Lead (II) Remotion in Solution Using Lemon Peel (*Citrus limonum*) Modified with Citric Acid

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Abstract**—Lead remotion was evaluated in a synthetic solution with 100 µg L^{-1} of Pb (II), using the lemon peel as a biosorbent. The adsorption capacity of the lemon peel at different pH values and particle sizes was studied.A maximum adsorption capacity of 19.556 mg g^{-1} was achieved with 0.5 g of biosorbent dose at pH 6, being able to remove up to 97.78% with the unmodified biomass and 93.83% after the cross-linking process of the adsorbent material.The adsorption kinetics is based on a Pseudo Second Order model for the biomass of lemon pre-treated with citric acid (R^2 = 0.9586) and not pre-treated (R^2 = 0.9408). It is concluded that lemon peel is a good precursor of lead adsorbent in aqueous solution.**

Keyword - Biosorption, adsorption kinetics, Freundlich isotherm, lead.

I. INTRODUCTION

The increase in the concentration of heavy metals in water bodies caused by effluent discharges from anthropogenic activities is a growing environmental problem, because even at very low concentrations they are highly toxic[1], [2].Being cadmium, chromium, zinc, mercury, lead and nickel, the metals commonly found in wastewater; and of these, lead can affect the central nervous system, cause cancer and in more critical cases death due to its high toxicity even at low concentrations by binding with organic molecules[3], [4].

Once the metals enter the aqueous and terrestrial media, they participate in chemical interactions of complexing, oxide-reduction and precipitation, modifying the characteristics of toxicity and bioavailability by converting from one chemical form to another, varying their toxic effect according to the chemical species of the ion, the degree of acidity-basicity and organic and inorganic components of the environment; factors determining the chemical behaviour of the ion in the formation of soluble or insoluble chemical forms that condition risks to biota and public health[5]–[9].

Various technologies have been used for the removal of metal ions, among which are highlighted: chemical precipitation, chemical coagulation, oxidation, reduction, ion exchange, filtration, ultrafiltration, nanofiltration, adsorption (activated carbon, zeolites, silica gel), membrane technologies (reverse osmosis), electrochemical treatment (electrodialysis and electrocoagulation) and application of artificial wetlands (some stabilization), among others, resulting in many cases inefficient and costly [10]–[13]. Consequently, it is important to develop new detoxification technologies for such effluents and to chemically stabilize the compound[14]. This is why the development of new technologies based on domestic raw materials is a pending task for researchers from developing countries such as Colombia. Several studies have shown that the biomass of different species of lignocellulosic waste, bacteria, fungi and algae, are able to retain in their structures, metal ions that are found in aquatic environments [15]–[17].

Biosorption is a physicochemical process that includes the phenomena of adsorption and absorption of molecules and allows the retention of metal ions dissolved by materials with bioadsorbent capacity [18], [19].Containing the biosorbents of plant origin macromolecules (proteins, carbohydrates, carboxyl groups, hydroxyl, sulphates, phosphates and amino) that can trap metal ions by attracting opposing charges, thus favouring adsorption, depending on this process of pH, temperature, ionic force of the medium, chemical characteristics of the metal, as well as the adsorbent capacity [20]–[23].

The search for low-cost materials with adsorbent capacity, such as agricultural waste and biological materials that allow ion stability and are resistant to disintegration and dissolution in the medium, have been tested to evaluate the efficiency of removal of soluble metal ions [24], [25].In addition, in order to improve the adsorption capacity of various materials, some authors have induced physical or chemical changes in different structures in order to increase the specific surface area of contact in two ways: between the bioadsorbent material and the ion and the number of loads and activity of the binding groups [26], [27].Among the vegetable residues recently used for adsorption of Pb (II) are African palm pre-treated with citric acid, olive pits modified with HNO_3, H_2SO_4 and NaOH, red seaweed, orange peel and tuna, dried or crushed orange peel, with and without cross-linking treatment (with $CaCl_2$) .In this context, the main objective of this work was to demonstrate the use of pre-treated lemon waste materials with citric acid as a source of biomass to remove Pb (II) from industrial wastewater[28]–[31].

