Chitosan-orange peel biosorbent for hexavalent chromium removal from aqueous solutions

Biosorbente a base de quitosán-cáscara de naranja, para la remoción de cromo hexavalente en agua

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Abstract: chromium is one of the most important water pollutants being Cr(VI) the one with the greatest environmental impact. The objective of this work is to evaluate the adsorption capacity of a biosorbent formed by chitosan-orange peel (CTS-OP) to remove hexavalent chromium from water. The novelty of this work is the evaluation of the drying process effect (oven, vacuum, and freeze-drying) on chromium adsorption capacity. Adsorbents are characterized using X-ray diffraction, FTIR spectroscopy and adsorption kinetics and isotherms measuring Cr(VI) concentration using UV-Vis absorption at 540 nm after complexing with 1,5-diphenylcarbazide. Adsorption capacity is enhanced at pH 2.0 and OPW particle size of 0.300 microns. The shoulder that appears at 944 cm⁻¹ after Cr(VI) adsorption in all three kind of CTS-OPW beads, indicate that chromate ion is bonding with the sorbent. The chi-squared analysis ($\chi^2$) indicate that Freundlich isotherm fits better that Langmuir isotherm for all CTS-OPW beads, and the best fit is obtained with Elovich model for kinetic studies. The adsorption capacity of the CTS-OPW beads was also evaluated for the three types of drying. It can be concluded that vacuum oven-dried beads have the highest hexavalent chromium adsorption capacity, 33.89 mg g⁻¹, followed by freeze-dried beads, 32.4 mg g⁻¹, and finally oven-dried beads with a $q_{max}$ value of 27.5 mg g⁻¹.

Keywords: chitosan, orange peel, hexavalent chromium, drying method; isotherms; Freundlich; beads; biocomposite.

Resumen: el cromo es uno de los contaminantes más importantes del agua siendo el Cr(VI) el de mayor impacto ambiental. El objetivo de este trabajo es evaluar la capacidad de adsorción de un biosorbente formado por quitosán-cáscara de naranja (CTS-OPW) para eliminar cromo hexavalente del agua. La novedad de este trabajo es la evaluación del efecto del proceso de secado (en horno, en horno de vacío y liofilización) sobre la capacidad de adsorción de cromo. Los adsorbentes se caracterizan mediante difracción de rayos X, espectroscopía FTIR y cinética de adsorción e isothermas midiendo la concentración de Cr(VI) mediante absorbación UV-Vis a 540 nm después de formar complejos con 1,5-difenilcarbazida. La capacidad de adsorción se mejora a pH 2.0 y tamaño de partícula OPW de 0.300 micrones. El hombro que aparece a 944 cm⁻¹ después de la adsorción de Cr(VI) en los tres tipos de perlas CTS-OPW indica que el ion cromato se está uniendo al adsorbente. El análisis de chi-cuadrada ($\chi^2$) indica que la isoterma de Freundlich se ajusta mejor que la isoterma de Langmuir para todas las perlas CTS-OPW, y que el mejor ajuste para la cinética de adsorción se obtiene con el modelo de Elovich. También se evaluó la capacidad de adsorción de las perlas CTS-OPW para los tres tipos de secado. Se puede concluir que las perlas secadas al horno de vacío tienen la mayor capacidad de adsorción de cromo hexavalente, 33.89 mg g⁻¹, seguidas de las perlas liofilizadas, 32.4 mg g⁻¹, y finalmente las perlas secadas al horno con un valor $q_{max}$ de 27.5 mg g⁻¹.

Palabras clave: quitosán; cáscara de naranja; cromo hexavalente; método de secado; isothermas; Freundlich; perlas; biocomposite.
1. Introduction
The world’s average annual freshwater use was about 4 trillion m$^3$ in 2014 for 7.2 billion people (Ritchie & Roser, 2018). Global water demand will increase by 1% per year until 2050 for 9.8 billion people, and still, three out of ten people do not have access to safe drinking water (World Water Assessment Programme, 2019). Chromium is one of the most important water contaminants being Cr(VI) the one with the greatest environmental impact because it is highly oxidizing, toxic, carcinogenic, and mutagenic character. It scarcely occurs naturally in the environment but is rather produced by industrial processes such as pigments for textile dyes, wood preservatives, corrosion inhibitors, metal finishing and chrome plating, and leather tanning; and can be released into the environment by leakage or inappropriate water waste disposal (South Australia Health, 2022; United States Environmental Protection Agency, 2022). Due to its toxicity, several removal technologies have been investigated for its removal such as reduction, filtration, reverse osmosis; ion exchange, foam flotation, electrolysis, chemical precipitation, liquid-liquid extraction, and surface adsorption; however, some of these processes are associated with high operational costs, limitations in scale-up and sludge generation and disposal issues (Owlad et al, 2009; Kalidhasan et al., 2019). Solid-liquid extraction using biopolymers or biomass is a green option for Cr(VI) removal since it is a low-cost process with good metal-binding capacity and minimization of chemical products and biological sludge; moreover, biosorbents can be regenerated and metals recovered (Owlad et al, 2009).

