Hexavalent Chromium Adsorption from Aqueous Solution Using Orange Peel Modified with Calcium Chloride: Equilibrium and Kinetics Study

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Abstract

Background: Adsorption technology using residual biomass has gained attention as a low-cost alternative for removing Cr (VI) ions from aqueous solutions. **Objectives:** This work attempts to study the effect of orange peel modification with CaCl$_2$ on Cr (VI) ions uptake in batch and continuous system. In addition, pH and particle size were evaluated to determine suitable values for carrying out adsorption process. **Methods/Analysis:** OP-CaCl$_2$ and OP biosorbents were characterized by FT-IR analysis in order to identify their functional groups. The pH of heavy metal ions solutions was adjusted to 2, 3, 4 and 6 and adsorbent particle size was varied in 0.355, 0.5 and 1 mm. Experimental data for batch experiments were used to calculate adsorption isotherms and kinetic. The results of adsorption on packed-bed columns were fitted to dynamic models. Desorption process was also studied to determine reusability of biomass. **Findings:** It was found that hydroxyl, carboxyl and aliphatic groups are the main contributors to adsorption process. The highest removal yield (86%) was achieved at pH of 2 and particle size of 0.355 mm. The chemical reticulation with CaCl$_2$ did not improve adsorption capacity of orange peel biosorbent. Kinetic and isotherm models that best fit experimental data were Elovich´s and Freundlich´s, respectively. Regarding continuous systems, data obeyed Yoon-Nelson and Dose-response models with R^2 =0.99. Desorption study with HCl reported a removal yield of 43.7% for second cycle of biosorbent use. **Novelty/Improvement:** These results suggested that orange peel is a suitable biosorbent alternative for removing Cr (VI).

Keywords: Adsorption Kinetics, Biosorption, Chromium Hexavalent, Isotherms, Removal

1. Introduction

Heavy metals in water sources have been a major issue due to its toxicological effect on environment and health. These pollutants get absorbed and accumulated in human body, causing serious health diseases such as cancer, damaging of nervous system, organ damage and even death[1,2]. They do not degrade physical o chemically and can bioconcentrate on moving up in the food chain[3,4]. Chromium is considered one of the 14 most noxious heavy metals and it is widely used in electroplating, leather tanning, metal finishing and chromate preparation[5,6]. The maximum concentration of chromium allowed in drinking water is 0.05 mg/L[7]. Hence, the removal and recovery of chromium is important for environmental protection, human health and economic reasons[8]. Chemical procedures as reverse osmosis, coagulation, chemical precipitation, electro dialysis and ultra-filtration are widely employed to wastewater

treatment[9]. Among these methods, adsorption has gained importance in the purification of all types of waters as it is environment friendly and a low cost technology[10]. Several materials have been tested to adsorb heavy metal ions from water solutions, however, agricultural waste products represent unused and widely available resource with great potential to be used as adsorbents[11]. Different biosorbents have been obtained from residual biomass to adsorb Cr (VI) in batch and continuous system as: pecan nut husks[12], olive stone[13], mustard oil cake[14], activated carbon from *Swietenia mahogani* fruit shells[15], rice straw[16], $ZnCl_2$ impregnated activated carbon derived by *Jatropha curcas* seed hull[17], among others. Orange peels are one of the valuable waste materials discarded from juice industry with great potential to remove pollutants from wastewater[18]. Therefore, this work attempts to study adsorption equilibrium and kinetic of Cr (VI) ions using orange peel (*Citrus sinensis*) biosorbent and evaluate the effect of its chemical modification with $CaCl_2$ on removal yield.

2. Material and Methods

2.1 Materials

Potassium dichromate, calcium chloride, sodium hydroxide and hydrogen chloride were purchased from Merck in analytic grade. Orange peel (*Citrus sinensis*) biomass was obtained from a local fruit market.

