

Mass-Transfer Processes Of Toxic Hexavalent Chromium Adsorption Onto Food Waste Adsorbent

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Abstract. Heavy metal pollution caused by industrial operations is a global environmental issue. Chromium, used in chrome plating, textile dyeing, wood preservation, and metal finishing, is classified as a highly toxic agent to humans and other living organisms. To minimize health risks, these contaminant should be removed from the aquatic ecosystem. In the present study, a bioadsorbant was fabricated from vegetable waste biomass : potato peels (PP) was tested for the adsorption of toxic hexavalent chromium [Cr(VI)] from simulated wastewater. Due to the health effects associated to Cr(VI) toxicity, it is mandatory to treat chromium-bearing wastewaters before disposal in to the environment to avoid consequent health problems. The research of cheaper, locally available and renewable materials as precursors for producing activated carbon with comparable functionalities to the commercial product. The purpose of this study is to highlight vegetable waste and to examine the efficiency of potato peels towards the removal of hexavalent chromium from aqueous solution. The physicochemical and textural characterization of the prepared adsorbent was accomplished by using available techniques. The influence of the operating parameters were investigated in batch mode. Eight bottles were used during the batch experiments under the following operating conditions: Mass of PP and PAC: 0.25 g to 1.5 g, time: 0-60mn, pH: 2-12, initial concentration of Cr (VI): 10-30mg/l, Temperature: 30 to 60°C. Adsorption kinetics was assessed by fitting the experimental data with the chosen kinetic models. The ability of potato peels to adsorb Cr(VI) ion was determined from the adsorption isotherms plots and the thermodynamic parameters were estimated. Furthermore, a comparison of the results obtained is carried out with commercial powdered activated carbon (PAC). The best removal efficiencies are obtained at pH of order 2 and 12 for PAC and PP respectively, an optimal mass of PP at 0,5 g and 1 g of PAC at 300 rpm. The most appropriate model is Langmuir model and the kinetics are the pseudo second order. The adsorption reaction is a chemisorption according to Elovich's model and the diffusion is extraparticle by Webber and Morris model. The results obtained from this study suggest that the

adsorbent prepared from plant biomass could be an interesting low-cost adsorbent to remove chromium VI.

Keywords: Chromate VI, bioadsorbent, adsorption, kinetic, isotherms

1. Introduction

Trivalent chromium Cr(III) is essential in human as well as for plants and animals at trace concentrations, the hexavalent Cr(VI) has been considered more hazardous to public health due to its mutagenic and carcinogenic properties [1]. It is also moving readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin [2]. A wide range of physical and chemical processes is available for the removal of Cr(VI) from waste water, such as electrochemical precipitation, ultrafiltration, ...etc.[3-5]. Most of these methods suffer from high operational costs. Therefore, it is necessary to develop new treatment processes that are not only effective, but also feasible in terms of cost. Adsorption is one of the most economically favorable and a technically easy method [6].

In the present work, we prepared bioadsorbent from waste which is potato peels and used it to adsorb Cr (VI) ions in a batch system. The effects of the process parameters such as pH, temperature, mass adsorbent, contact time on the removal were investigated. In order to have better understanding of the adsorption process, some isotherm, kinetic and thermodynamic models were employed. A comparative study was carried out with a commercial powdered activated carbon (PAC).

2. Experimental procedure

2.1. Chemicals

Potassium dichromate ($K_2Cr_2O_7$), sodium hydroxide (NaOH, 0.1N), chloridric acid (HCl, 0.1 N), potassium nitrate (KNO_3), sulfuric acid (H_2SO_4), ethanol 98% and

1,5-Diphenylcarbazyde were Aldrich products. Commercial powdered activated carbon is provided by Prolabo.

The adsorbent (potato peels: PP) comes from the Oued Souf region. The peels were washed in tap water to remove impurities, followed by drying in the open air for 72 hours.

2.2. Characterization of the PP adsorbent

Infrared spectra was performed using Thermo Nicolet iS-10 IRTF Spectrometer, piloted by par Omnic 9 software. The surface morphology of the adsorbent was visualized with a scanning electron microscope (Quanta 650, Germany). The scanning electron microscopy (SEM) enabled us to direct observation of the changes in the surface microstructures of the adsorbent.

