eq (7)}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}).

The value of the mean free energy of adsorption, E (J mol^{-1}), could be obtained as:

$$E = \frac{1}{\sqrt{2\beta}} \qquad \text{Eq (8)}$$

From the magnitude of this parameter, the type of adsorption can be distinguished: E = 1-8 kJ mol^{-1} for physical adsorption and $E > 8$ kJ mol^{-1} for chemical adsorption processes (Hu and Zhang, 2019).

2.3.2. Kinetics of biosorption

With the aim of evaluating the kinetics of Ni (II) biosorption on lemon peel, the pseudo-first order and pseudo-second order models were used:

Pseudo-first order equation:

$$q_t = q_e(1 - \exp(-\mathrm{k}_1 \mathrm{t})) \qquad \text{Eq (9)}$$

Pseudo-second order equation:

$$q_t = \frac{q_e^2 \mathrm{k}_2\, \mathrm{t}}{1 + (q_e \mathrm{k}_2\, \mathrm{t})} \qquad \text{Eq (10)}$$

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

2.3.3. Thermodynamic study

The thermodynamic parameters as the Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and the entropy ($\Delta S°$), were obtained as:

$$\Delta G° = -R\ T\ lnk_D \qquad \text{Eq (11)}$$

$$Lnk_D = -\frac{\Delta H^{°}}{RT} + \frac{\Delta S°}{R} \qquad \text{Eq (12)}$$

$$\Delta G° = \Delta H° - T\Delta S° \qquad \text{Eq (13)}$$

where T (K) is the temperature and k_D is distribution coefficient (dimensionless). The values of $\Delta H°$ (J mol^{-1}) and $\Delta S°$ (J mol^{-1} K^{-1}) were obtained from the values of the slope and the intercept by plotting lnk_D versus $1/T$.

2.3.4. Evaluation of model performance

The fitting of the experimental data was carried out using the non-linear form of isotherm and kinetic models by varying the model parameters and, simultaneously, minimizing the error of predictions. This error was evaluated by the root mean square errors (RMSE) obtained as:

$$RMSE = \sqrt{\frac{\sum_1^m (q_{exp} - q_{model})^2}{m}} \qquad \text{Eq (14)}$$

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

With the aim of evaluating properly results from different models, parity plots for model prediction versus experimental values have been studied. The coefficient of determination (R^2) of this regression analysis was obtained to measure the accuracy of models.

2.4. Characterization

The adsorbent (before and after modification) was characterized by Attenuated Total Reflection Fourier-transform infrared spectroscopy (FTIR-ATR) and by scanning electron microscopy (SEM). The surface morphology was studied on a JSM-840 Scanning Electron Microscope (JEOL, United States). The evaluation of surface functional groups was carried out using a FTIR spectrometer (Model Vertex70) with the Golden Gate Single Reflection Diamond ATR System (Bruker, United States). The spectra were recorded by 64 scans in absorbance mode from 4000 to 500 cm^{-1} range with a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Effect of contact time and pH

The effect of contact time on adsorption of Ni ions on lemon peel has been evaluated to determine the equilibrium time for the maximum uptake (Figure 1). Results show that the uptake increases rapidly within the first hour keeping constant for higher contact times. The equilibrium time selected was 3 h for further experiments in order to ensure the maximum adsorption of Ni (II). As can be seen, the adsorption capacity within 10 min represents more than 50% of the equilibrium adsorption capacity. The high adsorption percentage of metal in very short time has been previously associated with the high affinity of pectin from lemon to interact with metal ions via carboxylic groups (Meseldzija et al., 2019).

