Application of Lemon (C. *Limonum*) Peels Biomass Chemically Modified with Citric Acid for Chromium (VI) Ions Removal

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Abstract- The increasing pollution of water resources with heavy metal ions coming from industrial activities has threatened the ecosystem biodiversity as well as human health. Several alternatives have been addressed to treat wastewater before discharging into the environment. In this work, chromium adsorption was evaluated using lemon peels biomass, which was also modified with citric acid attempting to increase adsorptive properties. Physicochemical characterization of adsorbent was conducted via FT-IR technique and compositional analysis (proximate and ultimate). The batch adsorption experiments were performed using stock solution of Cr (VI) ions at 100 ppm, room temperature and 0.5 g of adsorbent. The effect of solution pH, particle size and initial concentration was evaluated to identify optimum operating conditions. Experimental results were used to calculate parameters of kinetic models of pseudo-first order, pseudo-second order and Elovich. Results revealed the presence of functional groups such as carboxylic that have been proved to enhance adsorption performance. The optimum condition for adsorption experiments using lemon peels biomass without chemical modification is pH=6 and particle size of 0.5 mm. The effect of initial concentration was also evaluated, and results revealed that chemically modified biomass was superior over the unmodified for all concentrations, with a maximum removal yield reached of 79.54% at 25 ppm. The kinetic modeling of results showed that Elovich model best fitted experimental data with R2 of 0.98 and 1 for LP and LP-CA adsorbents, respectively.

Keywords – Valorization, agricultural residues, removal, heavy metal, chromium

I. INTRODUCTION

The need to reduce the concentration of heavy metal ions present in industrial effluents below the levels allowed by international legislation on environmental conservation has led to the development of various separation techniques such as: coagulation , differential precipitation, ion exchange, solvent extraction, flotation and adsorption [1]. Some heavy metals associated with the most toxic industrial residues are chromium, lead and nickel. Chromium hexavalent is discharged by different industries such as pigment manufacturing, leather tanning and electroplating

[2]. This heavy metal is considered one of the most noxious metals because of its toxicological properties leading to irreversible physical health problems such as skin cancer, kidney damage and nervous system disorder [3]. The treatment of wastewater polluted with heavy metals like chromium has received great interest in the scientific community owing to its difficult removal, toxicity and its non-biodegradability [4].

The most common methods used in the removal of chromium, as well as other heavy metal ions, are economically unfeasible (conventional ion exchange, liquid or electrolytic extraction, electrodialysis) or technically complicated (precipitation, cementation, osmosis reverse) with disadvantages such as low efficiencies, high operating costs, involved implementation [5]. Among these, adsorption appears to be a good alternative capable of overcoming the deficiencies of traditional methods, which promotes the use of low-cost renewable natural materials that have adequate characteristics such as adsorptive materials coming from sugarcane bagasse, banana peels, rice husk and coconut fiber [6]. To date, several works have addressed lignocellulosic materials from agricultural activities to be used as adsorbent for the removal of heavy metal ions from aqueous solution [7].

Acosta et al. [8] studied the adsorption capacity of tamarind peels to remove chromium hexavalent and reported total removal of 50 mg/L occurring after 30 minutes of contact time, pH=1 and 28°C. This material showed great capacity of removal at the concentrations evaluated, also efficiently removes the metal in situ, (94.65% removal, 6 days of incubation, 5 g of biomass). A study conducted by Bhatnagar et al. [9] used lemon peels for adsorptive removal of cobalt ions. They reached the maximum adsorption capacity of 22mg /g. The models of simplified kinetics (pseudo-first order, pseudo-second order, Weber and diffusion models) were tested to describe the adsorption process. Kinetic parameters, speed constants, equilibrium adsorption capacity, and related correlation coefficients on kinetic models were determined. Lemon peel residues can be beneficially used in the treatment of industrial effluents that contain heavy metal ions. In this work, lemon (*C. Limonum*) peels biomass was modified chemically with citric acid to evaluate the enhancement of adsorptive properties of this agricultural waste. The effect of particle size, initial solution pH and initial concentration was assessed for chromium hexavalent onto the biomass.