Water content: The water content was determined by weighing a known quantity of material, before and after drying at 105°C to constant mass. The water content (WC%) calculated according to the formula:

$$WC = \frac{m_1 - m_2}{m_1 - m_0} * 100$$

Where m_0 and m_1 are weights (g) of the wet and dried potato peels, respectively. This value reflects the hydrophilic character of the resin type.

2.3. Experimental protocol

Preparation of solutions: solution of chromium (VI) was prepared by dissolving 1.47g $K_2Cr_2O_7$ in 1L bi-distilled water. All batch experiments were carried out with adsorbent samples in 250 mL conical flasks with 100 mL Cr (VI) aqueous solutions on a rotary shaker (SIGMA 2-16P) at 200 rpm. The concentration of Cr(VI) ions was determined spectrophotometrically (Spectromètre UV/Visible Jenway 6300) at 540 nm using diphenylcarbazyde as the complexing agent.

Adsorption study:

The different parameters influencing the adsorption were studied according to the following conditions: pH: 2 to 12, contact time: 0-60 mn, adsorbents mass (PP and PAC): 0.25 to 1.5 g, initial concentration of chromium solution: 10, 20, 30 mg/L, Temperature: 30 to 60°C.

The adsorption data were treated according to Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{K_1 q_m} + \frac{C_e}{q_m}$$

Where q_e the adsorbed value of Cr (VI) ions at equilibrium concentration (mmol/g), q_{max} is the maximum adsorption capacity (mmol/g) and K_1 is the Langmuir binding constant which is related to the energy of adsorption (L/mmol), C_e is the equilibrium concentration of Cr (VI) in solution (mmol/L) [7, 8].

The Freundlich empirical relationship describes the multilayer adsorption of heterogeneous systems. It can be expressed logarithmically as :

$$\ln q_e = \ln K_f + \frac{1}{n_F} \ln C_e$$

Where, K_f and $1/n_F$ are Freundlich constants. The values of K_f and $1/n_F$, which roughly correspond to the adsorption capacity and the heterogeneity factor.

Kinetic of adsorption:

The models used for study of kinetic of adsorption are:

- a. Pseudo first order established by Lagrege

$$\log(q_e - q_t) = \log q - \frac{K_1 t}{2.303}$$

q_t : adsorbed quantity at time t in mg/g, q_0 : adsorbed quantity at equilibrium in mg/g.

- b. Pseudo second order

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{1}{q_e} t$$

- c. Intraparticle diffusion model established by Webber and Morris

$$q_t = K_{int} \cdot t^{1/2} + C$$

K_{int} : the intra-particle diffusion constant in (mg/g. min^{1/2}); C: represents the value of the thickness of the limit layer.

- d. Boyd Model

$$F = 1 - \frac{1}{\pi^2} \exp(-Q_t)$$

With $B_t = -0.4977 - \ln(1 - F)$

where $F = q / q_e$

- e. Elovich model

$$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$$

α is the initial adsorption rate in mg/g min and β is the desorption constant in g/mg

The thermodynamic parameters of adsorption reaction were obtained from the treatment of K_1 values at different temperature according to Van't Hoff equation [24]

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

where ΔH° and ΔS° are enthalpy and entropy changes, R is the universal gas constant and T is the absolute temperature (K). The Gibbs free energy of adsorption (ΔG°) at different temperatures was calculated using the following relation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S$$

3. Experimental procedure

3.1. Infrared Transform Fourier Spectrometer analysis (IRTF)

The IRTF spectrum of potato peel adsorbent is shown in Figure 1. The band spectrum of PP (Figure 1) had a vibrational band at 3400- 3200 cm^{-1} , corresponding to the -OH stretching band in hydroxyl groups indicating the presence of alcohols and phenols. The band at 2400-3200 cm^{-1} is due to the N-H stretching vibrations of the ammonium ion. The band located at 1615-1700 cm^{-1} corresponds to the elongation vibrations of the C-N group with C=O. The band at 1320-1242 cm^{-1} corresponds to the deformation vibration of the C-O-H aldehyde group of lignin, cellulose and hemicellulose. The band at 1220-1260 are due to the stretching vibrations of the C-O of the

ether and aromatic group. The band at 1100-1300 cm^{-1} corresponds to the C-O stretching vibrations of the ester group. The band at 1000-1100 cm^{-1} correspond to the C-O-C elongation vibrations of the cellulosic functions. These results agree with the data of the literature where it is reported that the potato herbaceous plant contains pectin, lignin, cellulose and hemicellulose.

