

Removal of Cr (VI) from Aqueous Solution using Orange Peel-based Biosorbents

C. Tejada-Tovar, A. D. Gonzalez-Delgado* and A. Villabona-Ortiz

Department of Chemical Engineering, University of Cartagena, Cartagena, Bolivar, Colombia;
ctejadat@unicartagena.edu.co, agonzalezd1@unicartagena.edu.co, avillabonao@unicartagena.edu.co

Abstract

Background: Now-a-days, adsorption has been recognized as an effective method to remove heavy metals ions in water sources. Objectives: This work is focused on studying removal of chromium (VI) from aqueous solution by orange peel-based adsorbents (OP, OPAC, OP-CaCl₂ and OP-Chitosan). Effects of pH and adsorbent dosage on the adsorption of Cr (VI) were evaluated in order to determine suitable conditions for carrying out adsorption process. **Methods/Analysis:** OP-CaCl₂ and OPAC biosorbents were obtained by chemical modification using CaCl₂ and H₃PO₄ acid solution, respectively, while OP-Chitosan was synthesized in acetic acid solution. FT-IR analysis was performed to OP and OP-Chitosan materials. The pH of heavy metal ions solutions was adjusted to 3, 4 and 5 and adsorbent dosage was varied in 2, 4 and 6 g/L. Batch experiments were carried out in a magnetic stirrer plate at 30°C using 100 ppm Cr (VI) ions solution. Experimental data of equilibrium were used to calculate adsorption isotherms. **Findings:** The adsorption of Cr (VI) was found to be maximum for OPAC biosorbent and its highest removal yield (66.8%) was achieved at pH 3 and dosage of 6 g/L. Application of the Langmuir isotherm to OP biosorbent yielded a maximum adsorption capacity of 911.21 mmol/g and the data for OPAC and OP-Chitosan obeyed Freundlich isotherm with KL of 0.25 mmol/g and 8.17 mg/g, respectively. The heterogeneity factor (1/n) indicated that OPAC obeys to cooperative adsorption and OP-Chitosan to chemisorption. **Application/Improvement:** Compared to the various other adsorbents reported in the literature, the orange peel-based adsorbents in this study show very good promise for practical applicability.

Keywords: Adsorption, Biosorbent, Chromium, Heavy Metal, Removal

1. Introduction

Recently, wastewater pollution has increased due to economic growth and industrial development. Heavy metal contaminants can result in various undesirable consequences because of their toxicological and physiological effects on the environment¹. Many heavy metals such as Pb, Zn, Ni, Cr and Hg are generally found in industrial wastewater effluents, which are highly toxic and carcinogenic even at low concentration and are not biodegradable².

Chromium is considered one of the 14 most noxious heavy metals and is the most common heavy metal as a groundwater contaminant^{3,4}. This heavy metal is known to cause wide ranging human health effects including mutagenic and carcinogenic risks³. The main sources of chromium pollution are mining, leather tanning process, cement industries, uses dyes, electroplating, production of steel and other metal alloys, photographic material and corrosive paints⁵.

*Author for correspondence

Various kinds of physical, chemical and biological processes are being applied for the removal of chromium from wastewater such as precipitation, ion exchange adsorption and membrane separation^{3,6}. Nevertheless, adsorption has been used by most of the researchers during the last few decades and it has proved to be a very efficient and economic process⁷. This technology has been considered as attractive and is widely employed in industries due to its low cost, simplicity of design, ease of operation, insensitivity to toxic pollutants and smaller amounts of harmful substances⁸. Use of different adsorbing materials like activated carbon, clay, metal oxides, various synthetic and natural polymers etc. have already been reported⁹. Activated carbon is the most effective and frequently used adsorbent, however its relatively high cost has led to develop low-cost adsorbents made from agricultural waste, construction waste, food waste, among others^{6,10}.

Many researchers have worked on production of activated carbon from renewable resources such as industrial and agricultural waste. Orange, as a kind of biological resources is available in large quantities in many parts of the world¹¹. Orange peel is widely discarded from juice industry, which produces more than 60 million ton¹². This waste is mostly composed of cellulose, pectin, hemicellulose, lignin, chlorophyll pigments and other low molecular weight hydro-carbons¹³. The present work focuses on modifying and preparing orange peels as biosorbents by physical-chemical treatment in order to evaluate their adsorption capacity for removing Cr (VI) in aqueous solution.

2. Material and Methods

2.1 Materials

Orange (*Citrus sinensis*) Peels (OP) were purchased from a local fruit market, washed in order to eliminate dust and other residues. Then, they were dried at 70°C during 24 hours and washed with alcohol to remove polymer insoluble in water. The dried samples were milled and screen-sieved using 0.355 mm mesh. Potassium dichromate, sodium hydroxide, sulfuric acid (0.2 N),

phosphoric acid (85% by weight), diphenylcarbazide and chitosan (85% analytical grade) were purchased from Sigma-Aldric.