Biopolymers such as chitosan, cellulose, lignin, and lignocellulose, are useful for heavy metals removal from water (Kalidhasan et al., 2019). Chitosan (CTS) is a biodegradable, biocompatible and non-toxic biopolymer. Several investigations show that CTS can be a good biosorbent for Cr(VI) removal with adsorption values ranging from 325.2 to 7.5 mg g$^{-1}$ (Vakili et al., 2018; Kousalya et al., 2010; Aydin & Aksoy, 2009; Wan Ngah et al., 2006; Sankararamakrishnan et al., 2006; Rojas et al., 2005). Regarding cellulotic materials, several agricultural wastes have been tested for metal removal like rice husk, coconut fiber, peanut shell, wheat shell, banana peel, and orange peel. Orange peel (OP) is a natural, non-toxic, easily available, and low-cost material. Several studies report the use of OP as a biosorbent for the removal of Cr(VI) with removal adsorption values ranging from 107.5 to 1.9 mg g$^{-1}$ (Pavithra et al., 2021; Pehlivan et al., 2012; Mandina et al., 2013; López-Téllez et al., 2013). Moreover, there is a trend for preparing mixtures, blends, composites, and chemically modified biopolymers to improve the individual adsorption capacities of each biosorbent: chitosan-graphene oxide nanocomposite membranes for Pb$^{2+}$ removal (Croitoru et al., 2020), chitosan supported onto agave fiber-postconsumer HDPE composites for Cr(VI) adsorption (Pérez-Fonseca et al., 2012), and oil palm shell charcoal coated with chitosan for removal of heavy metals (Nomanbhay & Palanisamy, 2005) among others. There are few studies for a biosorbent prepared with chitosan and orange peel, to evaluate the adsorption capacity as an alternative for water treatment but also for contributing to the management of agro-industrial solid waste reuse (Pavithra et al., 2021). The objective of this work is to evaluate the adsorption capacity of a biosorbent formed by chitosan-orange peel (CTS-OP) to remove hexavalent chromium from water. The novelty of this work is the evaluation of the drying process effect (oven, vacuum, and freeze-drying) on chromium adsorption capacity.

2. Methods, techniques and instruments
Chitosan medium molecular weight with 83% degree of deacetylation and viscosity of 328 cP (Batch Num. STBC1894V) was obtained from Sigma Aldrich. Orange peel raw material was obtained as waste material from a local juice store. Ethanol (assay 99.8%), glacial acetic acid (assay 99.7%), acetone (assay 99.7%), sulfuric acid (assay 98.1%), hydrochloric acid (assay 99.4%), sodium hydroxide (flakes), sodium tripolyphosphate (Na$_5$P$_3$O$_{10}$), potassium dichromate, and 1,5-diphenylcarbazide were obtained from Sigma and Baker. Orange peel was cleaned by hand—to separate residual pulp—, best pieces were selected and cut into 1-cm small pieces and washed with water thoroughly under mechanical stirring for 30 minutes. Finally, the orange peel was dried at 100 °C for 24 h, this resultant material is named orange peel washed with water (OPW). OPW material was grounded in a blade mill and sieved into different
particle size: 0.6, 0.425, 0.3, and 0.073 mm corresponding to mesh # 30, 40, 50 and 200 according to the ASTM standard. EII-61, respectively.

OPW with particle size 0.073 mm was dispersed into a 2 % w/v CTS solution in aqueous acetic acid (1 vol %) to obtain a 1:1 ratio CTS:OPW and stirred for 1 h. The obtained dispersion of OPW in CTS solution was dropped into a 1 % w/v sodium hydroxide and 0.5 % w/v sodium tripolyphosphate (ratio 2:1) and left to stand for 24 h. The obtained beads were washed with distilled water until a neutral pH was obtained (figure 1 left). Excess water was removed, and beads were placed in a Petri dish and dried in the oven at 60 °C for 24 h, until constant weight.

2.2. Beads characterization
The changes in the infrared spectrum due to chromium adsorption onto the composite beads, were evaluated using a Thermo Scientific Nicolet iS5 with an ATR accessory from 4000 to 550 cm⁻¹. Crystalline structure is evaluated with XRD using a TNX Easy600 benchtop diffractometer from 5 to 80 in 2θ with a step size of 0.05.

![Figure 1. CTS-OPW beads after coagulation into the NaOH and Na₃P₂O₁₀ solution (left), and different particle size of orange peel treated with water, grounded, and sieved (right).](image)

2.3. Particle size and pH effect on adsorption kinetics
Particle size and pH were evaluated in the same experiment for CTS powder and OPW powder. Four particle sizes (0.600, 0.425, 0.300, and 0.073 mm, figure 1 right) of OPW and a sample of powdered CTS are evaluated (total of 5 samples). We added 0.05 g of each biosorbent sample into a 10 mL of 100 mg L⁻¹ Cr(VI) solution prepared in each flask, and the pH is adjusted to 2.0 or 3.0 using 0.1 M sulfuric acid. All solutions (ten) were agitated in an orbital shaker for 6 h. After the contact time has elapsed, solutions were centrifuged at 3500 rpm for 15 min, and supernatant was separated and diluted with a factor of 10C. pH must be adjusted between 1.5–2.0 if necessary and 0.05 mL of 1,5-diphenylcarbazide (DPC) solution —DPC solution prepared according to literature (Environmental Protection Agency, 1992) — were added to each solution, stirred, and left to stand for 5 to 10 min until Cr(VI)-DPC complex is developed and intense violet color arises. Absorbance is then measured at 540 nm using a Perkin Elmer Lambda 2 UV/Vis spectrophotometer to obtain the equilibrium concentration of hexavalent chromium and thus determine the adsorption capacity per gram of adsorbent.
Once the absorbance has been measured, the equilibrium concentration, \( C_e \), of Cr(VI) can be obtained using the fitted equation from calibration curve obtained with standard samples of 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mg L\(^{-1} \), where \( b = 0.66753 \) is the slope, \( a = 0.0107 \) is the intercept, and \( FD = 100 \) is the dilution factor and \( R^2 = 0.9972 \).

\[
C_e = \left( \frac{(Abs-a)}{b} \right) \times FD
\]  
\( (1) \)

