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Adsorption Kinetics of Orange Peel Biosorbents for Cr (VI) Uptake from Water

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Abstract

Adsorptive materials have been widely investigated for removing heavy metal water pollutants and agricultural residues such as fruit peels seems to be a promising alternative due to its low cost and availability. This work attempts to study kinetics of Cr (VI) adsorption onto different orange peels-based biosorbents (OP, OPAC and OP-Chitosan). The activated carbon from orange peels was obtained by carbonizing the biomass and its activation with H_3PO_4 acid solution. The OP-Chitosan was prepared by immersing orange peels into chitosan-acetic acid gel. The OP biomass was characterized by ultimate analysis in order to determine the composition of main elements (carbon, nitrogen and hydrogen). Batch experiments were carried to analyse adsorption process over time and fit the experimental data to kinetic models such as pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion. It was found that elemental composition of orange peels biomass was C (%) 42.02, H (%) 5.44 % and N (%) 0.7. The pseudo-second order model best fits adsorption results for OPAC and OP-Chitosan with $q_{e,2}$ value of 17.27 and 17.24 mg/g, respectively. For OP biosorbent, pseudo-first order describes appropriately the data with parameter ($q_{e,1}$) value of 18.21 mg/g.

Keywords: Orange peels, biosorbent, kinetics, adsorption

1. Introduction

Contamination of water source with various toxic compounds has become one of the major environmental interests of many researchers around the world over the past decades [1]. Industrial wastewaters contain pollutants which are hazardous to living creatures and environment [8]. Unlike organic pollutants, heavy metals once introduced into the environment cannot be biodegraded [2]. Health metal contamination come from diverse industries such as metal plating facilities, batteries, as well as agricultural sources where fertilizers are intensively used [3]. Cr (VI) represents an environmental risk to the bodies of receiving water and damages to the health of living organisms, due to its mutagenic and cytogenetic effects widely reported [4, 5]. Different technologies have been used for decontamination of wastewater such as chemical precipitation, membrane filtration, biological processes and ion exchange [6]. However, these techniques exhibit disadvantages such as high reagent cost, energy requirements and sludge generation [7]. Of all treatment methods that have been developed, adsorption is the one most promising method for removing pollutants from aqueous solution [8]. It is well known that efficiency of adsorption depends on nature of both adsorbent and sorbate, hence, many studies have been reported about the use of some types of agricultural wastes employed as alternative biosorbents as fruit peels [9]. Among these biosorbents, orange peels are being considered for pollutant removal from wastewater due to its low cost and availability as residue of juice industry [10, 11]. In this work, orange peels biomass was used to prepare different biosorbents (OP, OPAC and OP-Chitosan) by physicochemical modifications in order to use them for removing Cr (VI) from aqueous solution. In addition, adsorption kinetics was studied to determine the kinetic model (pseudo first order, pseudo second order, Elovich and intraparticle diffusion) that best fits experimental data.

2. Materials and Methods

2.1. Preparation of orange peels biosorbent: Orange (*Citrus sinensis*) peels were collected from local fruit market. They were initially washed with distilled water and ethanol, several times. Then, this biomass was dried at 70°C during 24 hours. The dried biomass was ground and sieved using 0.355 mm mesh.

2.2. Activated carbon from orange peels (OPAC): The orange peels biomass was carbonized at heating rate of 7°C/min up to 420°C. Afterwards, 85 wt. % H_3PO_4 acid solution was added per gram of carbon and heated at 600 °C with a muffle. The neutralization of pH was carried out by adding distillated water and activated carbon was dried using a vacuum oven.

2.3. Coating with chitosan: This procedure was based on Babel & Kurniawan's research [12]. The chitosan was treated with acetic acid solution under stirring at 150 rpm in order to form a homogenous gel. Then, orange peels biomass was immersed into this gel (dose ratio of chitosan and OP= 1:5). The resulting material was washed, dried and neutralized with 0.5 % w/v NaOH solution. The chitosan gel beads (OP-Chitosan) were washed with abundant deionized water and dried.

2.4. Characterization of biosorbents

The orange peels biomass was characterized by ultimate analysis in order to determine its elemental composition according to the analytical methods listed in Table 1.