2.2 Biosorbent Preparation

2.2.1 OPAC

An OP sample was carbonized up to 420°C at a heating rate of 7°C/min and held for 1 h. Then, an 85 wt. %H₃PO₄ acid solution was mixed with 1 g carbon and placed in a muffle at 600°C during 1 min per gram of sample. After cooling to room temperature, distilled water was used to attain neutral pH. The sample was then dried in a vacuum oven and activated carbon from orange peel (OPAC) was obtained.

2.2.2 OP- CaCl₂

Pectin in biomass can be reticulated by chemical modification with CaCl₂, which improves biosorbent performance. Hence, 20 g of OP sample was mixed with 500 mL of 0.2 M CaCl₂ solution under constant agitation during 24 hours. Afterwards, the sample was rinsed with distilled water to remove excess of chlorine and calcium. Finally, OP-CaCl₂ was filtered and dried up to 40°C.

2.2.3 OP-Chitosan

Chitosan was added to 0.5% vol. acetic acid solution under stirring during 24 h to obtain a homogenous gel. OP was mixed with this gel (1:5, chitosan to biomass ratio) and stirred during 12 h at 150 rpm. Then, the gel was soaked and dried three times until obtain a chitosan thick layer in the biomass. Activation and neutralization was carried out with 0.5 % w/v NaOH during 3 h. The chitosan gel pearls were rinsed with deionized water and dried.

2.3 Characterization of Biosorbents

The biosorbents (OP, OPAC, OP-CaCl₂ and OP-Chitosan) were characterized to determine elements and organic compounds according to analytical methods summarized in Table 1. In thermogravimetric analysis, weight loss of biomass served as an indicator of degradation of its components as a function of temperature¹⁴. FT-IR stud-

Table 1. Analytical methods for chemical characterization

Parameter	Method
Carbon (%)	AOAC 949.14
Hydrogen (%)	AOAC 949.14
Nitrogen (%)	AOAC 984.13
Sulfur (ppm)	Digestion
Ashes	Thermogravimetric analysis
Functional groups	Fourier transformed infrared(FT-IR)

ies pre- and post-adsorption were recorder by a Fourier Transform Infrared Spectrophotometer in the range between 4000 and 500 cm^{-1} .

2.4 Batch Adsorption Experiments

Stock solution of chromium (100ppm) was prepared by dissolving required amount of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in deionized water. The experiment of adsorption was mainly performed with adsorbent dose of 2, 4 and 6 g/L for OPAC, OP and OP-Chitosan and 5 g/L for OP- CaCl_2 . The flask containing chromium solution and biosorbent mixture was placed on a stirrer during 24 h with a rotating speed of 600 rpm under environmental temperature (30°C). The effect of pH analyzed by adjusting pH to 3, 4 and 6 with HCl and NaOH solutions. The residual Cr(VI) concentration in the solutions was measured in triplicate using UV/Vis Shimadzu UV 1700. The adsorption capacity of biosorbents for chromium was determined using mass balance equation as stated¹⁵.

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where C_0 (mg/L) is the initial Cr(VI) concentration in the solution, C_e (mg/L) is the Cr(VI) concentration

in the solution at equilibrium, m (g) is the dried mass of used OP, OPAC, OP-Chitosan and OP- CaCl_2 , and V (L) is the volume of the Cr(VI) solution. In order to determine heavy metal concentration by UV/Vis spectroscopy technique, it is required to perform a calibration curve. Initially, an aliquot (2.5 mL) of stock solution was diluted to 50ppm and four samples were obtained by adding 0.25, 0.5, 1 and 2 mL of this diluted solution to water and 2.5 mL of diphenylcarbazide acid solution. The sample of reference was prepared by mixing 2.5 mL diphenylcarbazide and water until complete capacity of 50 mL flask. Then, 1 mL of 0.632% w/v. KMnO_4 was added and heated at 50°C until disappearance of violet coloring. The sample was kept at rest during 10 min and 2.5 mL of diphenylcarbazide acid solution was added to achieve a solution with red-violet coloration.

3. Results and Discussion

3.1 Characterization of Biosorbents

3.1.1 Compositional Analysis

To determine elemental composition of OP biosorbent, analytical methods summarized in Table 1 were carried out and the results were shown in Figure 1. It is observed that carbon; pectin and cellulose were the components that are in greater proportion in OP, with a percentage of

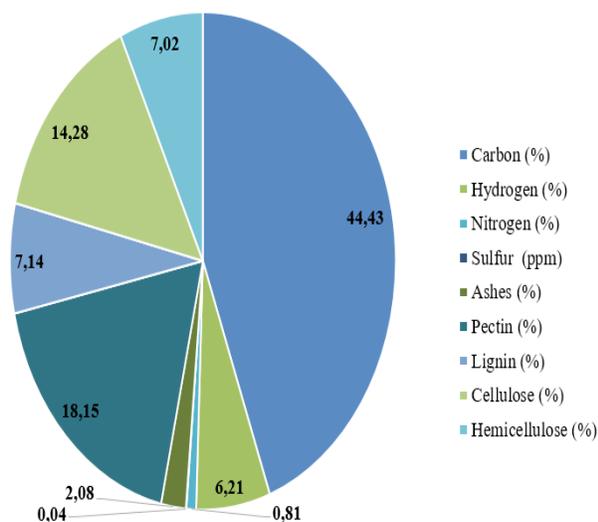


Figure 1. Elemental analysis of OP.