Where: the equilibrium concentration units are mg L\(^{-1} \), and the equilibrium adsorption capacity of the biosorbent can be determined, with the following equation:

\[
q_e = (C_0 - C_e) \left( \frac{V}{m} \right) \quad \text{or} \quad q_e = \frac{C_0 - C_e}{m/V}
\]  
\( (2) \)

Where: \( q_e \) is the amount of Cr(VI) adsorbed at equilibrium per unit mass of adsorbent (mg g\(^{-1} \)), \( C_0 \) is the initial concentration of Cr(VI) in the solution (mg L\(^{-1} \)), \( V \) is the volume of the solution (L), and \( m \) is the amount of adsorbent used (g). There are two important parameters in this equation that impose an upper limit for the value of \( q_e \), the solid/liquid ratio \( m/V \) (sometimes referred as sorbent dose or sorbent concentration), and \( C_0 \); if \( \frac{m}{V} = 1 \), then \( q_e \) is proportional to \( C_0 \) and the ideal upper limit occurs when the adsorbent adsorbs all the metal present (i.e., \( C_e = 0 \)); if \( \frac{m}{V} < 1 \), then we are using a small adsorbent quantity and \( q_e \) values will tend to be high, on the contrary if \( \frac{m}{V} > 1 \), then \( q_e \) values will be small. Therefore, kinetic experiments with an initial metal concentration that report a metal removal efficiency (%) removal should be careful analyzed and only \( q_e \) values must be compared.

For kinetics analysis 0.10 g of biosorbent were added into a flask with 20 mL of Cr(VI) solution of 100 ppm initial concentration and agitation in a shaker at ambient temperature. Aliquots are taken at different times and quantified using the DPC method. Three kinetic mathematical models are commonly used for adsorption experiments: the pseudo-first order model, proposed by Lagergren in 1898, the pseudo-second order model proposed by Blanchard et al. (1984), and the Elovich model originally proposed by Roginsky and Zeldovich (1934, cited in Tran et al., 2017). According to Ho (2004) and Tran et al. (2017), the authors who first propose a theoretical model should always be given credit for their contributions via correct citation.

The pseudo-first equation (PFO) is:

\[
q_t = q_e (1 - e^{-k_1t})
\]  
\( (3) \)

Where: \( q_t \) (mg g\(^{-1} \)) is the amount of adsorbate uptake per gram of adsorbent at time \( t \) (min), \( q_e \) is the amount of adsorbate adsorbed at equilibrium, and \( k_1 \) (min\(^{-1} \)) is the rate constant of the PFO model. The pseudo-second order equation (PSO) is:

\[
q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}
\]  
\( (4) \)

Where: \( q_t \) (mg g\(^{-1} \)) is the amount of adsorbate uptake per gram of adsorbent at time \( t \) (min), \( q_e \) is the amount of adsorbate adsorbed at equilibrium, and \( k_2 \) (g mg\(^{-1}\)min\(^{-1} \)) is the rate constant of the PSO model (Tran et al., 2017). The Elovich model is:

\[
q_t = \frac{1}{\beta} \ln (1 + a \beta t)
\]  
\( (5) \)
Where: \( q_t \) (mg g\(^{-1}\)) is the amount of adsorbate uptake per gram of adsorbent at time \( t \) (min), \( \alpha \) (mg g\(^{-1}\)min) is the rate constant—the rate of chemisorption at the beginning of the process—, and \( \beta \) (mg g\(^{-1}\)) is the desorption constant associated to the extent of the surface coverage and activation energy of chemisorption (Ghaneian et al., 2017), so this model assumes that the rate of adsorption of solute decrease exponentially as the amount of adsorbed solute increases (Kajjumba et al., 2019), or that the number of available sites for adsorption decreases exponentially with the number of sites occupied (Aharoni & Tompkins, 1970). The experimental data might be represented by one of these kinetic models, but the adsorption cannot be described by just fitting the data to a model. In the last years, several works reported a chemisorption mechanism just because data is well fitted to the PSO model, which is an erroneous conclusion (Kajjumba et al., 2019) since there is no single criterion to distinguish with no doubt chemical adsorption from physical adsorption (Gundry & Tompkins, 1960). Indeed, the Elovich model has been applied extensively to chemisorption kinetics (Taylor & Thon, 1952; Low, 1960; McLintock, 1967; Ghaneian et al., 2017), but it also describes properly different adsorption systems.

2.4. Batch adsorption

0.05 g of biosorbent were added into a flask with 10 mL of Cr(VI) solution of different initial concentration (10, 25, 50, 100, 200, and 250 mg L\(^{-1}\)) and pH was adjusted to 2.0 at ambient temperature and agitated in a shaker for 72 h. The solution was filtered to remove the biosorbent and added with 0.05 mL of DPC solution for 10 minutes until color is developed. Light absorption is determined at 540 nm and Cr(VI) equilibrium concentration was calculated using the calibration curve Eq.(1). A plot of \( q_e \) vs \( C_e \) is generated for the CTS-OPW beads with different drying method: oven, vacuum oven, and freeze-drying. Finally, experimental data is non-linear fitted using IGOR Pro software with Langmuir and Freundlich models. The Langmuir equation assumes a fixed number of adsorption sites at the sorbent surface with the same energy, that the adsorption is reversible, that a site can only be occupied once and no further adsorption can occur, and that there is no interaction between adsorbate species, which indicates a monolayer adsorption at the homogeneous surface sites of the beads:

\[
q_e = \frac{Q_{\text{max}}K_LC_e}{1 + K_LC_e}
\]  

(6)

Where: \( Q_{\text{max}} \) (mg g\(^{-1}\)) is the maximum adsorption capacity of the adsorbent at monolayer saturation and \( K_L \) (L mg\(^{-1}\)) is the Langmuir isothermal constant related to the affinity between de adsorbate and adsorbent. On the other hand, the Freundlich isotherm can also describe the adsorption process of a heterogeneous Surface:

\[
q_e = K_F C_e^n
\]  