2.2 Biosorbent Preparation

2.2.1 Orange Peels (OP)

Orange peels were washed with enough water to remove impurities and soluble compounds such as surface tannins, reducing sugar resin and pigments that can affect adsorption process. They were dried to 90°C during 24 hours and milled to 1, 0.5 and 0.355 mm particle size.

2.2.2 Modification with $CaCl_2$

The content of pectin in orange peels can be reticulated using different chemicals as $CaCl_2$ in order to improve its adsorption capacity[19]. In this study, 20 g of OP dried biomass was kept in contact with 500 mL of 0.2 M $CaCl_2$ solution during 24 hours. Afterwards, the sample was washed with distillated water and filtered to remove excess of chlorine and calcium. Finally, OP-$CaCl_2$ was dried in an oven during 3 hours[20].

2.3 Characterization of Biosorbents

The OP-$CaCl_2$ biosorbentwas characterized by Fourier Transform Infrared Spectroscopy to identify chemical groups in biomaterial molecules. The FT-IR analysis of samples was recorded on Nicolet 6700 spectrophotometer in the range between 4000-500 cm^{-1}.

2.4 Batch Adsorption Experiments

The experiments of adsorption on batch mode were performed in a shaker at room temperature (25°C) during 2 hours. Stock solution of chromium (100 ppm) was prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) in deionized water. Then, 100mL of this solution was mixed with 0.5 g of biosorbent inside a flask placed on a stirrer plate. The effect of pH on adsorption process was evaluated by adjusting pH to 2, 3, 4 and 6 with 0.5 N HCl and NaOH solutions. The residual heavy metal ions concentration was measured using diphenylcarbazide acid solution using anUV/Vis Shimdzu UV 1700 spectrometer. The concentration of Cr (VI) ions retained by biomass was calculated according to Equation 1, where C_o (mmol/L) is the initial Cr (VI) concentration in the solution, C_f (mmol/L) is the Cr (VI) concentration in the solution after adsorption, V_o (L) is the initial volume of Cr (VI) solution, V_f is the final volume of Cr (VI) solution and m is the dried mass of used OP-$CaCl_2$ biosorbent.

$$q = \frac{C_o V_o - C_f V_f}{m} \qquad (1)$$

2.5 Kinetic Studies and Adsorption Isotherms

The adsorption kinetic of lignocellulosic materials was studied in order to determine the required contact time to attain adsorption equilibrium. In brief, 0.5 g of OP and OP-$CaCl_2$ biosorbent were shaken with 100 mL of 100 ppm Cr (VI) ions solution on a reciprocating shaker at 150 rpm at a constant temperature of 25°C. Suitable pH and particle size operating conditions were considered in these experiments. Aliquots of 5 mL were taken periodically between 10-330 minutes. Pseudo-first order, pseudo-second order, Elovichand intra-particle diffusion models were selected to explain the adsorption process of Cr (VI) and OP-$CaCl_2$. Experimental data for fitting to isotherms model were taken under same conditions as described above and using different initial Cr (VI) concentration

(25, 50, 75 and 100 ppm). Empirical isotherms (Langmuir and Freundlich) were selected to evaluate the adsorption equilibrium of OP-CaCl$_2$-Cr (VI).

2.6 Bioadsorption Experiments in Continuous Systems

The adsorption experiments in continuous system were carried out on lab-scale equipment based on 4 packed-bed columns with diameter of 3.5 cm and height of 18.5 cm. The system required a pump and 9 valves to distribute 0.1 mL/s of Cr (VI) solution throughout these columns. Aliquots of 5 mL were taken after 270 minutes of contact time in order to analysis the behaviour of biomass to remove heavy metal ions and the time in which the packed-bed achieved breakthrough concentration (5% of initial concentration). The experimental data were fitted to Yoon-Nelson, Thomas, Dose-response and Bohart-Adams models that are frequently used in literature.