44.43%, 18.15% and 14.28% respectively. On the other hand, sulfur, ashes and nitrogen are attributed percentages of 0.04ppm, 2.08% and 0.81% respectively¹⁵ reported similar values for ultimate analysis: C (wt%) 44.34, H (wt%) 5.91, N (wt%) 1.14 and O (wt%) 48.61¹². Also performed proximate and ultimate analysis: C (wt %) 43, H (wt %) 5.9, N (wt %) 0.9 and O (wt %) 50.2. It is observed that carbon content obtained in this research is very close to those reported in other studies.

3.1.2 FT-IR Analysis

A FT-IR spectrum of OP biosorbent is illustrated in Figure 2. The peak observed at 3337.61 cm^{-1} is assigned to O-H stretching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds such as alcohols, phenols and carboxylic acids as in pectin, cellulose and lignin¹³. The peak at 2923.78 cm^{-1} can be attributed to C-H stretching vibrations of methyl, methylene and methoxy groups. The peak around 1732.7 cm^{-1} in OP spectrum correspond to C=O stretching vibrations in carboxyl groups of biomass studied. The peak at 1615.6 cm^{-1} is assigned to C=C, which indicated the presence of benzene or aromatic rings in lignin. Aliphatic acid group vibration at 1233.53 cm^{-1} may be assigned to deformation vibration of C=O and stretching formation of -OH of carboxylic acids and phenols¹⁶. Peak at 1010.34 cm^{-1} may be due to stretching vibration of C-OH of alcoholic groups and carboxylic acids. The adsorbents studied in this research exhibited chemical modifications by adding compounds as CaCl_2 and H_3PO_4 , which do not contribute with functional groups that enhance chemical interactions between adsorbent and heavy metal ions solution. However, chitosan has amino and hydroxyl groups that affect significantly the FT-IR spectrum of OP. The FT-IR spectra of OP-chitosan is shown in Figure 3, in which both amine (NH) and hydroxyl (OH) groups of chitosan

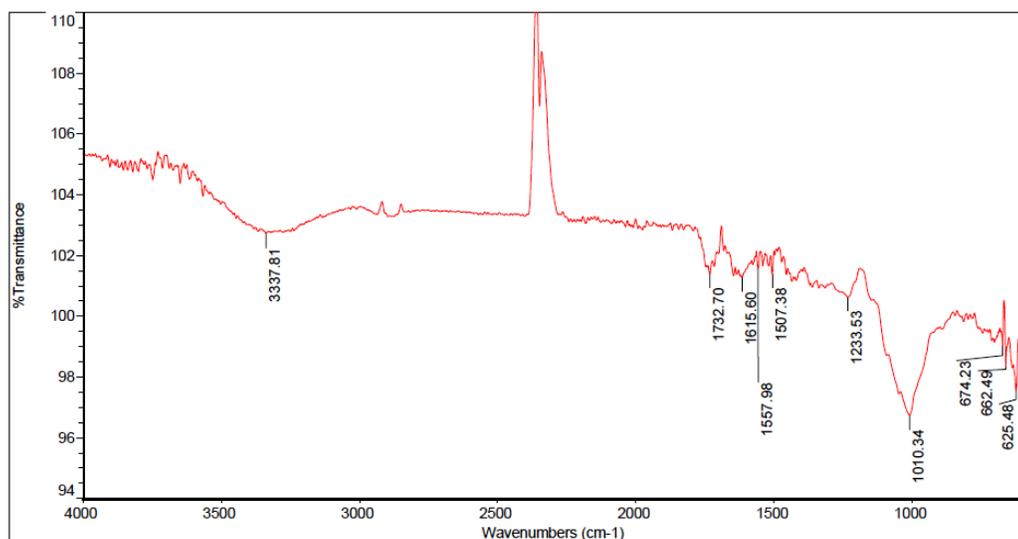


Figure 2. FT-IR spectra of OP biosorbent.

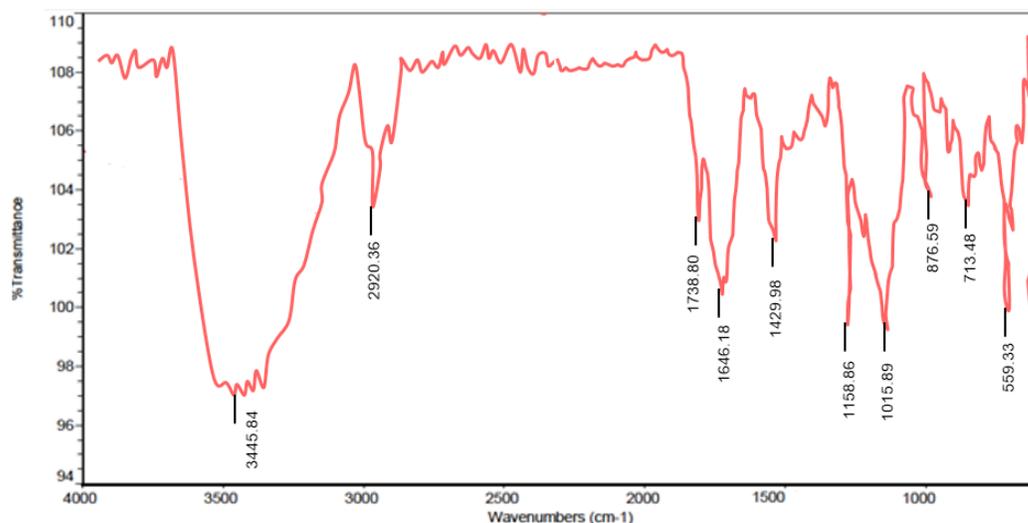


Figure 3. FT-IR spectra of OP-Chitosan biosorbent.