(7)

In this case, \( K_F \) (mg g\(^{-1}\))(mg L\(^{-1}\))^n and \( n \) (dimensionless) are the Freundlich constant and the intensity parameter, respectively. Freundlich isotherm cannot describe the saturation effect at high concentrations (i.e., the saturation behavior of the adsorbent). The intensity parameter indicates the magnitude of the adsorption driving force or the surface heterogeneity. Moreover, from Langmuir isotherm the dimensionless separation factor or equilibrium parameter, \( R_L \), can be calculated by:

\[
R_L = \frac{1}{1 + K_L C_0}
\]  

(8)

It follows that there is a \( R_L \) separation factor for each adsorption experiment at different \( C_0 \), and the isotherm shape can be predicted analyzing the separation factor, \( R_L \) (Langmuir), and the intensity parameter \( n \) (Freundlich). The
isotherm shape is irreversible (horizontal) when \( R_L = 0 \) and \( n = 0 \), it becomes linear when \( n = 1 \) and \( R_L = 1 \), favorable when \( n < 1 \) and \( R_L < 1 \) (concave), and unfavorable (convex) when \( n > 1 \) and \( R_L > 1 \) (Tran et al., 2017).

3. Results and discussion

Adsorption capacity is enhanced at pH 2.0 and OPW particle size of 0.300 microns (Figure 2). Adsorption capacity is also higher at pH 2.0 for CTS powder (only one particle size). Cr(VI) removal is commonly performed at low pH since the surface of the biosorbent may be surrounded by hydronium ions which results in a positive surface that attracts the negative charge of the chromate (HCrO₄⁻) and dichromate (Cr₂O₇²⁻) ions presents at low pH (Szabó et al., 2018).

CTS powder shows a higher adsorption capacity compared to OPW powder of 0.300 mm at pH 2 and initial Cr(VI) concentration of 100 ppm, using the same sorbent dosage of 5 g L⁻¹ for 6 h. The higher adsorption of chitosan is probably related to the -NH₂ functional groups in addition to the -OH groups while orange peel (OPW) functional groups (-OH and -COOH) might not be as effective (Moussout et al., 2018). We also must consider that oxygens of chromate acid and dichromate ions must attach to the positive sorbent surface at certain distances imposed by steric positions.

Figure 2. Adsorption capacity of OPW powder at different pH and particle size and CTS adsorption capacity at different pH after 6 h equilibrium time.

In Figure 3 is possible to observe morphology and particle size of wet CTS-OPW beads after coacervation process (A); CTS-OPW beads after drying in oven (B); CTS-OPW beads after drying in vacuum oven (C); and CTS-OPW beads after lyophilization (D). Wet beads are about 3-mm diameter and freeze-dried beads have a similar diameter since lyophilization is a process that evaporates solvent without a drastic change in volume, maintaining the morphology of wet beads. CTS-OPW beads dried in a conventional oven and vacuum oven have a smaller size due to shrinkage of polymer during the drying process; diameter of beads is around 0.5 mm which means that beads volume is around...
80-100 times smaller for the oven-dried and vacuum oven-dried beads compared with freeze-dried beads. A cross section of a freeze-dried bead is shown in (E), it is possible to observe a porous morphology. After the freeze-dried beads were in contact with chromium, the biosorbent color changes from a light yellowish into an intense yellow color due to Cr(VI) adsorption.

Figure 3. Biosorbent composite beads: (A) wet; (B) oven dried; (C) vacuum dried, and (D) freeze dried, and freeze-dried beads before; (E) and after (F) chromium adsorption.

Figure 4 shows infrared spectra for CTS and OPW before and after chromium adsorption experiment in the range from 2000 to 550 cm\(^{-1}\). Chitosan spectrum shows the characteristics bands for amide I at 1648 cm\(^{-1}\) (C-O stretching of the acetyl group), amide II band at 1558 cm\(^{-1}\) (N-H stretching), and amide III band at 1313 cm\(^{-1}\) (Shigemasa et al., 1996; Kam et al., 1999; de Queiroz Antonino et al., 2017). Vibrations at 1420 and 1375 cm\(^{-1}\) are attributed to the asymmetrical C-H bending of the CH\(_2\) group, while the absorption at 1150 cm\(^{-1}\) is attributed to the anti-symmetric stretching of C-O-C bridge, and at 1060 and 1026 cm\(^{-1}\) to the skeletal vibrations involving a C-O stretching. The C-H deformation of the \(\beta\)-glycosidic bond corresponds to the peak at 895 cm\(^{-1}\) (Kumirska et al., 2010; de Queiroz Antonino et al., 2017). Orange peel powder (OPW) spectrum shows a peak at 1732 cm\(^{-1}\) attributed to the C=O bond due to carboxyl groups (-COOH) and esters (-COOCH\(_3\)) present in pectin. The peak at 1606 cm\(^{-1}\) may be attributed to C=C aromatic stretching or C=O stretching of carboxylate group (Lugo-Lugo et al., 2012) and the peak at 1645 cm\(^{-1}\) might be a water peak (Doshi et al., 2019). The bands at 1575 and 1455 cm\(^{-1}\) correspond to the asymmetric and symmetric stretching vibrations of ionic carboxylic groups (-COO\(^-\)), the peak at 1015 cm\(^{-1}\) may be attributed to the C-O group. Moreover, the peaks in the range of 850-1150 cm\(^{-1}\) were attributed to the C-O, C-C and C-O-C of the polysaccharide chain having a glycosidic bond and pyranose ring (Doshi et al., 2019). There are no differences before and after chromium adsorption in the O-H region with a broad band centered at 3300 cm\(^{-1}\) (that accounts for O-H stretching, intermolecular hydrogen bonds, and N-H stretching for chitosan), and the corresponding peaks for C-H stretching at 2920 and 2850 cm\(^{-1}\), for cellulose, pectin, lignin, and chitosan O-H and C-H groups (see Figure 5).
There are no differences in the spectrum of CTS and OPW taken before and after Cr(VI) adsorption. The only noticeable difference is the absence of the 1606 cm⁻¹ peak for OPW after chromium adsorption which, according to Lugo-Lugo et al. (2012) is attributed to the C=O stretching vibration of the carboxylate groups; hence, the chromate ion might be bonded into the OPW through this group.