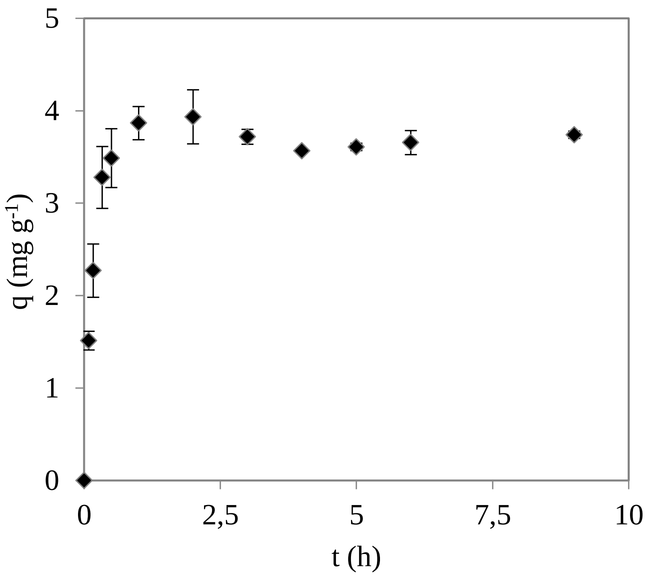

Figure 1. Effect of contact time on adsorption of Ni (II) on raw lemon peel (pH=5; C_0=100 mg L^{-1}, S/L=10 g L^{-1}).

The pH value is one of the most relevant parameters affecting the adsorption processes. Therefore, the dependence of biosorption of Ni (II) on the initial pH value of the aqueous solution in the range 2-6 has been investigated (Figure 2). For these pH values, nickel is mainly present as Ni (II) cation (Anoop Krishnan et al., 2011). As expected, the adsorption efficiency of Ni (II) is significantly lowest for a pH value of 2. These results are associated not only with the competition between Ni (II) cations and protons for the sorbent active sites but also with the repulsion between species positively charged. Also, it should be considered that lower pH entails the protonation of some surface functional groups which hinders the formation of Ni-surface complexes.

However, no important differences in adsorption capacity were observed for pH values from 3 to 6. Based on results, the selected pH value for further essays was 5 since the pH value of the aqueous Ni (II) solution was close to this value.

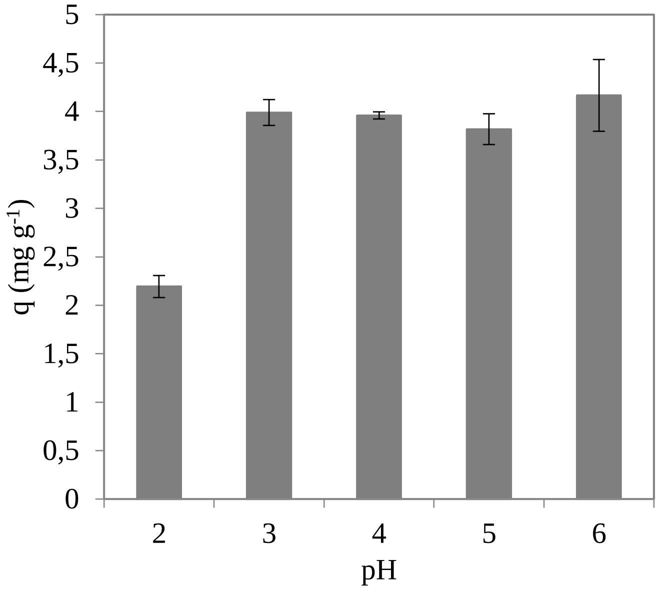

Figure 2. Effect of pH on adsorption capacity of Ni (II) by raw lemon peel. (C_0=100 mg L^{-1}, S/L = 10 g L^{-1}).

3.2. Surface pretreatment

With the aim of improving the efficiency of lemon peel to remove nickel ions, different reagents were used to pretreat the biosorbent surface. As can be observed, the surface modification had an important influence on the adsorption capacity (Figure 3). The ratio of adsorption capacity for acid-modified surfaces with respect to the non-modified surfaces were 0.82, 0.87, and 1.24 for HNO_3, HCl and H_3PO_4, respectively. Decrease in adsorption capacity could be associated with the surface protonation, which reduced the available surface sites for metal binding (Marshall and Johns, 1996; Ranasinghe et al., 2018). Contrary, previous works explained the improvement in adsorption capacity for acid-modified surfaces by the increase of adsorption sites for metal uptake as result of hydrolysis of cellulose, which entails the conversion of macropores to micropores (Ranasinghe et al., 2018). Other authors suggested that protonated peels showed a significantly higher negative surface charged comparing with original biosorbent which ease the metal cation uptake (Schiewer and Balaria, 2009). The use of $CaCl_2$ to modify the sorbent entails an increase of twice the adsorption capacity. The adsorption capacity for lemon peel modified with NH_3 and NaOH represent about 2.5 times than that of the untreated peel. The improvement of alkali-treated surface could be explained by the conversion of lignin structure into negative surface charges favouring adsorption of metal cations (Min et al., 2004). Also, the increase of adsorption capacities could be because of micro-precipitation of metal hydroxides. Based on results, NaOH was selected as surface modifier.