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

2.5. Adsorption kinetic study

The adsorption kinetics were determined through batch experiments at solution pH of 3 and biosorbent dosage of 2 g/L. In brief, stock solution of Cr (VI) was obtained by dissolving potassium dichromate in deionized water. The residual concentration of Cr (VI) ions in 5 mL aliquots was measured between 10-270 min by Shimdzu UV 1700, UV–visible spectrophotometer with 1,5-diphenylcarbazide in acidic medium [12]. The experimental data was fitted to kinetic models summarized in Table 2 in order to further understand the adsorption process of hexavalent chromium onto orange peels based biosorbents.

Table 2. Adsorption kinetic models

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

*Foo et al.[13] and Pérez et al.[14]

3. Results and Discussion

3.1. Characterization of biosorbents: The ultimate analysis for OP biosorbent is shown in Figure 1. It was found that carbon and hydrogen are the elements that are in greater proportion in OP biomass, with a percentage of 42.02 and 5.44 %, respectively.

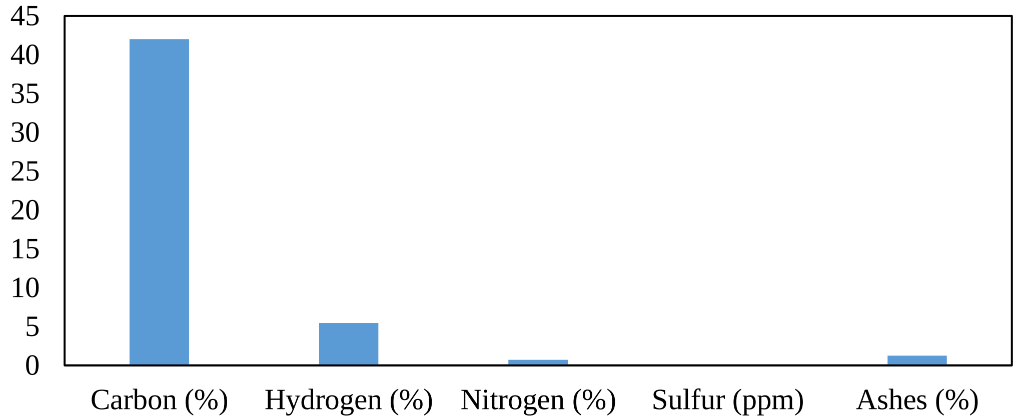

Figure 1. Elemental analysis of orange peels biosorbent

Other studies reported a carbon composition ranged in 40.24-43% for different biomaterials as summarized in Table 3. All these biomasses exhibit property to bind and concentrate heavy metals from even very dilute aqueous solutions [15]. Emilia eta al. [10] carried out ultimate analysis to orange peels biomass and found similar values to those obtained in this work. Pinzón & Cardona [16] stated that biomass with high carbon content has good performance for Cr (VI) uptake.

Table 3. Ultimate analysis for different biomaterials

Biomaterial	Elements (%)			Source
	Carbon	Hydrogen	Nitrogen	
Orange peels	43.00	5.9	0.9	[10]
Banana peels	40.24	6.14	1.3	[17]
Citrus peels	38.51	6.20	0.64	[17]
Pomegranate peels	43.13	7.17	0.66	[18]

3.2. Adsorption kinetics: The data obtained from kinetic study were analyzed in accordance with pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion kinetic models to find out the mechanism of adsorption. The corresponding kinetic parameters are listed in Table 4. Figure 2 represents the adsorption rate curves generated for Cr (VI) ions adsorption on OP, OPAC and OP-Chitosan biosorbents. It was observed a rapid uptake of metal ions within the first 50 min and then, the process continues slowly, which was expected due to due to a larger surface area of the adsorbent being available for the adsorption of the metals [19]. The repulsive forces between cations already set and the free ones in solution affect rate of adsorption overtime [18].