2.7 Desorption Studies

Desorption of Cr (VI) ions was performed to study the reusability of biomass in adsorption cycles. This process was carried out by adding 10 g used OP to 25 mL of 0.2 M HCl in a recipient placed on a shaker at 150 rpm during 30 minutes, followed by a washing with abundant distillated water to remove acid traces.

3. Results and Discussion

3.1 Characterization of Biosorbent

In order to determine chemical structure of biosorbent materials and their functional groups that can have affinity with Cr (VI) ions, OP and OP-CaCl$_2$ biosorbents were characterized by FT-IR analysis. Figure 1 shows infrared spectra of OP and OP-CaCl$_2$ before and after adsorption process. The peak at 3300 cm^{-1} is assigned to hydroxyl group (OH) stretching vibrations, which are reported in 3400-3000 cm^{-1} range[21]. In addition, it was identified peaks at 1732 cm^{-1}, 1615-1684 cm^{-1}, 1558 cm^{-1} and 1235 cm^{-1} attributed to C=O, C=C, C-H and C-O stretching vibrations, respectively[22]. These functional groups are characteristic of carboxyl, aromatic rings, hydroxyl, methyl and methoxy present in main components of lignocellulosic biomass as pectin, hemicellulose and lignin[23].

3.2 Batch Adsorption Experiments

3.2.1 Effect of Solution pH and Biosorbent Particle Size

The pH of the solution is an important parameter for carrying out adsorption because it modifies charge of biosorbent surface, ionization degree and speciation of sorbate species. As is well known, adsorption process
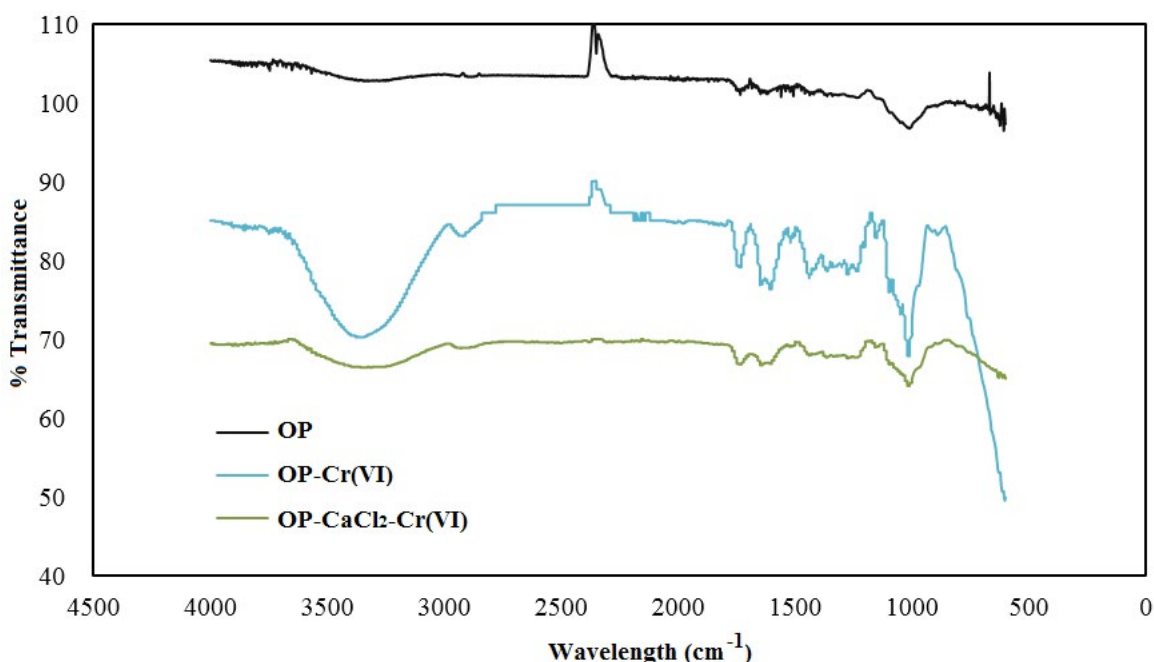

Figure 1. FT-IR spectra of OP and OP-CaCl$_2$ biosorbents before and after Cr (VI) adsorption.

takes place on pores surface. The amount of solute that can be adsorbed is directly proportional to volume, hence, to surface area that is significantly affected by particle size of biosorbents. The effect of pH and particle size on removal yield of Cr (VI) ions using OP and OP-CaCl$_2$ biosorbents are shown in Figure 2.