In Figure 5 we can see infrared spectra for chitosan powder, orange peel powder (OPW), and CTS-OPW beads with different drying methods (oven, vacuum, freeze dry) before and after chromium adsorption batch experiment in the range of 4000 to 2200 cm⁻¹. CTS and OPW powder and CTS-OPW oven-dried beads show no difference before and after the adsorption process. CTS-OPW freeze-dried, and vacuum-dried beads show an important reduction in the O-H, N-H infrared absorption region after chromium adsorption, which could be indicative of chromate ion bonded to those functional groups. However, there is no clear evidence of chromium adsorption in this region of the infrared spectra, since Itankar et al. (2021) suggest coordination between metal and biomass (wood apple shell) as they report a shift of the band from 3448 cm⁻¹ to 3391 cm⁻¹ attributed, probably, to the complexation of H-bonded -OH with Cr(VI) ions. On the other hand, Murugesan et al. (2013) do not observe any change at 3435 cm⁻¹ (-OH stretching vibration of H-bonded hydroxyl groups of the carbonized corncob pile); neither Almughamisi et al. (2019) observe any difference between Cr(VI) loaded composites chitosan-metal hydroxide/oxide [Cu(OH)₂ and CuO], and Vieira et al. (2014) do not even report the infrared spectra in the 4000-2000 cm⁻¹ range for chitosan-based sorbents, they only discuss the region between 2000-1000 cm⁻¹ and assume that the nitrogen atoms (amino groups) are the main adsorption sites for Cr ions.
Figure 5. Infrared spectra for chitosan powder, orange peel powder (OPW), and CTS-OPW beads with different drying methods (oven, vacuum, freeze dry) before and after chromium adsorption batch experiment in the 4000 to 2200 cm⁻¹ region. For more convenient representation, the spectra are shifted in relation to each other along the ordinate axis.

In Figure 6 we can see infrared spectra for CTS-OPW beads with different drying methods (oven, vacuum, freeze dry) before and after the chromium adsorption batch experiment in the range of 2000 to 550 cm⁻¹. The first difference is the shift of the 1647 and 1560 cm⁻¹ bands between 20-35 cm⁻¹ to 1627 and 1525 cm⁻¹, moreover, both peaks reduce their intensity after Cr(VI) adsorption. The peaks at 1414 and 1378 cm⁻¹ do not shift but both reduce their intensity. Another noticeable shift is observed in peaks at 1067 and 1026 cm⁻¹ that shifted to 1055 and 1020 cm⁻¹, respectively. The peak at 890 cm⁻¹ does not shift but it reduces its intensity, and finally, a shoulder at 944 cm⁻¹ appears after Cr(VI) adsorption for all kinds of beads. Venugopal and Mohanty (2011) indicate that the shifting of peaks and their intensity (intensity reduction) confirmed that carboxyl, amine, alkane, and amide groups were the leading Cr binding group. According to Hoffmann et al. (2001), who studied the chromate, bichromate, and dichromate in ambient solutions with infrared spectroscopy, there is a band at 949 ± 1 cm⁻¹ corresponding to the CrO₃⁴⁻ stretching asymmetric vibration (νas) of HCrO₄⁻ and Cr₂O₇²⁻ species. The shoulder that appears at 944 cm⁻¹ after Cr(VI) adsorption in all three kinds of CTS-OPW beads indicates that chromate ion is bonding with the sorbent.
Figure 6. Infrared spectra for CTS-OPW beads with different drying methods (oven, vacuum, freeze dry) before and after chromium adsorption batch experiment in the 2000 to 550 cm⁻¹ region. For more convenient representation, the spectra are shifted in relation to each other along the ordinate axis.

In Figure 7 we can observe the x-ray diffraction patterns of CTS and CTS-OPW before and after adsorption. Several authors report the diffraction pattern of chitin with two peaks at 2θ around 10° and 20°, while the diffraction pattern of chitosan shows the peak at 20° and a decrease in the band at around 10° due to deacetylation (Abdou et al., 2008; Kaya et al., 2014; Hwang et al., 2003), where the peak at 10° corresponds to the (020) plane and the peak at 20° corresponds to the (200) plane (Mogilevskaya et al., 2006; Zhang et al., 2005). The diffraction pattern of CTS before adsorption shows a broad peak at 20° and a broad low intense amorphous halo between 30-45° of 2θ, which is an indicative of high deacetylation degree and low crystallinity. After adsorption, the diffraction pattern shows no peak at 20° indicating that adsorption of chromate ion or dichromate ion modifies the crystal structure of native CTS. Gupta and Nayak (2012) reported that orange peel powder is amorphous, and their diffraction pattern shows a low intense broad peak around 22° and an amorphous halo between 30° and 50°, which is consistent with our diffraction pattern of CTS-OPW beads. Moreover, the adsorption process does not modify the diffraction pattern of CTS-OPW beads that might indicate the material is completely amorphous and chromate ion or dichromate ion does not affect that amorphous structure.
Figure 7. XRD diffraction patterns of CTS and CTS-OPW beads before and after chromium adsorption. For more convenient representation, the diffractograms are shifted in relation to each other along the ordinate axis.