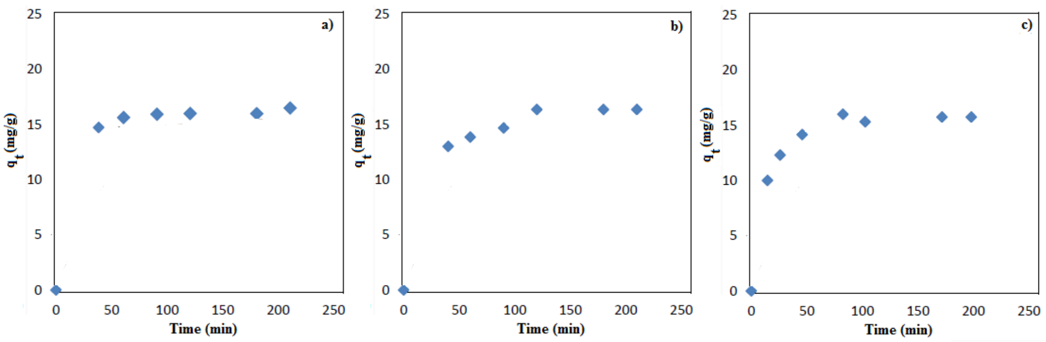

Figure 2. Kinetics study of Cr (VI) and: a) OP, b) OPAC and c) OP-Chitosan

The pseudo-first order model assumes that the rate of change in heavy metals ions adsorption over time is directly proportional to the difference in saturation concentration and the amount of adsorbent uptake over time [20]. The parameters of this model were calculated by plotting $\log(q_e - q_t)$ versus time(t). The $q_{e,1}$ values determined from the intercept are 18.21 mg/g, 16.14 mg/g and 2488.857 mmol/g for OP, OPAC, OP-Chitosan, respectively. The pseudo-second order model considers that adsorption of heavy metal ions onto biosorbent supports second order chemisorptions [21]. A linear plot of t/q_t vs. t was performed to obtain $q_{e,2}$ and k_2 values [22]. The activated carbon from orange peels biomass exhibited the highest value (17.27 mg/g) for $q_{e,2}$ parameter followed by OP-Chitosan and OP biosorbents. The Elovich equation is suitable to describe adsorption behavior that concurs with the nature of chemical adsorption [23]. In addition, the intraparticle diffusion model is used when the diffusion (internal surface and pore diffusion) of heavy metals ions inside the biosorbent is the rate-limiting step [9].

For orange peel biosorbent, the kinetic model enabled to properly describe the experimental data with square sum error (SSE) of 0.20 was pseudo-first order, which suggests that Cr (VI) ions can be adsorbed by two active sites of this biosorbent. For activated carbon from orange peels biomass, better fitting was obtained with pseudo-second order kinetic equation ($q_{e,2}$= 17.27 mg/g, k_2=0.00487 $\frac{\mathrm{g}}{\mathrm{mg\ min}}$ and SSE=0.59). For OP-Chitosan biosorbent, the correlation coefficient of 0.996 is very close to 1 indicating that the experimental data can be fitted very well by pseudo-second order model. Similar results were reported for Cr (VI) removal using orange peels, in which pseudo-second order appropriately describes adsorption kinetics [24].

Table 4. Parameters of main adsorption kinetic models for Cr (VI) uptake using OP and OP-$CaCl_2$ biosorbents.

Kinetic model	Parameter	OP	OPAC	OP-Chitosan
Pseudo-first order	$q_{e,1}\left(\frac{mg}{g}\right)$	18.21	16.14	2488.857^{+}
	$k_1(min^{-1})$	-0.05	0.037	0.051
	Correlation	0.20*	0.64*	0.804**
Pseudo-second order	$q_{e,2}\left(\frac{mg}{g}\right)$	16.66	17.27	17.241
	$k_2\left(\frac{g}{mg\ min}\right)$	0.02	0.00487	0.004
	Correlation	0.41*	0.59*	0.996**
Elovich equation	β	1.32	0.55	0.421
	α	1159.51	70.81	14.295
	Correlation	1.48*	1.41*	0.782**
Intraparticle diffusion	k	0.15	1.38	0.472
	Correlation	5.59*	58.44*	0.689**

* SSE; ** correlation coefficient (R^2); $^{+}$mmol/g

Conclusions

Adsorption technology has been widely applied for removing heavy metals ions from aqueous solution and kinetic study plays an important role on evaluating the performance of different adsorbents. From literature, orange peels are recognized as an agroindustrial residue with adsorptive properties and have been used in adsorption process. In this work, orange peels-based biosorbents were used to study kinetics of Cr (VI) adsorption. The ultimate analysis reported that carbon (42.02 %) is the element that is in greater proportion in orange peels biomass. Regarding batch experiments, pseudo-second order model fits adsorption data when OPAC and OP-Chitosan were used with parameter $q_{e,2}$ value of 17.27 and 17.24 mg/g, respectively. For OP biosorbent, better fitting was obtained using pseudo-first order with parameter ($q_{e,1}$) value of 18.21 mg/g. In addition, the biosorbents from orange peel biomass present a high adsorption rate within the first 50 minutes, suggesting that adsorption equilibrium is achieved at short contact times.

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