The rest of the paper is organized as follows. The methodology of bio-adsorbent synthesis and batch tests are explained in section II. Experimental results are presented in section III. Concluding remarks are given in section IV.

II. MATERIALS AND METHODS

2.1. Preparation of adsorbent-

The lemon (*C. Limonum*) peels was provided by a local market in Cartagena de Indias, Colombia, and washed thoroughly with distillated water to remove impurities that may affect adsorption process. This biomass was dried in an oven at 70°C for 24 hours and then washed with ethanol to remove water-insoluble polymers remaining in the material. After a second drying, the material was grounded and sieved to reduce particle size to 0.355 mm, 0.5 mm and 1 mm. The chemically modification of lemon peels was performed by mixing 0.6 M citric acid solution with biomass in a 1:5 ratio (g biomass: mL acid) [10]. The resulting mixture was kept under stirring at 60°C for 2 hours and then, washed with distillated water until neutral pH. Finally, the modified biomass was dried in an oven at 55°C for 24 hours.

2.2. Physicochemical characterization-

The lemon peels (LP) biomass was characterized by the analytical methods listed in Table 1. Elemental analysis was conducted to quantify the contribution of carbon, hydrogen, nitrogen and sulfur in the material. Besides, the presence of biopolymers (pectin, lignin, cellulose and hemicellulose) were identified using digestion-thermogravimetry and photocalorimetry. The effect of chemical modification with citric acid was observed via Fourier-Transform Infrared Spectroscopy (FT-IR) technique.

Table -1 Analytical methods for chemical characterization of biomass

Parameter	**Method**
Carbon (%)	**AOAC 949.14**
Hydrogen (%)	**AOAC 949.14**

Nitrogen (%)	**AOAC 984.13 KJELDAHL**
Sulfur (ppm)	**Digestion**
Ashes (%)	**Thermogravimetry**
Pectin (%)	**Digestion-thermogravimetry**
Lignin (%)	**Photocalorimetry**
Cellulose (%)	**Digestion-thermogravimetry**
Hemicellulose (%)	**Digestion-thermogravimetry**
Functional groups	**FT-IR**

2.3. Adsorption study-

To evaluate the adsorption performance of LP biomass before and after chemical modification, batch experiments were conducted using stock solution of chromium ions at 25, 50, 75 and 100 ppm. This solution was prepared by dissolving 0.05 g $K_2Cr_2O_7$ into 500 mL of deionized water. The adsorption tests were carried out following the methodology proposed by Li et al.[11]. Initially, solution pH was adjusted to 2, 4 and 6 using HCl and NaOH solutions. Then, 100 mL of stock solution was mixed with 0.5 g of adsorbent under stirring at 25°C and 150 rpm. After reaching the fixed contact time of 6 hours, samples were collected to quantify the remaining concentration of heavy metal ions using UV-VIS spectroscopy. The removal yield R (%) is calculated according to Equation 1, where C_o (mg/L) is the initial concentration of heavy metals and C_e (mg/L) is the remaining concentration of heavy metal ions [12].

$$R\ (\%) = \frac{(C_0 - C_e)}{C_0} \cdot 100 \qquad (1)$$

2.4. Kinetic modelling-

The adsorption mechanism was predicted by fitting experimental data with kinetic models (pseudo first order, pseudo second order and Elovich). Table 2 lists the mathematical expressions used to calculate the model parameters.