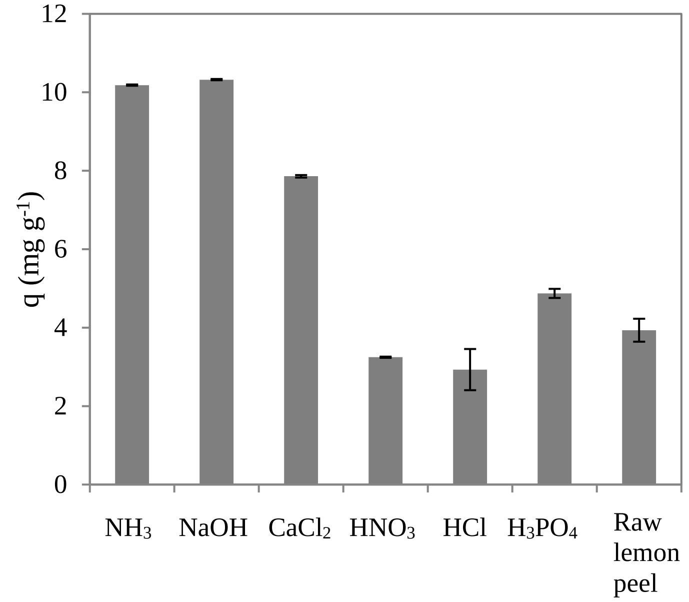

Figure 3. Adsorption capacity results for different surface treatments and raw lemon peel ($pH=5$, $C_0=100$ mg L^{-1}, $S/L=10$ g L^{-1}).

Figure 4 shows the FTIR-ATR spectra of lemon peel biosorbent before and after surface modification with NaOH and HCl, representative results of alkali and acid pretreatments. Results for Ni (II)-loaded biosorbent for unmodified and the alkali-modified peel are also shown. As can be observed, untreated and treated peels have similar spectra, which indicate the presence of similar functional groups contained in the most important component of peels: protein, pectin, cellulose and pigments. The broad peak around 3200-3400 cm^{-1} is indicative of carboxylic and hydroxyl functional groups. The OH stretching depends directly on the content of cellulose in the sample. The well resolved peaks corresponding to –OH and –CH stretching indicates the presence of functional groups for metal binding. The peak around 2900 cm^{-1} was mainly associated with alkyl groups ($-CH_n$) which could be altered during surface modification. The complex split of stretching vibration of CH_3 due to correlation field effects was detected for modified surfaces with NaOH and HCl. The peak at wavenumber around 1640-1750 cm^{-1} was related to the C=O bond of carboxyl groups, probably assigned to ester carbonyl group (Li et al., 2007). The peak at wave number at 1020-1300 cm^{-1} indicates the presence of compounds containing a C–O group. As can be observed, the surface modification with NaOH entails the removal of some functional groups. This trend has been previously associated with the removal of some organic substances, pectin and protein (Thirumavalavan et al., 2011). The disappearance of the peak associated with C=O (~1728 cm^{-1}) for NaOH-modified surface suggested the hydrolysis of this group into carboxyl group (Singh and Shukla, 2016). In general, after acid treatment, some new peaks have been detected due to chemical modification. After the adsorption of Ni (II) on raw and NaOH-treated lemon peel, some changes were observed. The peak intensity of C=O and C–O groups were reduced as a consequence of the adsorption of Ni (II). The peak associated with alkyl groups, around 2900 cm^{-1}, was also reduced after Ni (II) adsorption which has been associated with the possible formation of a metal-carbon bond (Thirumavalavan et al., 2011). Also, shift in wavenumber were detected after metal adsorption which suggested the change in energy of the functional group after adsorption. These results suggested the important role of the aforementioned functional groups as contributors in Ni (II) uptake (Iqbal et al., 2009).