3.1. Adsorption kinetics
Figure 8 shows the adsorption capacity of Cr(VI) as a function of time for CTS-OPW oven-dried beads when mixed with Cr(VI) at an initial concentration of 100 mg L\(^{-1}\). Data is adjusted to PFO, PSO, and Elovich models.
Figure 8. Adsorption kinetic data for CTS-OPW oven-dried beads. Pseudo-first order, pseudo-second order, and Elovich models are fitted using a non-linear method.

Figure 9. Adsorption kinetic data for CTS-OPW vacuum oven-dried beads. Pseudo-first order, pseudo-second order, and Elovich models are fitted using a non-linear method.
Figure 9 shows the adsorption capacity of Cr(VI) as a function of time for CTS-OPW vacuum oven-dried beads when mixed with Cr(VI) at an initial concentration of 100 mg L⁻¹. Data is adjusted to PFO, PSO, and Elovich models and the best fit is obtained with Elovich model. Figure 10 shows the adsorption capacity of Cr(VI) as a function of time for CTS-OPW freeze-dried beads when mixed with Cr(VI) at an initial concentration of 100 mg L⁻¹. Data is adjusted to PFO, PSO, and Elovich models and the best fit is obtained with Elovich model. Adsorption capacity at equilibrium for CTS-OPW oven-dried and vacuum oven-dried beads are very similar when fitted with PFO (7.6–7.7 mg g⁻¹) and PSO (8.7–10 mg g⁻¹) models, however this fitted value for CTS-OPW freeze-dried beads using PFO and PSO is lower than that for oven-dried and vacuum oven-dried (5.2–5.7 mg g⁻¹) at the same conditions.

![Graph showing adsorption kinetics data for CTS-OPW freeze-dried beads.](image)

**Figure 10.** Adsorption kinetic data for CTS-OPW freeze-dried beads. Pseudo-first order, pseudo-second order, and Elovich models are fitted using a non-linear method.

For all the samples, experimental data do not reach equilibrium after 72 hours even with agitation. However, the obtained values for $q_e$ using a non-linear adjustment for both pseudo-first and pseudo-second order equations are very similar, indicating a good agreement of the experimental data with both kinetic models (Simonin, 2016). Moreover, there is a better agreement of the data ($\chi^2$) with the PSO than for the PFO for all samples. Several works in the literature show a better fitting for the PSO model (Zhang et al., 2015; Chagas et al., 2019; El Nemr et al., 2020; Yang et al., 2020; Pavithra et al., 2021) than the PFO model. Even though our results show some dispersion and equilibrium is not completely reached, the behavior of the PFO and PSO models is in good agreement with previous reports on similar adsorbents.

Few works report kinetic adsorption fitting with the Elovich model, among them Aydin & Aksoy (2009) reported a better fitting for the PSO than for the Elovich model using 1300 micron chitosan flakes as adsorbent for Cr(VI). The results obtained by Yang et al. (2020) for hexavalent chromium adsorption (using chitosan/bentonite composite as adsorbent) indicate that their adsorption kinetic data are best fitted with the Elovich model, with is in good agreement with our results for CTS-OPW beads. Moreover, Yang et al. (2020) indicate that the adsorption of
Cr(VI) onto chitosan/bentonite occurs primarily by chemisorption, and it is reported by several works that the Elovich model is the most effective model for explaining chemisorption, but –as commented earlier– it is not possible to ensure that adsorption follows a chemisorption mechanism. Parameter $\alpha$ is 0.15 for CTS-OPW oven-dried beads, reduces for CTS-OPW freeze-dried beads (0.038), and the lowest value (0.021) for CTS-OPW vacuum oven-dried beads. This indicates that CTS-OPW oven-dried beads show a faster initial adsorption rate compared to the CTS-OPW freeze-dried and CTS-OPW vacuum oven-dried beads. This behavior is not expected since CTS-OPW oven-dried beads are not as porous as CTS-OPW freeze-dried beads.

3.2. Adsorption isotherm
To fit the experimental data by linear regression analysis for the three types of beads, the conventional models of Langmuir and Freundlich are used. The Langmuir equation indicates a monolayer adsorption at the surface sites of the beads, where $q_{\text{max}}$ is the maximum adsorption capacity of the adsorbent at monolayer saturation, $q_e$ is the amount of adsorbate adsorbed at equilibrium, $K_L$ is the Langmuir isothermal constant. While Freundlich model indicates adsorption at a heterogeneous surface—which cannot describe the saturation behavior of an adsorbent— with a Freundlich constant, $K_F$, that is not necessarily equal to the maximum adsorption capacity (it is only when $n \to \infty$), and an intensity parameter $n$ which indicates the magnitude of the driving force or the surface heterogeneity. The adsorption isotherm becomes favorable when $n > 1$. The chi-squared analysis ($\chi^2$) indicate that Freundlich isotherm fits better that Langmuir isotherm for all CTS-OPW beads, which indicates a heterogeneous surface that corresponds to the fact that it is a composite material.