is seen at 3445.84 cm^{-1} assigned to overlapping of the stretching vibrations. The bands at 2920.36 and 1429.98 cm^{-1} are due to the vibration of CH group of chitosan.

3.2 Adsorption Experiments

The removal yield of heavy metal in aqueous solution using OP, OPAC and OP-Chitosan biosorbents was cal-

Table 2. Removal yield of Cr (VI) using OP, OPAC and OP-Chitosan

Conditions		Removal yield (%)		
pH	Dosage (g/L)	OP	OPAC	OP-Chitosan
3	2	50.975	58.05	49.158
	4	62.718	68.05	53.512
	6	66.801	83.05	61.240
4	2	49.144	48.05	29.567
	4	60.718	53.05	34.573
	6	64.013	60.05	42.628
5	2	43.484	38.05	19.009
	4	57.142	48.05	30.220
	6	59.676	54.05	36.097

culated by Equation 2 varying parameter of pH and adsorbent dosage, which are summarized in Table 2.

$$\text{Removal yield(\%)} = \frac{(C_o - C_e) \cdot 100\%}{C_o} \quad (2)$$

It can be observed that the highest removal yield of chromium (83.05%) was achieved using activated carbon from orange peel as adsorbent at defined parameter (pH 3 and dosage 6 g/L). Under these conditions, adsorbent OP achieved 57.47% of removal yield. For all values of parameter pH and dosage, OPAC exhibited better adsorption performance than OP. These results suggested that activating carbon from Orange peel using H_3PO_4 acid solution may improve interactions with heavy metals in aqueous solution and enhance its uptake inside active sites of OPAC. Adsorption process is the surface phenomena involving the accumulation of solute from liquid to the solid surface, which is mainly affected by the capacity of adsorbent to chelation and interact chemically¹⁷. The removal yield of Cr (VI) using OP-Chitosan was reduced in comparison to OP, which is attributed to the absence of chemical interaction between functional groups of orange peel (carbonyl groups) and chitosan (amino groups). In⁴ affirms that chitosan exhibits high hydrophilicity and large number of hydroxyl groups of glucose units and functional groups (acetamido, primary amino and/or hydroxyl groups) in its structure that

make this biopolymer suitable for adsorbing heavy metals. Hence, synthesis was not carried out successfully and OP only suffered a physical modification by covering its surface by chitosan, probably due to insufficient stirring during reaction, therefore, adsorption interactions of carbonyl groups with greater affinity for heavy metals ions was diminished in absence of direct contact with heavy metal ions solution.

The adsorption results using biosorbent OP- $CaCl_2$ were not summarized in Table 2 due to the experiment was carried out at 5 g/L of dosage and pH 6, therefore, it did not provide enough information of the effect of both parameter on adsorption process. The removal yield of Cr (VI) achieved under these conditions was 20.95 %, value significantly low in comparison to OP, OPAC and OP-Chitosan, which subjected that chemical modification by $CaCl_2$ reduces the performance of OP during adsorption.

3.2.1 Effect of Adsorbent Dosage

The amount of adsorbent in heavy metal ions solution has great effect on the adsorption process as it determines the capacity of each adsorbent to remove a known initial concentration of Cr (V)⁴. As is presented in Table 2, removal of Cr (V) ions increased with increasing adsorbent dosage for all pH and adsorbents. The highest removal yield was achieved at dosage of 6 g/L, hence this value is selected as suitable condition for carrying out adsorption process.

Table 3. Optimal dosage for different adsorbent materials

Biosorbent	Removal yield (%)	Optimal dosage (g/L)	Reference
Orange peels	61.2	4	In ¹⁸
Orange peels	66.8 ⁺	6	This work
Coffee leaves	82.0	8.5	In ²⁷
Sawdust	92.2	10	In ²⁸

+Heavy metal ions solution with pH = 3

ture⁸. Claimed that increasing the dosage of adsorbent could reduce the availability of sites due to the effective surface area is likely to decrease although the amount of adsorption sites per unit mass remain constant. However, at optimal amount of adsorbent, there are enough sites available to interact with Cr (VI) ions in the solution and aggregation due to excess of adsorbent is not induced. Table 3 summarized optimal dosage for different bioso-

rbent materials obtained in other researches. According to¹⁸ highest removal yield was reached at dosage of 4 g/L, which differs from the results obtained in this work. However, other biosorbents as coffee leaves and sawdust exhibit optimal dosage higher than 6 g/L.