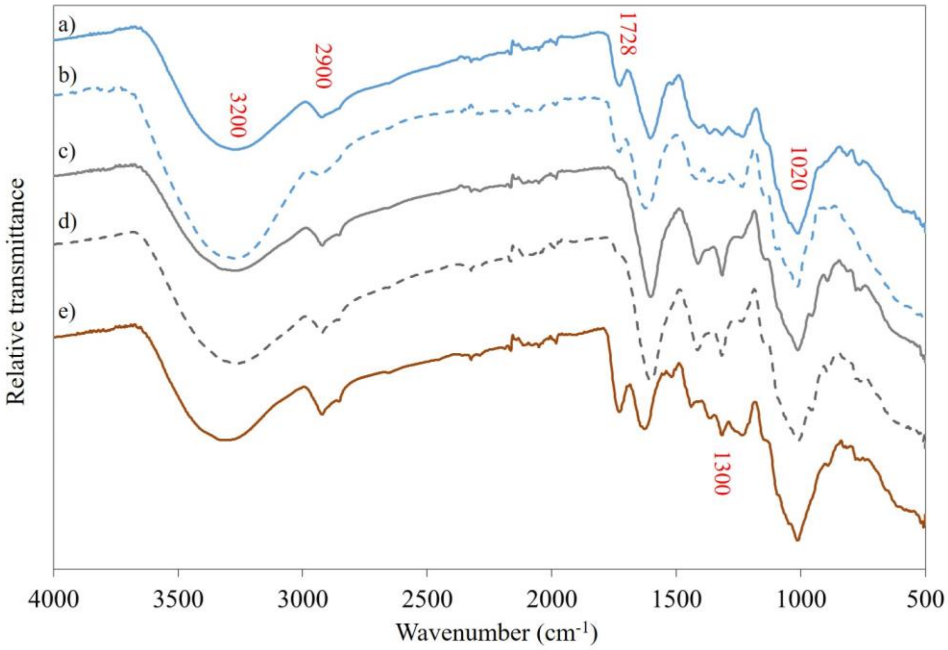

Figure 4. FTIR-AR spectra for: a) raw lemon peel, b) raw lemon peel + Ni(II), c) NaOH-modified lemon peel, d) NaOH-modified lemon peel + Ni (II), e) HCl-modified lemon peel.

The SEM micrographs of unmodified and modified with NaOH lemon peel before and after metal biosorption are presented in Figure 5. The biosorbent surface is mainly characterized by an irregular geometry (Figure 5.a). After modification with NaOH, the superficial structure was kept not being damaged (Figure 5.c). However, the chemical treatment entails variation in morphology, such as the surface structure, which is probably associated with the improvement of the adsorption capacity. The structure of the raw and treated lemon peel was not significantly changed by Ni (II) binding (Figure 5.b,d) which is in agreement with previous studies (Lugo-Lugo et al., 2012).