<p>| Table 1. Adjusted parameters for CTS-OPW with different drying methods with Langmuir and Freundlich isotherm models. |</p>
<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>CTS-OPW oven-dried beads</th>
<th>CTS-OPW vacuum-dried beads</th>
<th>CTS-OPW freeze-dried beads</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. datum</td>
<td>$q_{\text{e}, \text{exp}}$ (mg g$^{-1}$)</td>
<td>24.62</td>
<td>21.25</td>
<td>16.98</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$q_{\text{max}}$, cal (mg g$^{-1}$)</td>
<td>27.5(6.06)</td>
<td>33.889(10.4)</td>
<td>32.404(17.8)</td>
</tr>
<tr>
<td></td>
<td>$K_L$ (L g$^{-1}$)</td>
<td>0.0237(0.0146)</td>
<td>0.00891(0.00529)</td>
<td>0.0051(0.00464)</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>35.03</td>
<td>14.2061</td>
<td>13.1428</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$\chi_L$</td>
<td>0.144-0.808</td>
<td>0.310-0.918</td>
<td>0.440-0.952</td>
</tr>
<tr>
<td></td>
<td>$K_F$ (mg g$^{-1}$) / (mg L$^{-1}$)$^n$</td>
<td>1.6883(0.935)</td>
<td>0.81222(0.371)</td>
<td>0.44352(0.294)</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>0.52265(0.122)</td>
<td>0.63818(0.0971)</td>
<td>0.68832(0.136)</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>33.4569</td>
<td>10.289</td>
<td>1.3176</td>
</tr>
</tbody>
</table>

Note: Standard deviation in parenthesis.

In this case for all biosorbents tested, $n < 1$ and $R_L < 1$ indicating that the isotherms are favorable and concave.
Figure 11. Adsorption isotherm data for CTS-OPW oven-dried beads. Langmuir and Freundlich models are fitted using a non-linear method.

Figure 12. Adsorption isotherm data for CTS-OPW freeze-dried beads. Langmuir and Freundlich models are fitted using a non-linear method.
López-Téllez et al. (2011) analyzed the Cr(VI) adsorption of an orange peel pith with iron and iron oxide nanoparticles biocomposite and found that the maximum adsorption $q_{\text{max}}$ of Langmuir model is 5.37 mg g$^{-1}$ and compared this value with the maximum adsorption of orange peel powder of 1.90 mg g$^{-1}$ evaluated with Langmuir model. Same authors (López-Téllez et al., 2013) also analyzed iron oxide nanorods in orange peel pith biocomposite and found a maximum adsorption capacity of 7.44 mg g$^{-1}$. Pehlivan et al. (2012) analyzed sorption behavior of orange peel and orange pulp and found that the maximum adsorption of Cr(VI) using Langmuir model is 0.92 and 0.55 mmol g$^{-1}$ of orange (*Maclura pomifera*) pulp and peel, respectively; the reported adsorption capacity equals to 47.8 and 28.6 mg g$^{-1}$ (Cr molar mass of 51.9961 g mol$^{-1}$), respectively. Pavithra et al. (2021) prepared a novel CTS-based hydrogel composite containing numerous functional groups by grafting, blending, and crosslinking using bentonite, acrylamide, orange peel, and N,N-methylenbis-acrylamide (MBA) as crosslinking agent, and obtained a $q_{\text{max}}$ value of 107.498 mg g$^{-1}$ using Langmuir isotherm model. Mandina et al. (2013) reported maximum adsorption capacities for chromium (VI) removal using orange peel and modified orange peel with sodium hydroxide of 97.07 and 139.0 mg g$^{-1}$, respectively. Unfortunately, this reported value correspond to the Freundlich constant with units of (mg g$^{-1}$)/(mg L$^{-1}$)$^{n}$ and does not correspond to the maximum adsorption capacity of the sorbent (Tran et al., 2017). Moreover, when calculating $q_{e}$ values from Fig.8 of Mandina et al paper, we obtained values ranging from 128 to 13,830 mg g$^{-1}$, while the theoretical upper value for $q_{e}$ at $C_e$=100 ppm is 50 mg g$^{-1}$, so we conclude that their calculations are not correct, and it is not possible to compare with their results. Olea-Mejía et al. (2017) reported the removal of Cr(VI) from water using a composite of orange peel + nanostructured zero-valent-iron and reported a 100% removal from a 10 mL of 50 ppm initial Cr(VI) concentration solution using 0.4 g of sorbent for one hour at room temperature and pH of 3 under magnetic stirring. They do not report neither kinetic adsorption nor isotherm data. Adsorption capacity or performance is expressed as the amount of adsorbed Cr(VI) at equilibrium ($q_{e}$, mg g$^{-1}$) or the percentage of removed Cr(VI) ($\%\text{removal}$) from solution. However, Tran et al. (2017) indicates that $\%\text{removal}$ is an approximate unit that must be used with caution since it can cause misleading conclusions about relative adsorption.
performance. The value of $q_e$ in the 100 % Cr(VI) removal experiment of Olea-Mejia et al. (2017) corresponds to a $q_e$ value of 1.25 mg g$^{-1}$. Liang et al. (2020) reported a new adsorbent by crosslinking orange peel with ethylenediamine and found a $q_{\text{max}}$ value of 52.08 mg g$^{-1}$ with Langmuir isotherm model at pH 6 and 3 g L$^{-1}$ sorbent dose. Finally, Pertile et al. (2021) studied chromium removal by orange peel powder with grain size fraction < 0.5 mm and found a $q_{\text{max}}$ value of 31.4 mg g$^{-1}$ when fitting with Langmuir isotherm model.

Table 2. Maximum adsorption capacity of different orange peel based composites for Cr(VI) sorption using Langmuir isotherm.