The removal yield of heavy metal ions in aqueous solution using OP and OP-CaCl$_2$ biosorbents was calculated by eq. (2).

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

It was found that adsorption capacity of orange peel biomass is dramatically affected by pH exhibiting an increase in removal yield when pH decreases as is shown in Figure 2a). According to the highest adsorption removal yield (30.6%), it was selected pH= 2 as suitable value for carrying out further experiments. The experimental results can be explained by protonation of biosorbent surface due to high amount of H$^+$ ions increasing attraction between these and chromium anions[24,25]. In range of pH= 2-6, the predominant form is $Cr_2O_7^{2-}$ and $HCrO_4^-$ ions[26]; for higher pH chromium is present as CrO_4^{2-} ions and its affinity is relatively low in comparison to $Cr_2O_7^{2-}$ and $HCrO_4^-$. Figure 2b) shows that removal yield of Cr (VI) increased when particle size was reduced, which is attributed to high surface area of small size particles and porosity of biomaterials[27]. The highest value for removal yield was achieved using 0.355 mm particle size, similar results to those reported by[28].

3.2.2 Kinetic Studies and Adsorption Isotherms

The kinetic study was performed to stablish the adsorption mechanism of Cr (VI) on biosorbents from orange peels (OP and OP-CaCl$_2$) fitting experimental data to kinetic models of pseudo-first order, pseudo-second
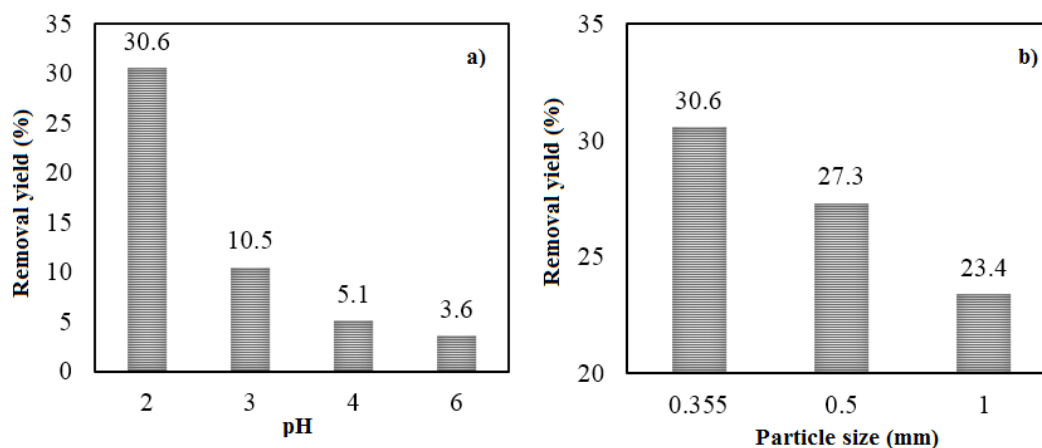

Figure 2.   Effect of: a) pH and b) particle size on removal yield of Cr (VI) ions.

Table 1.   Kinetic models of adsorption

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

Source: In[34]-[35]

order, Elovich and intra-particle diffusion. The mathematical expression for these models are presented in Table 1. The adsorption process involves: mass transfer of ions from solution to biosorbent surface, Cr (VI) ions adsorption in available sites of biosorbent and intern diffusion of solute onto biosorbent[29]. Hence, adsorption capacity-time curves was plotted and fitted to models using non-lineal regression by minimization of sum of squares (SS).