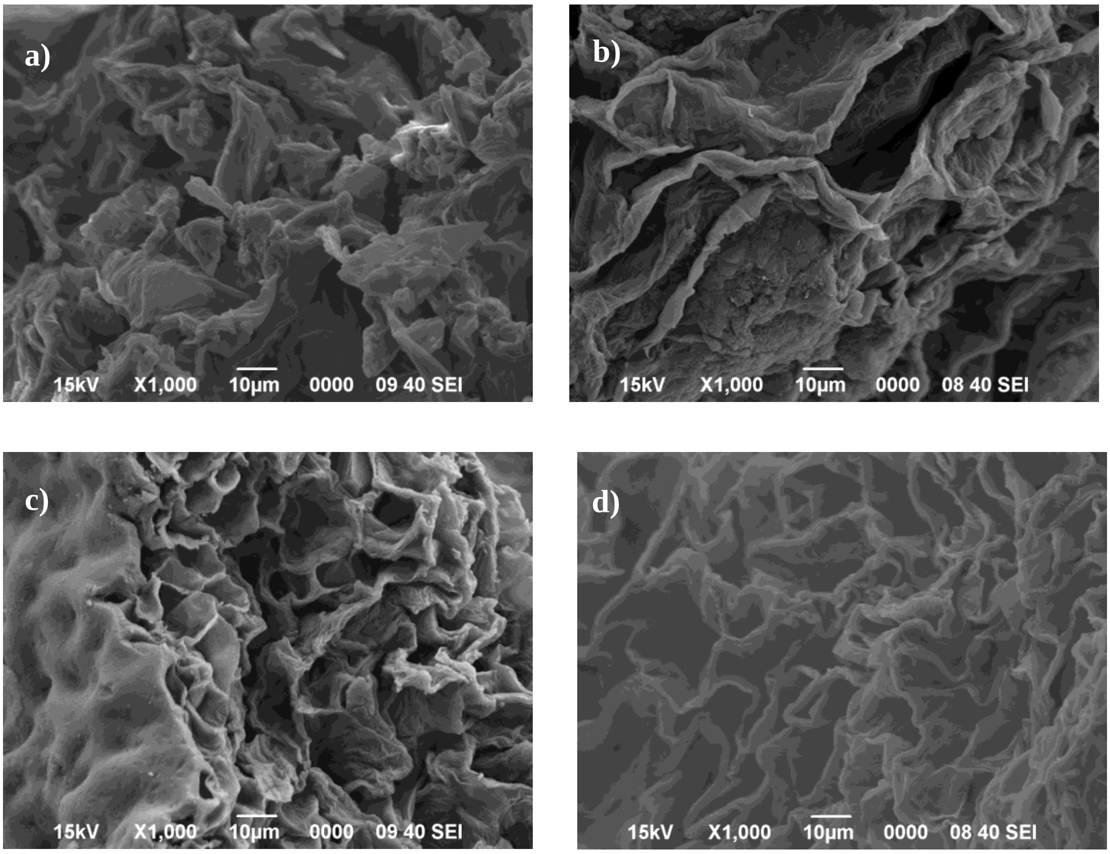

Figure 5. SEM micrographs of raw lemon peel a) before and b) after Ni (II) biosorption and NaOH-modified lemon peel c) before and d) after Ni (II) biosorption.

3.3. Effect of biosorbent dosage

The effect of dosage of NaOH-modified lemon peel samples on the removal of Ni (II) is presented in Figure 6. As expected, the percentage of metal removed increases with biosorbent dosage due to the increase of active sites available for adsorption of Ni (II). The percentage of Ni (II) removed reaches 100% for a biosorbent dosage of 5 g L^{-1}. Regarding adsorption capacity, in contrast, it decreases with increasing mass dosage of biosorbent. These results, for experiments in which the removal of Ni (II) was below 100%, has been previously associated with limited availability of biosorbent surface, reduction in the mixing, interferences between binding sites and electrostatic interactions (Suryavanshi and Shukla, 2010). On the other hand, based on results, use biosorbent dosage above 5 g L^{-1} does not entail any improvement of biosorption efficiency. On the contrary, high biosorbent dosage could involve biosorbent particle agglomeration and the subsequent reduction of the active surface area. According to results, the adsorbent dosage used for further experiments was 5 g L^{-1}.

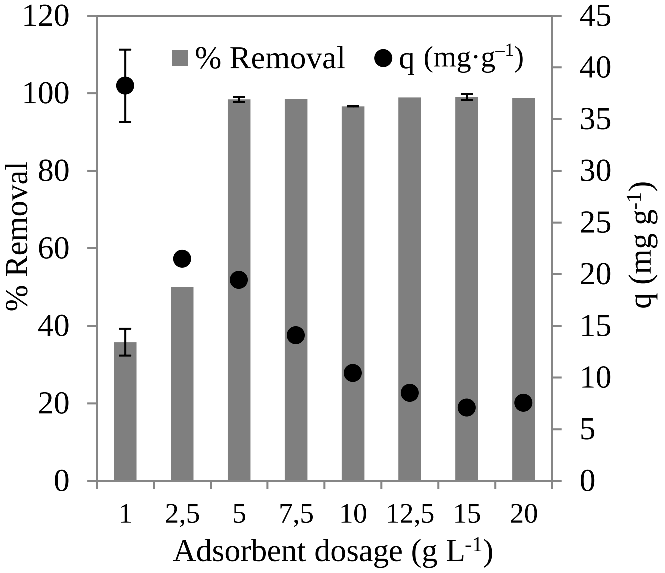

Figure 6. Effect of absorbent dosage on percentage removal and adsorption capacity of Ni (II) by NaOH-modified lemon peel. (C_0=100 mg L^{-1}, pH=5).