3.2.2 Effect of pH

The pH of the solution plays an important role in ion

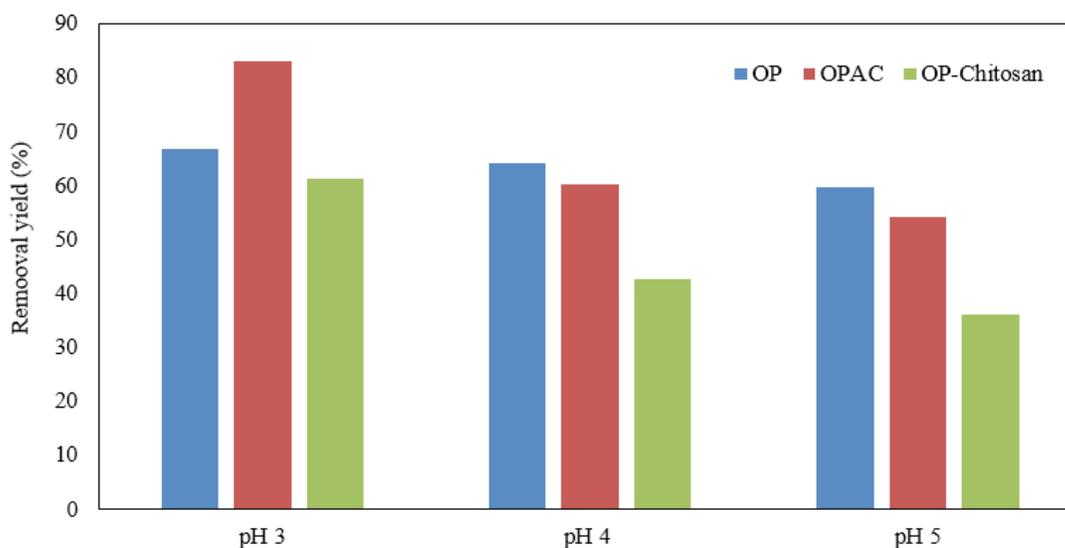


Figure 4. Effect of pH on removal yield of Cr (V) for OP, OPAC and OP-chitosan biosorbents at dosage 6 g/L.

Table 4. Optimal pH for different adsorbent materials

Biosorbent	Removal yield (%)	Optimal pH	Reference
Walnut	97.3	1.0	In ²⁹
Distillery sludge	82.0	3.0	In ³⁰
Tamarid seed	95.0	1.46	In ³¹
Wool	81.0	2.0	In ³²
Peanut shell activated carbon	45.0	2.0	In ³³
Groundnut husk activated carbon	97.0	3.0	In ³⁴

adsorption by affecting the ion speciation and surface charge properties of the adsorbents¹⁹. Figure 4 shows the effect of pH on removal yield of Cr (V) using different biosorbents synthesized in this study under optimal dosage (6 g/L). It is observed that the highest removal yield was achieved under acidic pH (pH=3) with values of 66.81, 83.05 and 61.24 % for OP, OPAC and OP-chitosan, respectively. At an acidic pH, chromium ions exist in two forms: as chromic acid H_2CrO_4 under pH 1-2 and as hydrogen chromate ions ($HCrO_4^-$) under pH 3-7¹. The high concentration of H^+ and H_3O^+ protonated from the hydroxyl and carbonyl could out-compete aqueous heavy metal ions for the available biosorbents binding sites at low solution pH, resulting in little or no adsorption⁸. At higher pH, deprotonation of functional groups that serve as binding sites become accessible to metal ions causing better sorption¹⁴. However²⁰, claim that the highest Cr (VI) removal at 3.4 was likely due to electrostatic attraction of sorbent surface and hydrogen chromate ions, value for pH similar to the obtained in this study. Table 4 summarizes removal yield of chromium at optimal pH using different biosorbents reported in other researches. It is observed that groundnut husk activated carbon and distillery sludge exhibit better removal yield when aqueous solution pH is adjusted to 3.

3.3 Adsorption Isotherms

The experimental equilibrium data were modeled using Langmuir and Freundlich model. The Langmuir model focuses on the theory that on the surface of the adsorbent, only a single layer of the adsorbate is formed⁶. Langmuir isotherm is expressed by the following equation²¹:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (3)$$

Where q_m is the maximum adsorption capacity of the biosorbent (mmol/g), C_e is the equilibrium concentration of heavy metal (mmol/l), q_e is the amount of heavy metal ions adsorbed per unit of adsorbent at equilibrium (mmol/g) and K_L is Langmuir constant (L/mmol). On the other hand, Freundlich model describes the adsorption process on a heterogeneous surface or a surface supporting different sites and is not therefore restricted to the formation of monolayer³⁰. The mathematic expression for this model is conveniently used in linear form as²³:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (4)$$

Table 5. Parameters of Langmuir and Freundlich models tested for adsorption of Cr (VI) onto biosorbents prepared from orange peels