Figure 3 shows kinetic models curves and experimental data for OP and OP-CaCl$_2$ biomaterials, in which Cr (VI) ions was rapidly removed from aqueous solution during first minutes. It was observed that Elovich model best fits batch adsorption results with sum of squares of 4.88 and 2.47. This suggested that hexavalent chromium ions uptake mainly obeys chemisorption with second order heterogenic reaction mechanism. However, batch adsorption results exhibited a reduction in adsorption potential of both biomasses. The highest removal yields of 43.7% and 21.2% were achieved for OP and OP-CaCl$_2$ biosorbents, respectively, which indicated that CaCl$_2$ agent did not interact or react with biomass; hence, OP only suffered a physical modification by covering its surface instead of chemical modification. This phenomenon can occur due to not complete carboxylation reaction, which is responsible of incorporating additional functional groups to the biomaterial[30]. It is suggested other modifications for further studies that can include carboxyl and hydroxyl groups to biomaterials chemical structure.

Table 2 summarized parameter models used in this work. According to Elovich model, initial adsorption rate (α) was higher for OP-CaCl$_2$ than for OP indicating the

rapid removal of Cr (VI) ions in aqueous solution using modified biomass, however OP biosorbent exhibited higher surface to uptake heavy metal ions.

Table 2. Parameters of main adsorption kinetic models for Cr (VI) uptake using OP and OP-CaCl$_2$ biosorbents

Kinetic model	Parameter	OP	OP-CaCl$_2$
Pseudo-first order	$q_{e,1}$	7.488	4.022
	k_1	0.028	0.079
	SS	11.761	6.285
Pseudo-second order	k_2	0.0037	0.029
	$q_{e,2}$	8.663	4.267
	SS	1.191	3.56
Elovich equation	β	0.592	2.062
	α	0.699	11.58
	SS	4.88	2.47
Intra-particle diffusion	k	0.526	0.292
	SS	13.33	10.198

The experimental equilibrium of solute in solid-liquid phase was modeled by Langmuir and Freundlich isotherm. These models describe the energy distribution of active sites that can be homogeneous or heterogeneous. In addition, they suggested monolayer or multilayer adsorption and interactions between adsorbed molecules[31]. Langmuir and Freundlich isotherms are expressed by Equations (3) and (4), respectively.
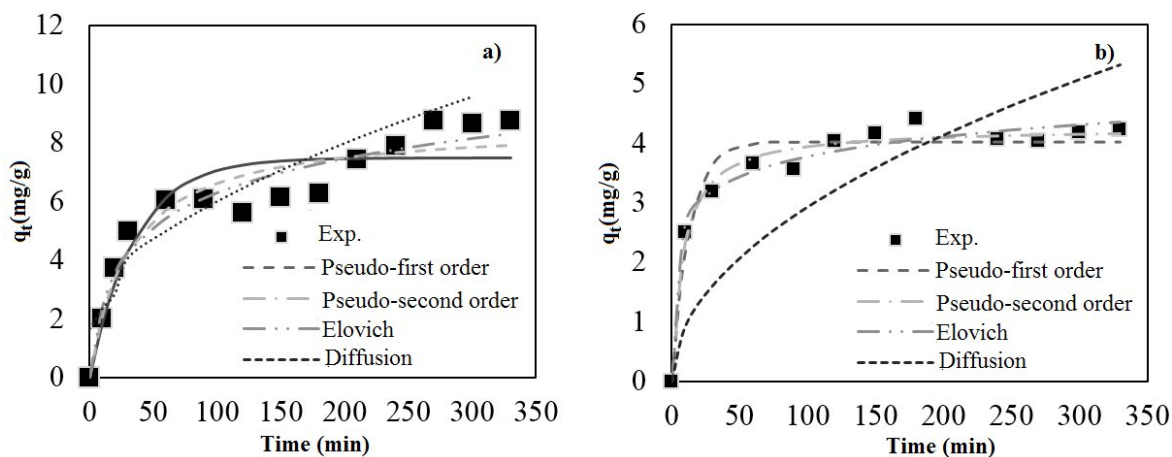

Figure 3. Cr (VI) adsorption experimental data fitting to kinetic models for: a) OP and b) OP-CaCl$_2$ biosorbents.