Table-2 Mathematical expressions of kinetic models

Kinetic model	Equation	Parameters
Pseudo-1st-order	$q_t = q_e(1 - e^{-kt})$	**q_e, Adsorption capacity at equilibrium (mg/g)** **k_1, pseudo-1st-order constant (min^{-1})**
Pseudo-2nd-order	$q_t = \frac{t}{\left(\frac{1}{(k_2 q_e^2)}\right) + \left(\frac{t}{q_e}\right)}$	**k_2 pseudo-2nd-order constant (g/mg.min)** **q_e, Adsorption capacity at equilibrium (mg/g)**
Elovich equation	$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$	**α, Elovich constant (mg/g min)** **β, Elovich exponent (g/mg)**

III. Experiment and Result

3.1. Biomass characterization-

In order to determine the composition of the biomass, the content of different elements present in the lemon peels was studied by elementary analysis, as well as the content of biopolymers. The ashes composition was quantified via proximate analysis. The results provided by these techniques are shown in Figure 1. The carbon most contributed to biomass composition with 38.39%, followed by hydrogen and nitrogen. Similar composition of lemon peels was found by Pathaket al. [13] as follows: C (%) 40.33, H (%) 5.96 and N (%) 1.27. The ashes content was calculated in 3.68%, lower than those reported by Janati et al.[14], in which ashes composition was 6.26%. The lemon (*C. Limonum*) peels reached 18.49% of cellulose, followed by lignin (7.22%), hemicellulose (6.07%) and pectin (5.41%). This high contribution of cellulose is attributed to the albedo, a cellulosic layer that represent the major part of the biomass [15]. Damma et al. [16] quantified the presence of biopolymers in lemon peels and obtained the following results: cellulose (23.1%), pectin (13 %), hemicellulose (8.09) and lignin (7.6%), which are similar compositions to those of this work. These polysaccharides represent an ally in adsorption due to their structure with functional groups such as alcohols, acids, phenolic hydroxides, aldehydes and ethers that are usually polar compounds improving the ion exchange capacity of the biomass [17].