Parameters		OP	OPAC	OP-Chitosan
Langmuir		911.21 ^a	5560.24 ^a	9.7 ^{a*}
		4.8x10 ^{-4b}	2.12x10 ^{-4b}	3.26 ^{b*}
	Correlation	0.86 ^c	0.78 ^c	0.979 ^{c*}
Freundlich		3.42 ^a	0.25 ^a	8.17 ^{a*}
		3.48	0.59	1.97
	Correlation	2.09 [*]	0.77 [*]	0.992 ^{**}

^a Values in ; ^b values in ; ^{a*} values in ; ^{b*} values in

^{*} Residual average; ^{**} correlation coefficient (R²)

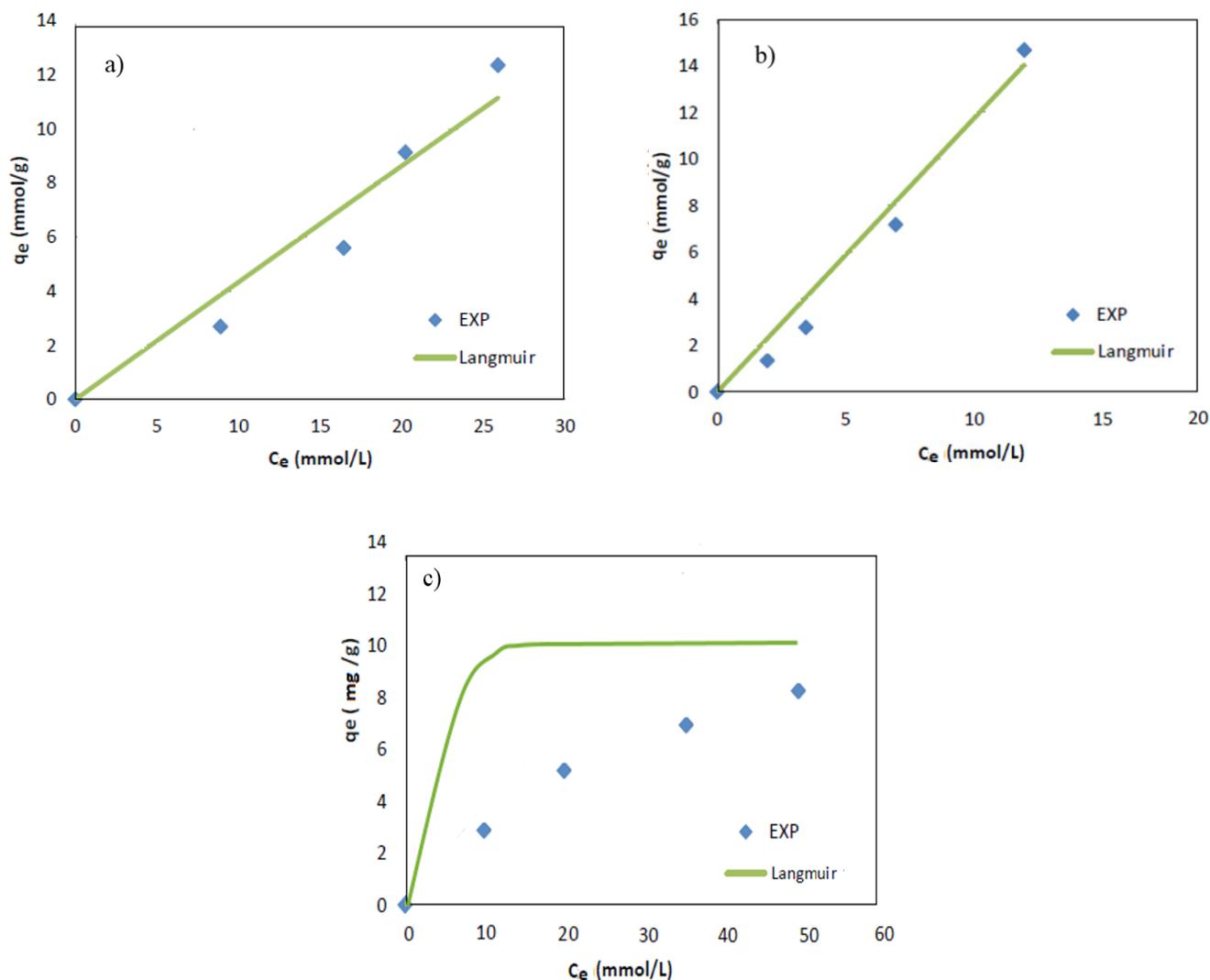


Figure 5. Experimental data of adsorption equilibrium and Langmuir model fitting using: (a) OP, (b) OPAC and (c) OP-Chitosan biosorbents.

Where and have the same definitions as those in the Langmuir equation cited above and are Freundlich constants related to adsorption capacity and heterogeneity factor, respectively. These constants can be determined from the intercept and slope of plotting \log against \log , respectively. Once it has been selected suitable values for both parameters evaluated in this work, pH and adsorbent dosage, experimental data for adsorption equilibrium were obtained under pH 3 and dosage of 6 g/L and it is shown in Figure 5, 6 for Langmuir and Freundlich model fitting, respectively. Sorption equilibrium provides fundamental physico-chemical data for estimating the appli-

cability of sorption procedures as a unit process²¹. The equilibrium uptakes for chromium ions solution using OP, OPAC and OP-Chitosan exhibit that the loading capacity of Cr (VI), after reaching the equilibrium, increases with increasing equilibrium ions concentration, since this concentration provides the necessary driving force to overcome the resistance to mass transfer of ions between biosorbent and solution²⁴. It can be seen that Langmuir model fitted experimental data for OP biosorbent, while equilibrium experimental data of OPAC is well fitted with Freundlich model. Parameters of both models are summarized in Table 5.