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>pH</th>
<th>Sorbent dosage (m/V), g L$^{-1}$</th>
<th>Isotherm model</th>
<th>$q_{\text{max}}$, mg g$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron nanoparticles embedded in orange peel pith</td>
<td>1</td>
<td>5</td>
<td>Langmuir</td>
<td>5.37</td>
<td>López-Téllez et al., 2011</td>
</tr>
<tr>
<td>Iron oxide nanorods over orange peel</td>
<td>1</td>
<td>5</td>
<td>Langmuir</td>
<td>7.44</td>
<td>López-Téllez et al., 2013</td>
</tr>
<tr>
<td>CTS-OPW oven-dried beads</td>
<td>2</td>
<td>5</td>
<td>Langmuir</td>
<td>27.5</td>
<td>This work</td>
</tr>
<tr>
<td>CTS-OPW vacuum-dried beads</td>
<td>2</td>
<td>5</td>
<td>Langmuir</td>
<td>33.9</td>
<td>This work</td>
</tr>
<tr>
<td>CTS-OPW freeze-dried beads</td>
<td>2</td>
<td>5</td>
<td>Langmuir</td>
<td>32.4</td>
<td>This work</td>
</tr>
<tr>
<td>Orange peel powder</td>
<td>2</td>
<td>3.33</td>
<td>Langmuir</td>
<td>28.6</td>
<td>Pehlivan et al., 2012</td>
</tr>
<tr>
<td>CTS-BENT-g-acrylamide-OP + MBA hydrogel</td>
<td>4</td>
<td>10</td>
<td>Langmuir</td>
<td>107.5</td>
<td>Pavithra et al., 2021</td>
</tr>
<tr>
<td>OP crosslinked with Ethylenediamine</td>
<td>6</td>
<td>3</td>
<td>Langmuir</td>
<td>52.08</td>
<td>Liang et al., 2020</td>
</tr>
<tr>
<td>Orange peel</td>
<td>1.1</td>
<td>20</td>
<td>Langmuir</td>
<td>31.4</td>
<td>Pertile et al., 2021</td>
</tr>
</tbody>
</table>

According to Langmuir fitting, CTS-OPW freeze-dried beads show the maximum adsorption capacity followed by CTS-OPW vacuum oven-dried beads and CTS-OPW oven-dried beads. The Elovich fitting indicates that CTS-OPW oven-dried beads show a faster initial adsorption rate compared to the CTS-OPW freeze-dried and CTS-OPW vacuum oven-dried beads. Then CTS-OPW oven-dried adsorbs Cr(VI) faster at early stages but adsorbs less Cr(VI) per adsorbent gram at equilibrium. On the contrary, CTS-OPW freeze-dried beads adsorb Cr(VI) at a slower rate but adsorb more Cr(VI) per adsorbent gram at equilibrium. It might be related to the pronounced reduction of –OH infrared signal for CTS-OPW freeze-dried beads compared to the CTS-OPW oven-dried beads in figure 5.

4. Conclusions

CTS-OPW with different drying process were analyzed for Cr(VI) adsorption. FT-IR analysis shows shifts of the 1647 and 1560 cm$^{-1}$ bands between 2C-35 cm$^{-1}$ to 1627 and 1525 cm$^{-1}$, shifts in peaks at 1067 and 1026 cm$^{-1}$ that shifted to 1055 and 1020 cm$^{-1}$, respectively, and the shoulder that appears at 944 cm$^{-1}$ after Cr(VI) adsorption indicates that for, chromate ion is present in all CTS-OPW beads since the band at 949 cm$^{-1}$ corresponds to the CrO$_3^-$ stretching asymmetric vibration ($\nu_{\text{as}}$) of HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ species. Using stereomicroscope images, the spherical and porous shape of the lyophilized beads could be seen, while the oven-dried and vacuum oven-dried beads showed a compact morphology. The adsorption capacity was evaluated by varying the pH and particle size. The highest adsorption capacities were reached at pH 2 with a granulometry of 0.3 mm. The adsorption capacity of the CTS-OPW beads was also evaluated for the three types of drying. It can be concluded that vacuum oven-dried beads have the highest hexavalent chromium adsorption capacity, 33.89 mg g$^{-1}$, followed by freeze-dried beads, 32.4 mg g$^{-1}$, and finally oven-
dried beads with a $q_{\text{max}}$ value of 27.5 mg g$^{-1}$. The manufacture of the beads contributes to improve the individual properties of these biosorbents, guarantees a lower use of CTS and a greater use of a solid agro-industrial residue such as orange peel. Adsorption isotherms can be modeled with the Langmuir isotherm, while vacuum oven-dried and freeze-dried beads fit the Freundlich model better. Our results for maximum adsorption capacity from Langmuir model are greater than those of López-Téllez et al. (2011), are in about the same range compared to the results of Pehlivan et al., (2012) and Pertile et al., (2021). All these works analyzed orange peel and/or orange peel with iron particles or nanoparticles. Finally, our results are slightly lower than those of Liang et al., 2020 and much lower than those of Pavithra et al., 2021, but it is important to consider that they analyzed orange peel crosslinked with ethylenediamine (process that uses also epichlorohydrin, N,N-dimethylformamide, and triethylamine) and CTS-BENT-g-acylamide-OP + MBA hydrogel (process that include the acrylamide polymerization using ceric ammonium nitrate as initiator and N,N’-Methylene bisacrylamide as cross-linking agent), respectively. This proposed method for beads manufacture is not as expensive as the latter two and the improving adsorption Cr(VI) capacity might be overcome with a non-expensive product.

5. Supplementary information
There is no additional information.

6. Acknowledgments
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Yanay Fernández-Reina performed the experiments and wrote the first draft. Pamela V. Sierra-Trejo supervised Fernández-Reina and collaborated with experiments. Rosalba Patiño-Herrera collaborated with infrared and x-ray diffraction analysis. Teresa del C. Flores-Flores collaborated with adsorption isotherms discussion. Guillermo González-Alatorre collaborated with adsorption kinetics discussion and writing. José F. Louvier-Hernández proposed the idea, principal advisor of Fernández-Reina and Sierra-Trejo, performed mathematical fitting and final draft.

Conflict of interest declaration
The authors declare no competing financial interest.

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References