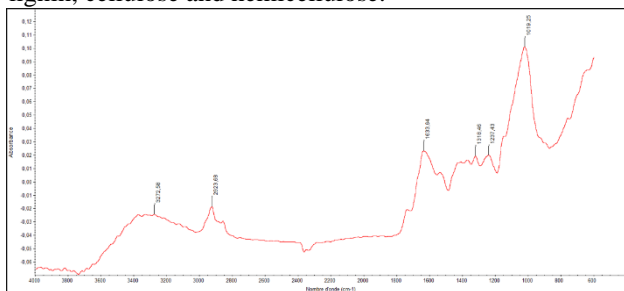


Figure 1. IRTF spectrum of potato peel adsorbent

3.2. Surface morphology

The SEM photomicrograph shows the presence of aggregates in elliptical form with swollen starch grains, which have different dimensions of 10 to 200 μm , between which there are voids.

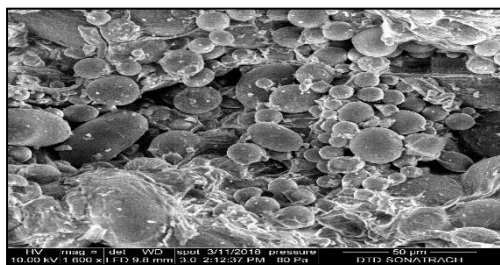


Figure 2. SEM photomicrography of PP adsorbent

3.3. Adsorption Study

Several parameters affecting the adsorption of chromium (VI) on PP and PAC have been studied, namely: the pH, the mass of the adsorbent, the temperature, the initial concentration of chromium and the equilibrium time.

In this study, two important isotherm models, the Freundlich and Langmuir models, were examined to identify the best fit model. The results are given in tables 1, 2 and 3.

Table 1. Constant values of Langmuir models for PAC adsorbent

Types	K_1 (l/mg)	q_{max} (mg/g)	R^2
Types I	1.8139	24.4259	0.9937
Types II	-1.2584	26.6801	0.9978
Types III	-1.7796	26.4270	0.9453
Types IV	1.6822	25.0941	0.9953
Types V	1.7937	25.5432	0.9937

Table 2. Constant values of Langmuir models for PP adsorbent

	K_1 (l/mg)	q_{max} (mg/g)	R^2
Type I	0.0027	13.7835	0.9827
Type II	0.0034	16.0179	0.9988
Type III	1.5723	14.9749	0.9766
Type IV	1.1419	15.6657	0.9893
Type V	1.8920	13.9545	0.9827

The results are presented in Figure 3, 4 and 5.