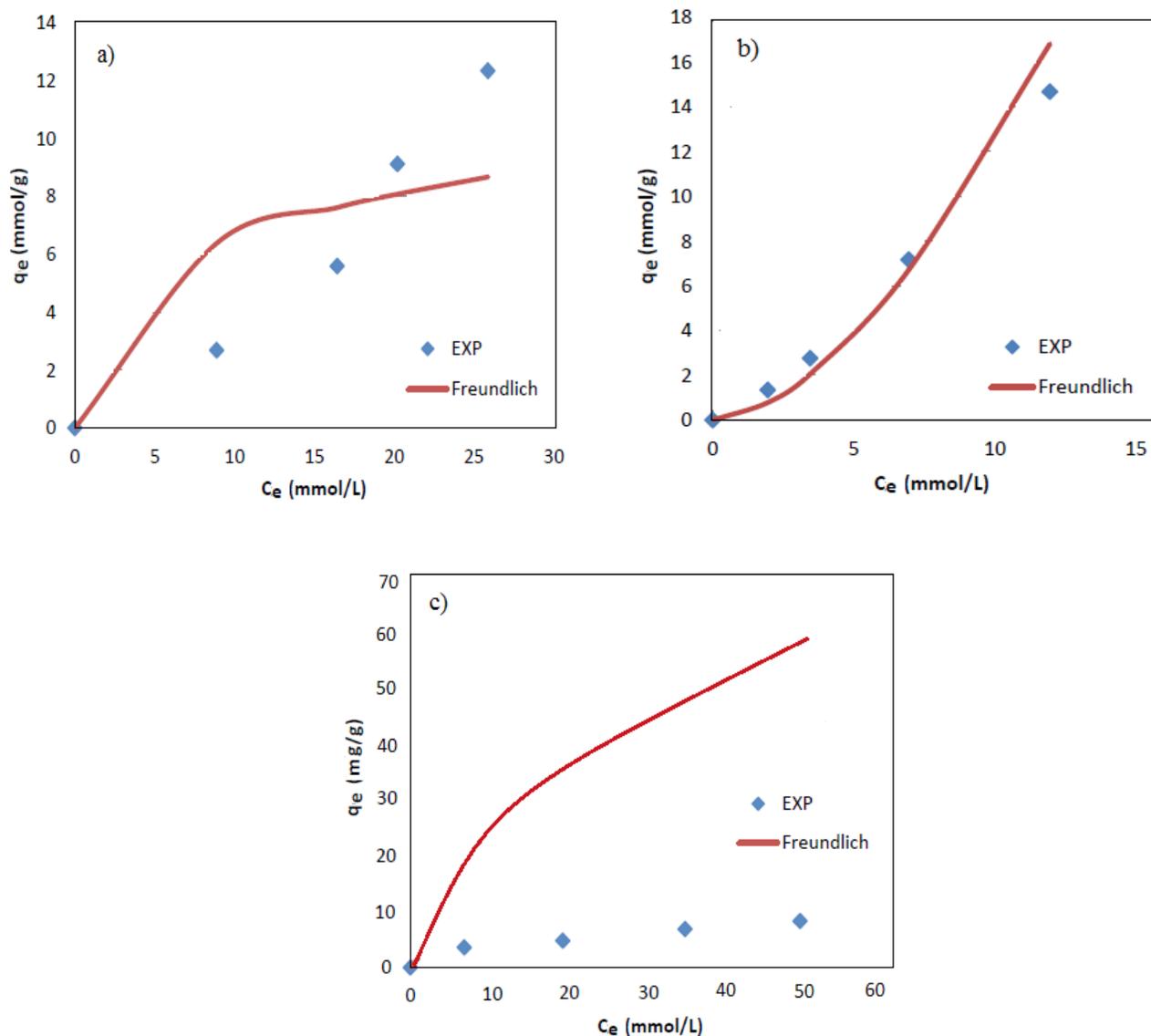


Figure 6. Experimental data of adsorption equilibrium and Freundlich model fitting using: (a) OP, (b) OPAC and (c) OP-Chitosan biosorbents.

Analysis of isotherm data in accordance with the isotherm models revealed that Langmuir model appropriately illustrated the adsorption process for OP biosorbent showing lower residual average value of 0.86 in comparison with Freundlich model with value of 2.09, which confirms monolayer sorption. The theoretical monolayer adsorption capacity (q_m) of OP for chromium was 911.21 mmol/g. It has been reported that the Langmuir constant K_L is related to the affinity of active sites, so that the

smaller the value of K , the higher the affinity of the adsorbent with the adsorbate²², hence, the K_L value obtained in this study suggested that orange peel biosorbent can interact with high affinity with heavy metal ions solution. Freundlich model fits better with the isotherm data than Langmuir model for OPAC with residual average value of 0.77 indicating that this biosorbent has a heterogeneous surface with non-uniform distribution of heat of adsorption over the surface and adsorption process is multilayer.