3.4. Adsorption isotherms

The experimental results were simulated with non-linear forms of isotherm model Freundlich, Langmuir and Dubinin-Radushkevich (Figure 7). As can be seen, the Langmuir isotherm fits better with experimental data than the others, having RMSE value of 1.5, lower than those obtained for Freundlich and Dubinin-Radushkevich, 4.4 and 3.5, respectively. These results are in agreement with other studies dealing with fruits and vegetable peel as biosorbent (Basu et al., 2017; Ranasinghe et al., 2018) which described the biosorption process as a monolayer adsorption. According to Langmuir model, the maximum adsorption capacity (q_{max_L}) was 36.74 mg g^{-1} which is comparable to those obtained using various agricultural solid wastes such as modified coir pitch (38.9 mg g^{-1}), barley straw (35.8 mg g^{-1}), pine bark (20.58 mg g^{-1}) and cashew nut shell (20 mg g^{-1}) (Raval et al., 2016). Regarding the Dubinin-Radushkevich isotherm parameters, the value of β allowed to estimate the free energy of sorption as showed in Eq. 8. The value obtained, lower than 8 kJ mol^{-1}, indicates that the process is of physical nature (Hu and Zhang, 2019).

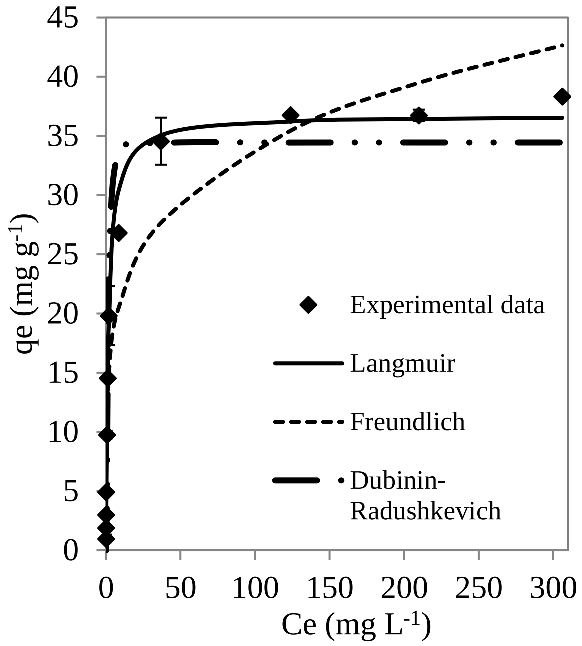

Figure 7. Equilibrium adsorption isotherm for the sorption of Ni (II) on NaOH-modified lemon peel. (pH=5, S/L=5 g L^{-1}).

Table 1. Equilibrium isotherm parameters for biosorption of Ni (II) on NaOH-modified lemon peel.

Model	**Parameters**	
Freundlich	k_f	13.22
	n	4.9
	RMSE	4.4
	R^2	0.913
Langmuir	k_L (L mg^{-1})	0.565
	q_{max_L} (mg g^{-1})	36.74
	RMSE	1.5
	R^2	0.992
Dubinin-Radushkevich	q_{max_DR} (mg g^{-1})	34.44
	β (mol^2 kJ^{-2})	0.34
	E (kJ mol^{-1})	1.21
	RMSE	3.5
	R^2	0.960