II. MATERIALS AND METHODS

A. Preparation of the bioadsorbent

The biomass was collected in the best possible condition to prevent its rapid decomposition, washed with abundant distilled water to eliminate tannins, reducing sugar resins and other impurities, which may intervene in the adsorption process.Then, it was dried in an oven at 90 °C for 24 h. The size was then reduced by a roller mill for 20 min. Sorting was carried out in a sieve shaker by selecting the sizes: 0.355 mm, 0.5 mm and 1 mm[28].

B. Adsorbent characterization

Once the bioadsorbent material had been prepared, the functional groups in the lemon peel were identified and the FTIR (Fourier Transformed Infrared Spectra) analysis was carried out[20].

C. Modification of lemon peel with Citric Acid

Once the lemon peel was conditioned, the modification was carried out with citric acid, for this purpose 40 g of biomass was mixed with 200 mL of a 0.6M citric acid solution. The mixture was left in agitation for 2 h at a temperature of 60°C, after this time, the biomass was washed with abundant deionized water, then dried in an oven for 24 h at 55°C[32].

D. Preparation of synthetic wastewater

A Shaking incubator IN-666 was used to perform the adsorption tests, which previously contained an Erlenmeyer with 0.5 g of biomass and a Pb (II) solution at 100 $\mu g\ L^{-1}$, which was prepared by adding 0.1 g of $Pb(NO_3)_2$ to one L of deionized water[31].

E. Bioadsorption tests

The adsorption tests were carried out at a temperature of 25°C and 150 rpm for 2 h, the pH values were 2, 4 and 6, which were controlled by the addition of 0.1N HCl and 0.5 % NaOH p v^{-1}[33].Final concentration analysis was performed by atomic absorption spectroscopy at 283.3 nm through mass balance[34]. After these tests the adsorption capacity was calculated using:

$$q_e(mg\ g^{-1}) = \frac{V(C_0 - C_f)}{m} \tag{1}$$

Where, q_e is the adsorption capacity in equilibrium (mg g^{-1}), C_o and C_f are the initial concentrations and equilibrium (mg L^{-1}) of Pb (II) in the solution, V is the volume (L) of solution taken and M is the mass (g) of adsorbent used[34].

F. Adsorption kinetics

In order to determine the Pb (II) remotion kinetics, batch-type experiments were carried out at 150rpm, by contacting different initial metal concentrations (25,50,75, 100 mg L^{-1}) for the unmodified lemon peel pre-treated with citric acid.The experiments were performed at pH 3, which was adjusted by adding drops of NaOH or HCl 0.1 N and 0.5 % w v^{-1}, respectively; and a ratio of 2 g L^{-1}. The experiments were placed in 1000 mL beakers and shaken with a magnetic stirrer for 4 h[28], [31].

III. RESULTS AND DISCUSSIONS

The chemical-proximal analysis of the natural lemon peel showed a high carbon content of 38.48%, followed by cellulose 18.49%, lignin 7.22% and hemicellulose 6.07%. In addition, it presented low ash content (3.68%). Fig. 1 shows an FTIR analysis of the lemon peel to determine the functional groups that favour the lead adsorption process, as well as the lemon peel pre-treated with citric acid.