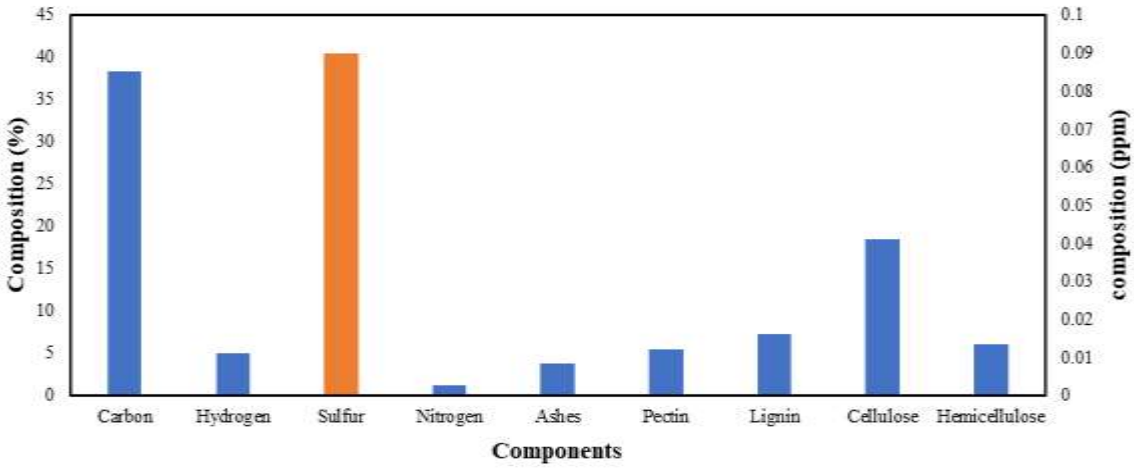

Figure 1. Chemical composition of LP biomass

The FT-IR spectra for the biomass before and after chemical modification are shown in Figure 2 and 3, respectively. It was identified the presence of carboxylic acids (-OH) and aldehyde (C=O) at 3293 cm^{-1} and 1734 cm^{-1}, respectively. The peak at 1650 cm^{-1} is assigned to the stretching vibrations of C=C (alkene, aromatic, amino acids). The absorption bands around 1560-1500 cm^{-1} are attributed to the symmetric bending of CH_3. The sharp band at 1048 cm^{-1} corresponds to the primary alcohol, C-O stretching, primary amine and CN stretching. The identification of these peaks proved the presence of alcohol, carboxylic groups and amides that contribute significantly to adsorption process [13]. After chemical modification with citric acid, changes in the bands 300-3200 cm^{-1} and 1700 cm^{-1} are observed, which corresponded to the hydroxyl and carboxylic acid groups, respectively, suggesting the lemon biomass adsorbed citric acid in a good way.