3.5. Kinetic study

In this work, the pseudo-first and the pseudo-second order models were applied to the experimental biosorption data of Ni (II) on the NaOH-modified lemon peel (Figure 8). With the aim of evaluating the influence of the initial metal ion concentration not only on the adsorption capacity but also on the kinetic parameters, different metal ion concentrations were essayed. As can be observed, most of the sorption (more than 90%) was detected in the firsts 10 minutes followed by a progressive rate decrease. Results from nonlinear regression analysis are presented in Table 2. The correlation coefficient for the pseudo-first order was found to be higher than that obtained for the pseudo-second order. Therefore, it could be concluded that the sorption of Ni (II) on lemon peel was better described as a pseudo-first order process. According to the results obtained, adsorption capacity (q_e) increases linearly with the initial Ni (II) ions concentration under the experimental conditions studied. The maximum adsorption capacity, 36.74 mg g^{-1}, would be obtained for an initial metal ion concentration of 200 mg L^{-1} in agreement with the adsorption isotherm results. For higher initial concentrations of Ni (II), the adsorption capacity will be maintained constant as can be concluded from Langmuir model. On the other hand, the value of the rate constant increased linearly with decreasing Ni (II) initial concentration which has been reported in previous studies (Ho et al., 1995; Ofomaja and Ho, 2007).

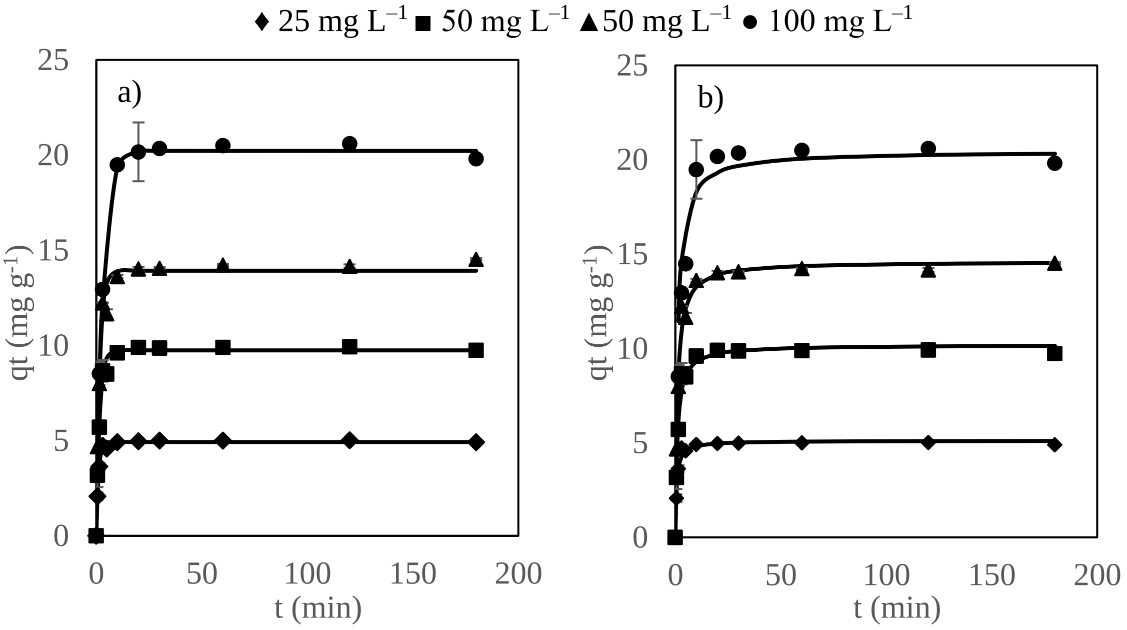

Figure 8. Kinetic studies of Ni (II) ions biosorption. a) first-order model and b) second-order model. Points represents experimental data, continuous lines correspond to fitting curves for NaOH-modified lemon peel. (pH=5, S/L=5 g L^{-1}).

Table 2. Kinetic model parameters.

Kinetic model		Ni (II) concentration (mg L^{-1})			
		25	**50**	**75**	**100**
Pseudo-first-order	k_1 (min^{-1})	0.977	0.640	0.615	0.315
	q_e (mg g^{-1})	4.925	9.740	13.928	20.006
	RMSE	0.132	1.295	0.682	0.667
	R^2	0.991			
Pseudo-second-order	k_2 (g min^{-1} mg^{-1})	0.326	0.103	0.068	0.041
	q_e (mg g^{-1})	5.121	10.193	14.609	20.450
	RMSE	0.185	0.398	0.526	1.449
	R^2	0.977			