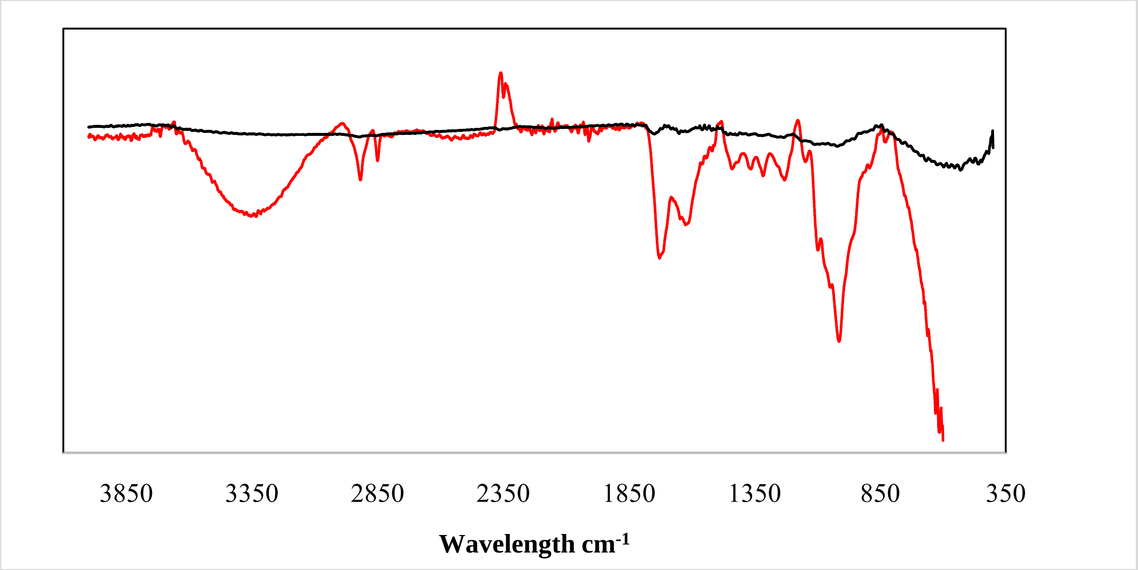

Fig. 1. FTIR analysis of modified (——)and unmodified (——) lemon peel before adsorption

Figure 2 shows the FTIR analysis of residual lemon biomass after adsorption without pre-treatment and modified with citric acid.

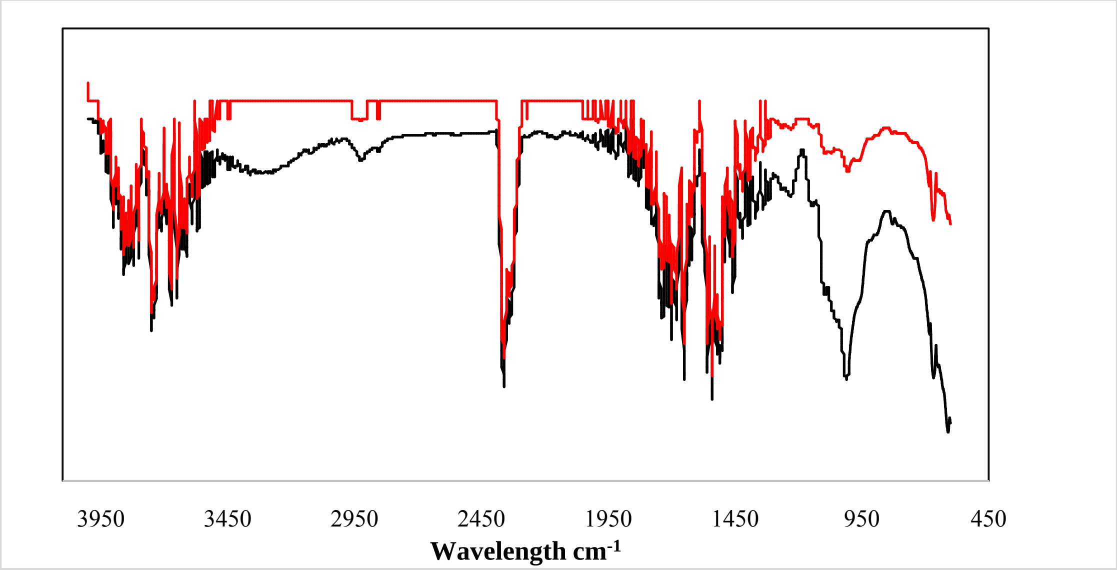

Figure 2. FTIR analysis of lemon biomass modified with citric acid (——) and unmodified (——) after adsorption of Pb (II).

A. Effect of pH and particle size on adsorption

In this study, it was evaluated the effect of pH for values of 2,4 and 6, shown in Fig. 3 as well as the effect of particle size on adsorption with residual lemon biomass.