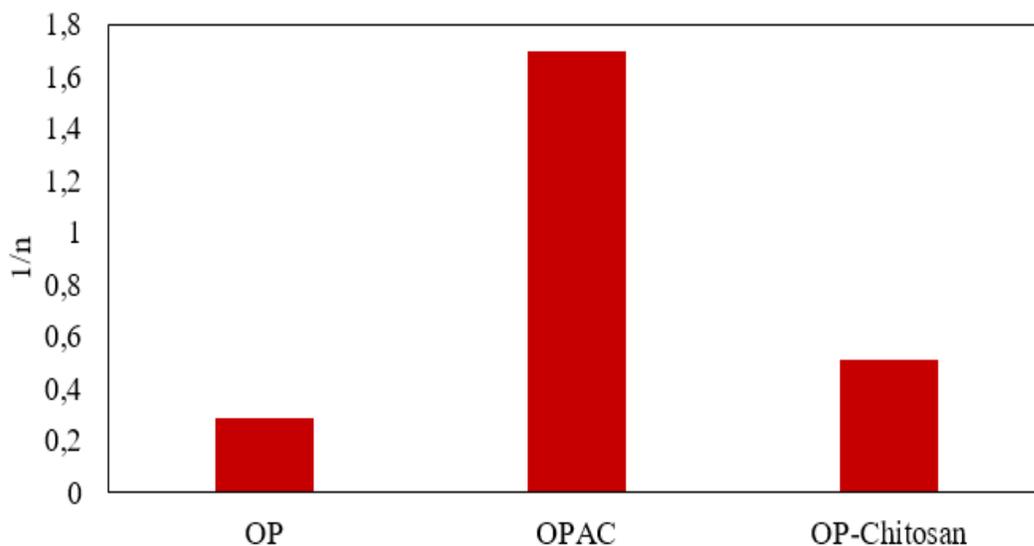


Figure 7. Heterogeneity factor of Freundlich adsorption model for orange peels-based biosorbents.

As is observed in Table 5, the K_F constant has a value of 0.25 mmol/g that indicates the adsorption capacity of biosorbent while n depicts the adsorption intensity¹³. Regarding OP-Chitosan biosorbent, the value of correlation coefficient (R^2) of 0.992 demonstrates that the Freundlich model fitted the experimental data well with K_F of 8.17 mg/g. The chromium removal from aqueous solution has been evaluated using other adsorbents in other works¹. Evaluate adsorption capacity of carbon nano-onions (CNOs) on removing Cr (VI) obtaining well fitting for both Langmuir and Freundlich isotherms. The K_F parameter value for Freundlich model was 2.339 mg/g, which is lower than the obtained in this study using OP-Chitosan indicating that OP-Chitosan exhibits better adsorption capacity than CNOs, hence, better performance for chromium uptakes. Figure 7 displays dimensionless factor ($1/n$) for OP, OPAC and OP-Chitosan adsorbents that offers information about adsorption mechanism and surface heterogeneity²⁵. OP and OP-Chitosan biosorbents show heterogeneity factor ($1/n$) of 0.29 and 0.51, respectively. It has been reported that values of $1/n < 1$ represented a chemical adsorption process and favorable adsorption¹⁹, suggesting that both adsorbent experiment chemisorption. The OPAC biosorbent has a heterogeneity factor of 1.69, which is assigned to cooperative (multilayer)

adsorption due to $1/n > 1$ ²⁵. Similar results were observed²⁶ using Chitosan/Clay Nanocomposite (CCN) to remove Cr (VI) ions with heterogeneity parameter value of 0.55, which is similar to the obtained for OP-Chitosan.

4. Conclusions

The present investigation emphasizes adsorption potential of orange-peels based biosorbents towards chromium. OP and OP-Chitosan biosorbents were analyzed by FT-IR in order to identify functional groups. The presence of carboxyl and amino groups was observed in biomass spectra playing key role in adsorption. The removal yield of Cr (VI) greatly depend on the solution pH due to it affects the adsorbent surface properties and ionic forms of Cr (VI) in solution. According to the highest removal yields achieved at pH 3, acidic solution was selected as suitable condition to perform adsorption process. The effect of dosage of adsorbent was also evaluated indicating that 6 g/L is the optimum value for enhancing heavy metal ions adsorption. The equilibrium data were fitted to Langmuir isotherm for OP with q_m of 911.21 mmol/g and K_L of 4.8×10^{-4} L/mmol, which indicated a monolayer adsorption mechanism. OPAC and OP-Chitosan equilibrium data were fitted to Freundlich model with K_F of 0.25

mmol/g and 8.17 mg/g, respectively. The heterogeneity factor obtained from Freundlich isotherm indicated that OPAC presents cooperative adsorption and OP-Chitosan presents chemisorption. Finally, the good performance of these biosorbents from orange peels in solutions at 100 ppm of Cr (VI) ions make them promising candidate for removing of heavy metals water pollutants.

5. Acknowledgments

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