3.6. Thermodynamic studies

The adsorption nature of Ni (II) on the modified surface of lemon peel was evaluated through the calculation of thermodynamic parameters using Eqs. 11 to 13. The values of the Gibbs free energy ($\Delta G°$), enthalpy change ($\Delta H°$) and the entropy change ($\Delta S°$) are presented in Table 3. As aforementioned, the values of $\Delta H°$ and $\Delta S°$ were determined from slope and intercept of the linear plot of $Ln\ k_D$ versus $1/T$. The value of the coefficient of determination (R^2=0.90) indicates a correlation of adsorption equilibrium with temperature. The biosorption process is endothermic in nature according to the positive value of $\Delta H°$. In other words, the adsorption of metals has been observed to increase with temperature (Sahmoune, 2019). The magnitude of $\Delta H°$, 14.05 kJ mol^{-1}, indicates that the adsorption of Ni (II) on lemon peel could be attributed to a physical adsorption process, which is in agreement with results obtained from isotherm studies. The negative values of $\Delta G°$ for Ni (II) indicates the feasibility and spontaneous nature of the adsorption process, while the positive value of $\Delta S°$ implies the increased of randomness at the solid-liquid interface during the biosorption process and the affinity of the biosorbents for Ni (II). The magnitude of $\Delta S°$ indicates no relevant structural changes in the biosorbent material (Ramasami et al., 2017).

Table 3. Thermodynamic parameters for Ni (II) adsorption in NaOH-modified lemon peel.

Temperature (K)	**$\Delta G°$ (kJ mol^{-1})**	**$\Delta H°$ (kJ mol^{-1})**	**$\Delta S°$ (J mol^{-1} K^{-1})**
293	-3.16	14.05	58.74
303	-3.75		
308	-4.04		
313	-4.33		
318	-4.63		

3.7. Desorption studies

The recovery efficiency of Ni (II) from loaded-biosorbent using HNO_3 and H_2SO_4 as desorbing agent within 5 consecutive cycles is shown in Figure 9. The desorption percentage after 5 cycles was close to 90% by both nitric and sulphuric acids. These results indicate that the biosorbent studied could be repeatedly used for Ni (II) adsorption without significant losses in it desorption capacity. Therefore, both acids are appropriate to be used as desorbing agent for continuous industrial applications.

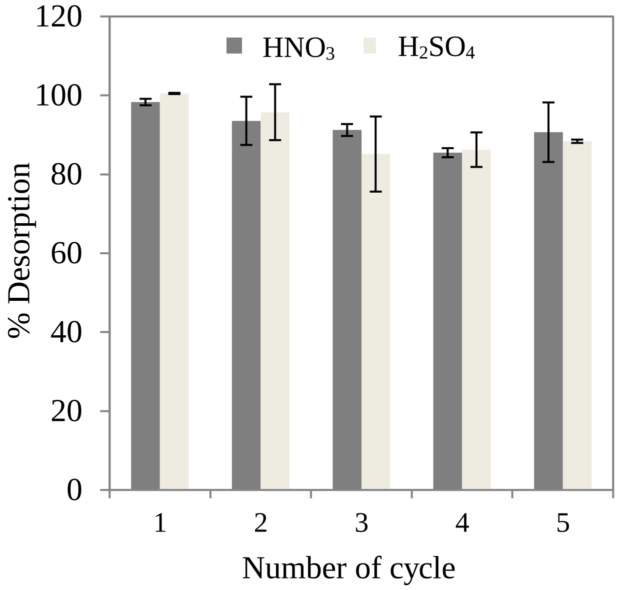

Figure 9. Desorption studies of NaOH-modified lemon peel using 0.1 M of HNO_3 and H_2SO_4 as desorbing agents.

4. Conclusions

The modification of lemon peel surface with NaOH has been probed to enhance, significantly, the adsorption capacity. The optimization of relevant parameters, such as the biosorbent dosage and contact time, revealed promising characteristics of the biosorbent under study to be used in columns applications. The maximum adsorption capacity according to Langmuir model was of 36.74 mg g^{-1}. The adsorption kinetics of Ni (II) on modified lemon peel followed the pseudo-first order model. Desorption studies revealed that using HNO_3 and H_2SO_4 as desorbing agents entails a recovery of Ni (II) of 90% after 5 cycles. Thus, the alkali-modified lemon peel studied presents promising characteristics to be used as an inexpensive biosorbent material for the recovery of wastewater contaminated with Ni (II).

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