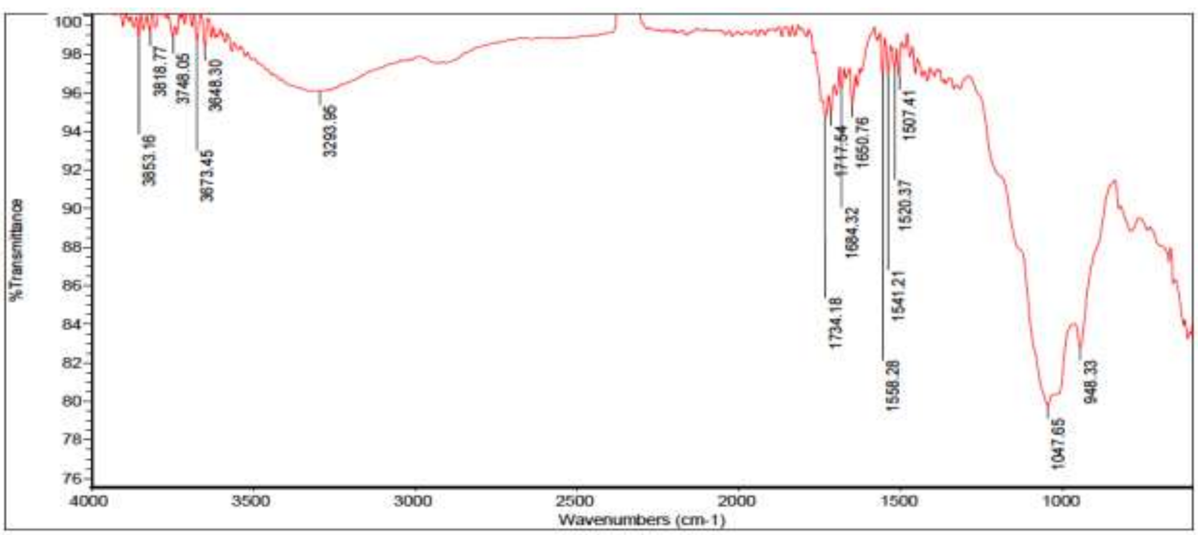

Figure 2. FT-IR spectra of lemon peel biomass

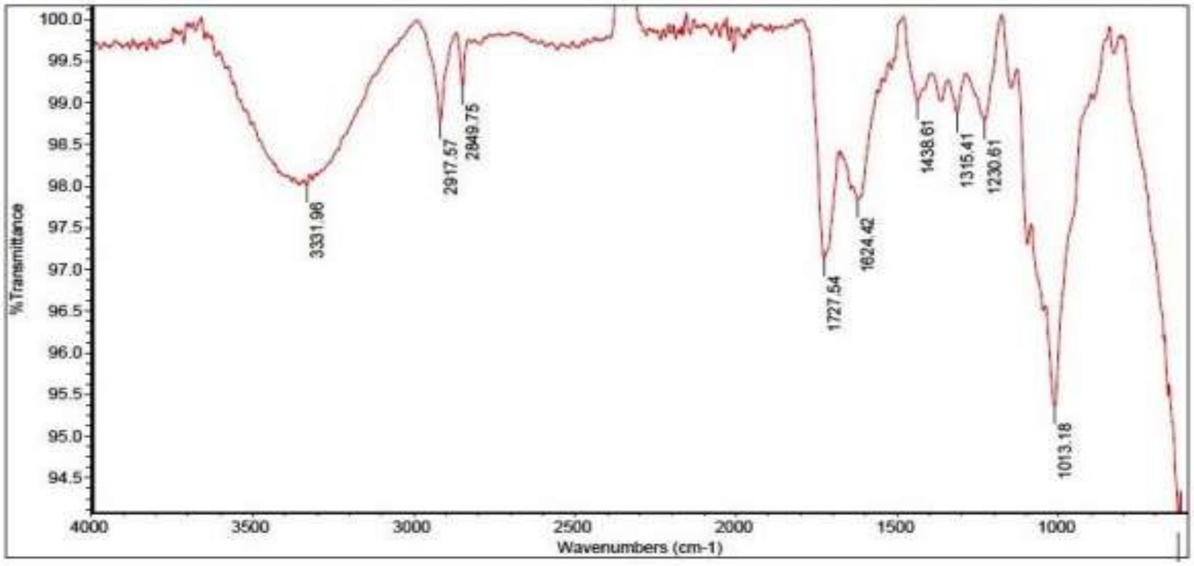

Figure 3. FT-IR spectra of lemon peel biomass chemically modified with citric acid

3.2. Adsorption study-

Effect of particle size and solution pH: Figure 4 depicts the removal yield of chromium ions reached by varying initial solution pH (2, 4 and 6) as well as biomass particle size (0.355 mm, 0.5 mm and 1 mm). It was found that chromium adsorption was highly pH dependent; the highest removal yield was reached at pH=6, followed by pH=4. The low adsorption when solution pH=2 is attributed to the presence of H^+ and H_3O^+ ions that compete with heavy metal ions for available active sites [18–20]. The particle size shows no significant contributions to heavy metal ions uptake; however, particle size of 1 mm reported the highest removal yields. The optimum condition for adsorption experiments using lemon peels biomass without chemical modification is pH=6 and particle size of 0.5 mm. Similar results were reported by Tejada-Tovar et al. [21] for the modification of biomass using citric acid, in which highest adsorption of 97% was achieved with particle size of 0.5 mm.