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

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

Where q_m is the maximum adsorption capacity (mmol/g), C_e is the equilibrium concentration of Cr (V) ions (mmol/l), q_e is the amount of Cr (V) ions adsorbed per unit of adsorbent at equilibrium (mmol/g), K_L is Langmuir constant (L/mmol), K_F is Freundlich constant and n is a heterogeneity factor.

The Cr (VI) adsorption process using both OP and OP-CaCl$_2$ biosorbents obeyed Freundlich isotherm model as is shown in Figure 4, which suggested a heterogeneous surface of biomass, multilayer formation and non-uniform distribution of heat of adsorption over the surface[24,32].

The Langmuir and Freundlich mathematical model parameters are presented in Table 3. The heterogeneity factor (1/n) determines adsorption favourability and depends on temperature and adsorbate/adsorbent properties. It has been reported that values of n>1 represented a chemical adsorption process and favorable adsorption[24]. In this study, both OP and OP-CaCl$_2$ biosorbents exhibited values of n equal to 1.8 and 10.2, respectively, suggesting that these materials experiment chemisorption. However, the maximum adsorption capacity parameter of Langmuir model was higher for OP biosorbent (12.29 mg/g) than OP-CaCl$_2$ biosorbent (4.95 mg/g). Therefore,

modification with CaCl$_2$ did not improve orange peel biomass performance for removing Cr (VI) from aqueous solution.

Table 3. Parameters of Langmuir and Freundlich models for adsorption of Cr (VI) onto OP and OP-CaCl$_2$ biosorbents

Parameters		OP	OP-CaCl$_2$
Langmuir	q_m (mg/g)	12.29	4.95
	K_L (L/mg)	0.029	0.33
	SS	30.62	30.61
Freundlich	(mg/g)	0.833	3.12
	$1/n$	0.555	0.098
	SS	0.6025	0.6023

3.3 Adsorption Experiments in Continuous System

The batch adsorption experiments provided suitable operating conditions of solution pH and biosorbent particle size for carrying out dynamic adsorption process in packed-bed columns. In order to design an adsorption column, it is necessary to predict the concentration-like profile and adsorption capacity of biosorbent for the selected adsorbate. Figure 5 shows breakthrough curve for sorption process in fixed bed using OP biosorbent. It
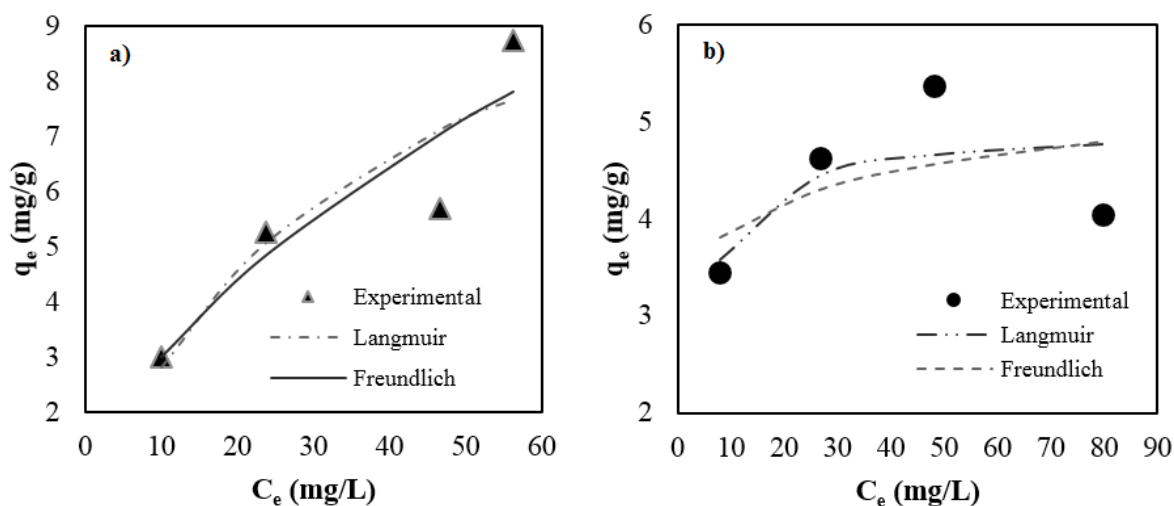