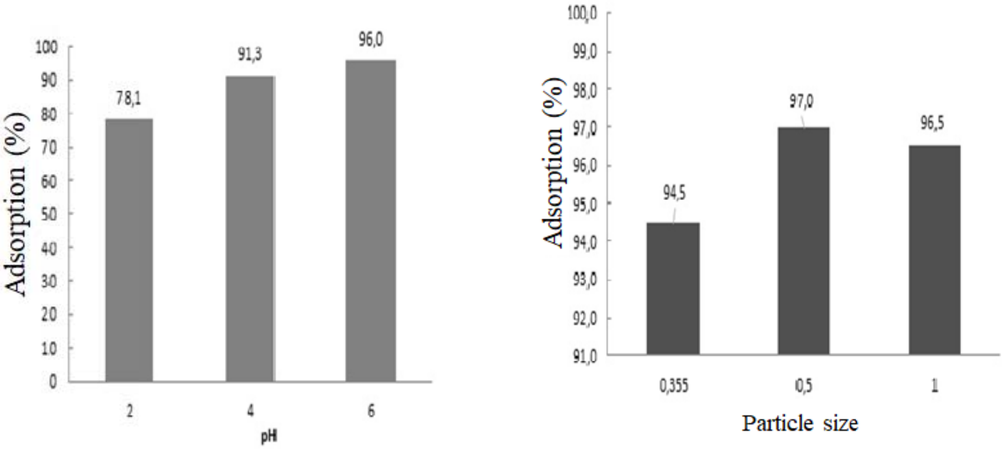

Fig. 3. Effect of pH (left) and particle size (right) on the adsorption of Pb (II)

B. Adsorption kinetics

To study adsorption kinetics, the Pseudo-first order, Pseudo-second order and Elovich models were taken into account. These mathematical models of non-linear fit were developed in the Microsoft Excel Solver tool.

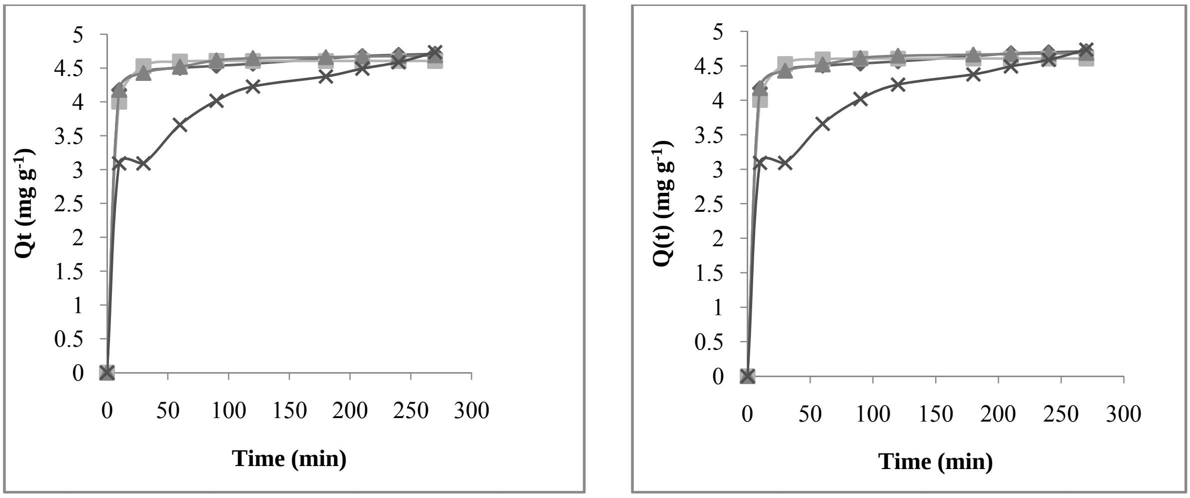

Fig. 4. Adjustment of the kinetic adsorption models of Pb (II) using lemon peel without pre-treatment (left) and modified with citric acid (right). Note: (—◆— xperimental, (—■— Pseudo-first order, (—▲— Pseudo-second order and (—✕— Elovich model.