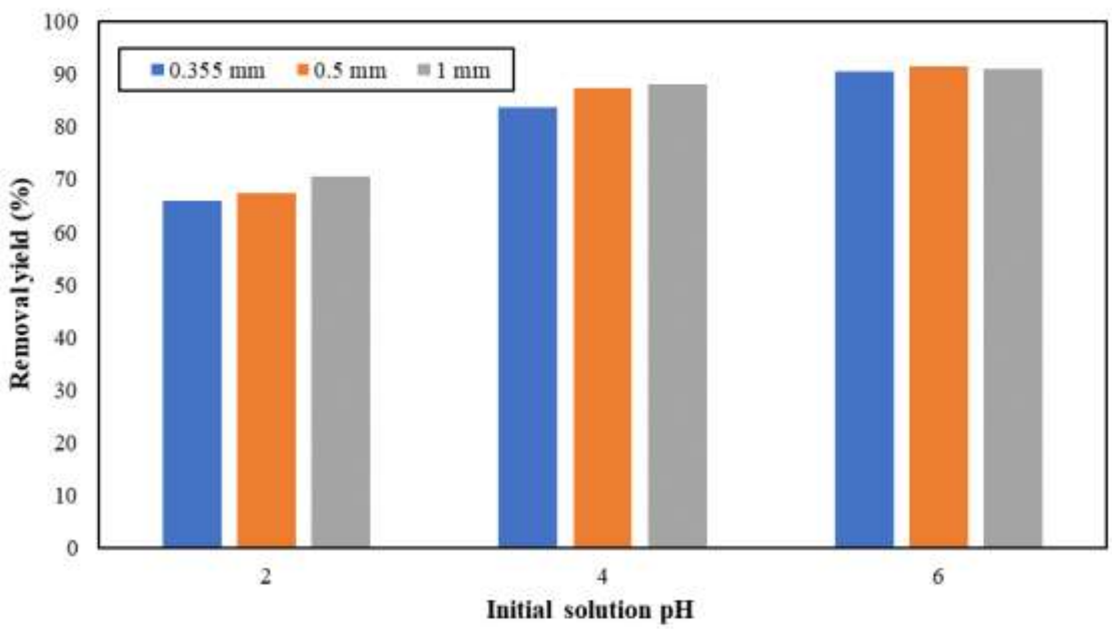

Figure 4. Effect of pH and particle size on removal yield of chromium using lemon peels biomass

Effect of initial concentration: Initial concentration of heavy metal ions play an important role during adsorption because of the saturation of the adsorptive material [22]. After selecting the optimum conditions of pH and particle size, the effect of initial concentration on removal yield was evaluated for both adsorbents LP and LP-CA. As shown in Figure 5, higher capacity of biomass to capture more metal ions on its surface is observed at lower initial concentration. For all concentrations, chemically modified biomass showed superiority over the unmodified, with a maximum removal yield reached of 79.54% at 25 ppm.

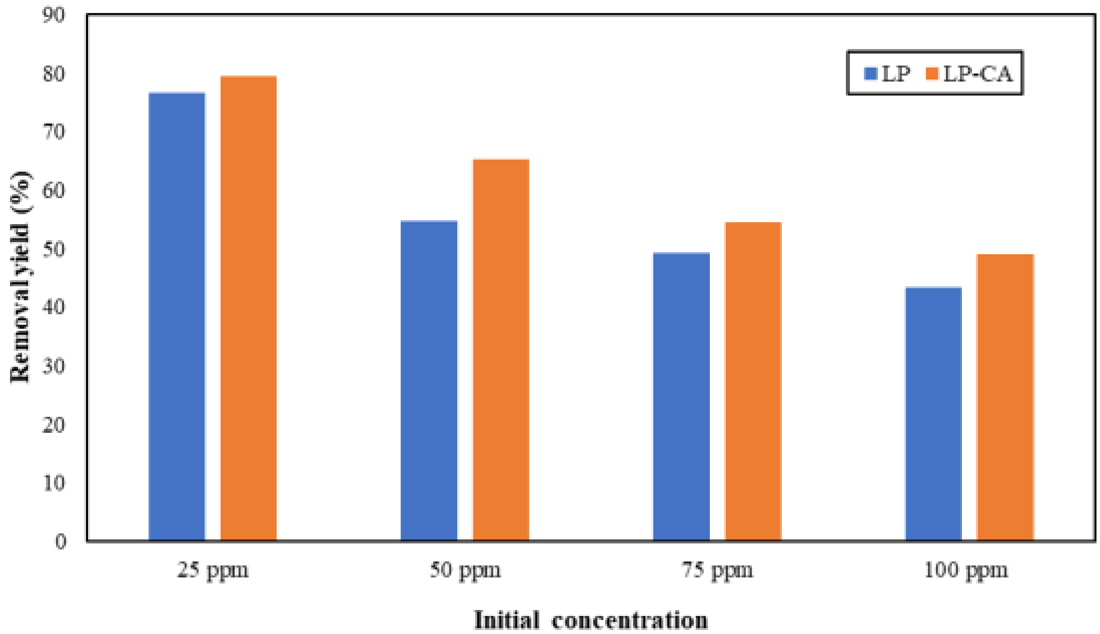

Figure 5. Effect of initial concentration on removal yield of chromium using LP and LP-CA adsorbents

3.3. Kinetic modeling

Studies of adsorption kinetics are important in the treatment of effluents, since these provide good information about the mechanism of adsorption. This process depends on the physical and chemical characteristics of the adsorbent as well as system conditions [23]. Figure 6 shows the adsorption performance of chromium onto LP and LP-CA adsorbents over time. The biomass modified with citric acid revealed a better adsorption performance in a time of 410 min with maximum removal yield of 49.85% compared to that obtained from LP biomass (43.7%).