Figure 4. Experimental data of adsorption equilibrium fitting to Freundlich and Langmuir model using: a) OP and b) OP-CaCl$_2$.
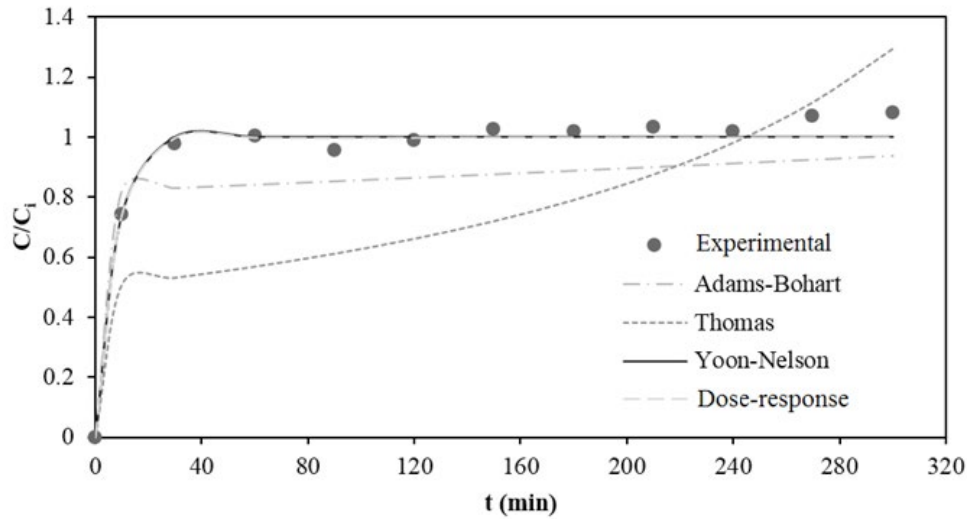
Figure 5. Models for the adsorption process of Cr (VI) in continuous systems using OP biosorbent.

was observed that break through time of OP was 120 min and adsorption capacity at this point (Q_{break}) was calculated by Equation 5, where the time is which outlet concentration is 5% of initial concentration, is flow rate in L/min and is biomass amount.

$$Qbreak\left(\frac{mg}{g}\right) = \frac{Q_v\tau_{5\%}C_o}{m} \qquad (5)$$

It was found that adsorption capacity at breakthrough time was 10.28 mg/g. In addition, the fitting of experimental data to different dynamic adsorption models is shown in Figure 5. Both Yoon-Nelson and Dose-response models best fitted the Cr (VI) uptake using OP biosorbent packed bed. Parameters of Yoon-Nelson, Thomas, Dose-response and Bohart-Adams models are presented in Table 4.