Because it is an organic material of vegetable origin, a high carbon content corresponding to 38.48% of the sample was observed, values that favor the adsorption of a metallic ion due to its porous characteristics.In addition, a great presence of cellulose with 18.49% was observed; the presence of these polysaccharides represents an ally in the adsorption due to their structure, which has the presence of groups such as alcohols, acids, phenolic hydroxides, aldehydes and ethers that usually improve the ion exchange capacity of biomass because they are polar compounds[28]. In the spectrum of Fig. 1, the wide and marked peaks of 3330 cm^{-1} correspond to the O-H vibrations due to the stretching of alcohols, phenols and carboxylic acids in pectin, cellulose and lignin, therefore, the presence of "free" hydroxyles on the adsorbent surface is established[24], [35].

The main components of the lemon peel are proteins, pectins, cellulose, pigments and lignin, so the spectrum shows numerous peaks of absorption indicating the complex nature of the adsorbent material[35].Moreover, a C-O stretch is observed in the spectrum 1030cm-1 after the cross-linking process with citric acid, as well as in the band 3500 cm^{-1} corresponding to the hydroxyl group[36].

In Fig. 2 corresponding to the FTIR spectra for modified and unmodified lemon biomass after lead ion adsorption (II), the change in the bands 300 to 3700 is observed, and in the own 2400 hydroxyl groups present in cellulose, lignin and pectin present in the biomaterial, which shows that the lemon biomass adsorbed citric acid well.In addition, a change is shown in the group that appears at 1700cm^{-1}, corresponding to the vibrations of ionic carboxylic acids -COO, thus establishing that there are carboxylic and hydroxyl groups in the native biomass and that plays an important role in the adsorption of the ion[36].On the other hand, it also presents the results of the FTIR analysis for lemon peel pre-treated with citric acid after the lead adsorption, a C-O stretch band is observed in 1000cm^{-1}, as well as in 1600cm^{-1} corresponding to the vibrations by stretching of the carboxylic ionic groups -COO.In addition, the 3700cm^{-1} band also shows vibrations, demonstrating that a high concentration of hydroxyl groups favors the removal of metals, since they allow chelation between the methyl ion to be treated and biomass[36].

The pH handled in the heavy metal solution influences the biosorption process due to the influence on the main surface sites and the nature of the metal.Figure 3 shows that at higher pH values (pH=6) the concentration of hydroxyl is increased, causing changes in the surface of the adsorbent and thus increasing the removal capacity of the metal ion, since the surface could be protonated favouring the adsorption of lead ions which favours the adsorption of lead in its anionic form,which is due to the influence of pH on surface electrostatic interactions between biomass and metal chemistry[37].

The influence of the particle sizes 0.355, 0.5 and 1 mm evaluated in this paper are shown in Fig. 3. It is observed that for an intermediate particle size of 0.5 mm the best metal removal rate was obtained with 97%; however, the three particle sizes tested are suitable for removal of the Lead (II) ion with lemon peel.Although, the decrease in adsorption capacity as the particle size decreases may be due to agglomeration of the particles in the pores of the biomaterial[36].Figure 4 shows that the model that best fits the lead data in the untreated lemon peel treated with citric acid is Pseudo Second Order with an R2 of 0.9586 and 0.9408, respectively.According to this, the ions are adsorbed in two active biomass sites, which in this case would be the hydroxyl and carboxyl functional groups, making a chemisorption. Removal percentages were obtained after 310 minutes of 97.78% and 93.83% contact with the untreated and pre-treated lemon, respectively, with better results with natural biomass were obtained[34], [37].

IV. CONCLUSION

According to the results obtained in this investigation, it was found that the lemon peel presents a great capacity of adsorption of Pb (II) ions in synthetic water, since it was able to remove up to 97.78% obtaining a maximum adsorption capacity of 19,556 mg/g with 0.5 g biosorbent dose, however once modified the adsorption capacity was reduced to 93.83%.The best conditions under which the Pb (II) ion adsorption process was performed were achieved using pH of 6 and 0.5 mm particle size.The fitting of the experimental data obtained for the different selected models indicates that the Pseudo Second Order model is the mathematical model that best describes the adsorption kinetics of Pb (II) for the residual biomass of lemon residual untreated and pre-treated with citric acid.On the other hand, the isothermal model that best describes the results obtained was the one proposed by Freundlich, which proved that the adsorption process is controlled by chemical reaction.

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