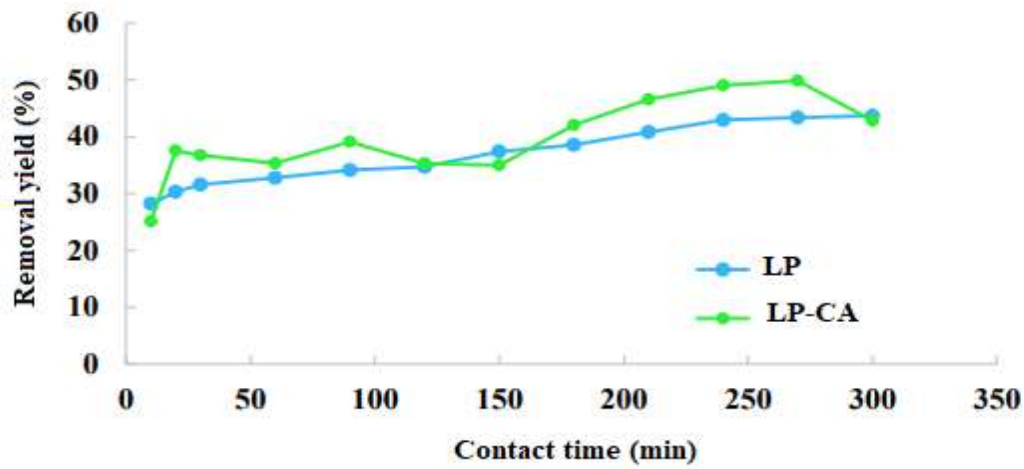

Figure 6. Adsorption curves over time using LP and LP-CA adsorbents

In order to analyze the adsorption behavior of lemon peels biomass before and after chemical modification, the kinetic model that best described the experimental data was determined by fitting results with pseudo-first order, pseudo-second order and Elovich models. These kinetic models account for the speed at which contaminants are adsorbed from the liquid medium. The parameters calculated with the different kinetic models and their corresponding correlation coefficients are summarized in Table 3. Based on the correlation coefficient (R^2), Elovich model best fitted experimental adsorption data with R^2 around 1, followed by pseudo-second order.

Table-3 Fitting parameter for kinetic models

Model	Parameters	LP	LP-CA
Pseudo –first order	q_e **(mg/g)**	**12.37**	**198.42**
	k_1 **(min^{-1})**	**1.49**	**0.59**
	R^2	**0.80**	**0.64**
Pseudo-second order	q_e**(mg/g)**	**11.07**	**50.93**
	k_2**(min^{-1})**	**5.3×10^{-3}**	**9.8×10^{-5}**
	R^2	**0.94**	**0.89**
Elovich	α	**33.04**	**46.01**
	β	**0.83**	**0.98**
	R^2	**0.98**	**1**

IV.CONCLUSION

The physicochemical characterization of lemon peels biomass via elemental analysis and FT-IR tecnique showed major contribution of carbon as well as cellulose in comparison with the other elements and biopolymers, respectively. The presence of alcohol, carboxylic groups and amides in the spectra allowed to predict biomass performance for metal ions uptake. It was found that chromium adsorption was highly pH dependent while particle size did not affect significantly the process. The optimum condition for adsorption experiments using lemon peels biomass without chemical modification is pH=6 and particle size of 0.5 mm. The effect of initial concentration was also evaluated, and results revealed that chemically modified biomass was superior over the unmodified for all concentrations, with a maximum removal yield reached of 79.54% at 25 ppm. The kinetic modeling of results showed that Elovich model best fitted experimental data with R^2 of 0.98 and 1 for LP and LP-CA adsorbents, respectively.

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