3.4 Desorption Studies

Desorption in batch system offers information about reusability of adsorbent reducing operational cost when it is applied to industrial scale. The orange peels biosorbent was subjected to three adsorption cycles after being desorbed by 0.2 M HCl. It was found that biomass after acid treatment can be reused for further adsorption process as shown Figure 6. The capacity for removing Cr(VI) ions decreased approximately to 20% and 10% during first and third cycle, suggesting that this biomass can be used several times in cycles without affecting its properties. On

Table 4. Experimental data fitting to models of adsorption in continuous system

Model	Parameter	Value
Thomas (Th)	k_{th} (mL mg^{-1} min^{-1})	0.04
	q_o (mg g^{-1})	1.11x10^{-14}
	R^2	0.79
	SS	0.088
Adams-Bohart (AB)	k_{AB} (L mg^{-1} min^{-1})	4.49x10^{-6}
	N_o (mg L^{-1})	7050.35
	R^2	0.0189
	SS	0.978
Yoon-Nelson (YN)	k_{YN} (min^{-1})	0.88
	τ (min)	8.80
	R^2	0.99
	SS	0.001
Dose-response (DR)	α	18.989
	q_O (mg g^{-1})	6.015
	R^2	0.993
	SS	0.1016

the other hand, the amount of heavy metal ions desorbed was 20 and 43.7% after 120 and 270 min, respectively, hence, it is recommended to evaluate other eluents in order to achieve higher desorption yield[33].
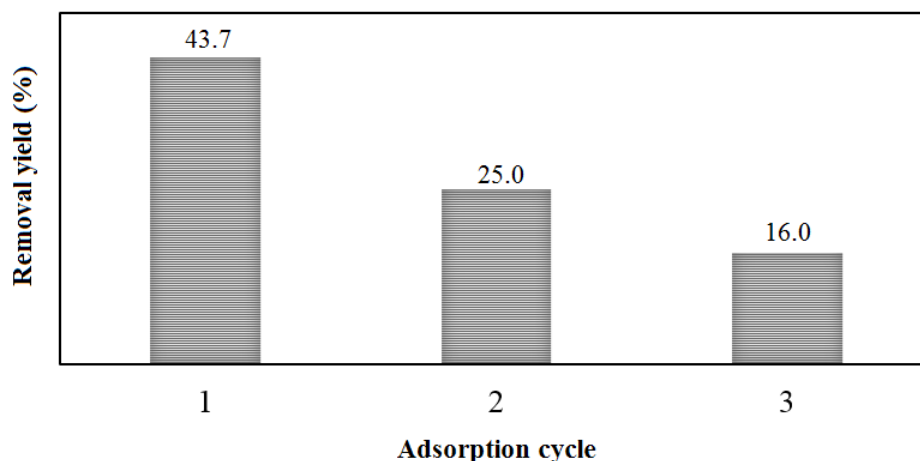
Figure 6. Desorption-adsorption experiments for Cr (VI) ions uptake using OP biosorbent in batch system.

4. Conclusions

This work was focused on studying adsorption process of Cr (VI) using orange peel biomass and evaluating the effect of biomass modification with $CaCl_2$ on removal yield. The FT-IR analysis performed to OP and OP-$CaCl_2$ showed the presence of hydroxyl and carboxyl groups on biosorbent surface. The highest removal yield on adsorption batch experiments was achieved under operating conditions of pH=2 and particle size = 0.355 mm. The kinetic and isotherm models that best fitted experimental data were those purposed by Elovich and Freundlich, respectively. The isotherm parameters suggested a chemisorptions process in multi-layers and heterogeneous surface of biosorbent. In addition, Cr (VI) adsorption capacity did not exhibit improvement with modification of orange peels biomass with $CaCl_2$. The adsorption dynamic process was studied on packed-bed columns and it was found rapid biomass saturation with breakthrough time of 120 min and adsorption capacity of 10.28 mg/g. The results of removal Cr (VI) on continuous system obeyed Yoon-Nelson and Dose-response models. Desorption of biomass revealed that OP biosorbent can be used repeatedly in removal process despite the reduction of its capacity. Hence, biosorbent from orange peels can be successfully used on Cr (VI) uptake.

5. Acknowledgments

6. References

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