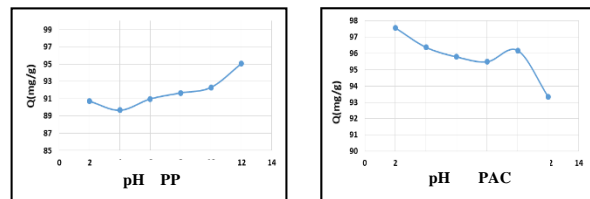


Figure 3. Influence of pH

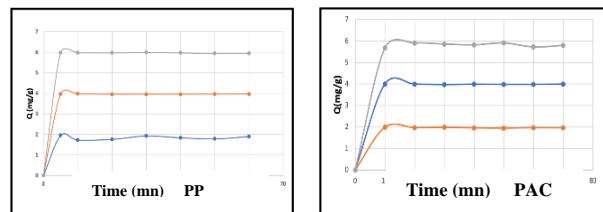


Figure 4. Influence of initial concentration of chromium ion

Table 3. Constant values of Freundlich model for PP and PAC adsorbents

Adsorbents	n	K_f (g/mg.min)	R^2
PAC	3.1557	12.8499	0.9094
PP	5.97	11.989	0.96

3.4. Discussion

The fixation of chromium VI on the PP and on the CAC is influenced by the variation of the pH, the adsorbent mass, the stripping speed. The best removal efficiencies are obtained at pH of order 12 for the PP respectively, an optimum mass of the PP at 0.5 g at a stirring speed of 300 rpm. The Langmuir model presents the best simulation of the experimental points. The pseudo second order model is better suited for modeling the kinetics with a coefficient of determination equal to 0.9993 and that the process of the adsorption reaction is a chemisorption according to the model. of Elovich. The Webber and Morris model shows that the diffusion is extra-particle and the Boyd model to confirm the Webber and Morris model.

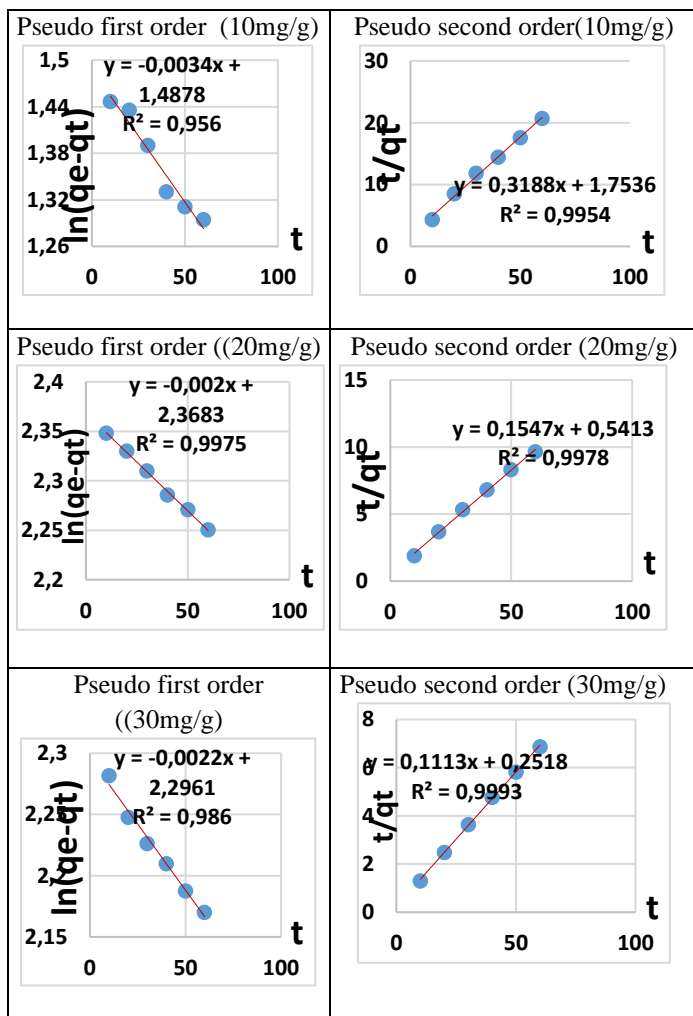


Figure 5 . Weber and Morris, Boyd models using PP adsorbent

4. Conclusion

Chromium VI adsorption on potato peels (PP) and commercial adsorbent (PAC) follows Langmuir isotherm with a coefficient of determination R^2 equal to 0.9988 and 0.9978 respectively. The kinetics showed that the quantity adsorbed increases with the increase in the concentration of chromium (VI). The pseudo second order model is better suited for modeling the kinetics with a coefficient of determination equal to 0.9993 and 0.9991 for the PP and the PAC respectively and that the process of adsorption reaction is chemisorption according to the Elovich model. The Weber and Morris model shows that the diffusion is extraparticle and the Boyd model confirms this. Therefore, it can be examined in more detail and considered as a cheaper alternative to commercial adsorbents. The nature of adsorption process is different for each adsorbent-adsorbate system: Cr(VI)-PP is exothermic and spontaneous; Cr(VI)-PAC is endothermic and spontaneous. The chromium molecules remain more ordered on the interface of the PP in the solution during the adsorption differ from the case of the PAC they remain less ordered. The results obtained suggest that potato peels could be an interesting low cost bioadsorbent to remove chromium VI from contaminated wastewater and could be used for field applications.

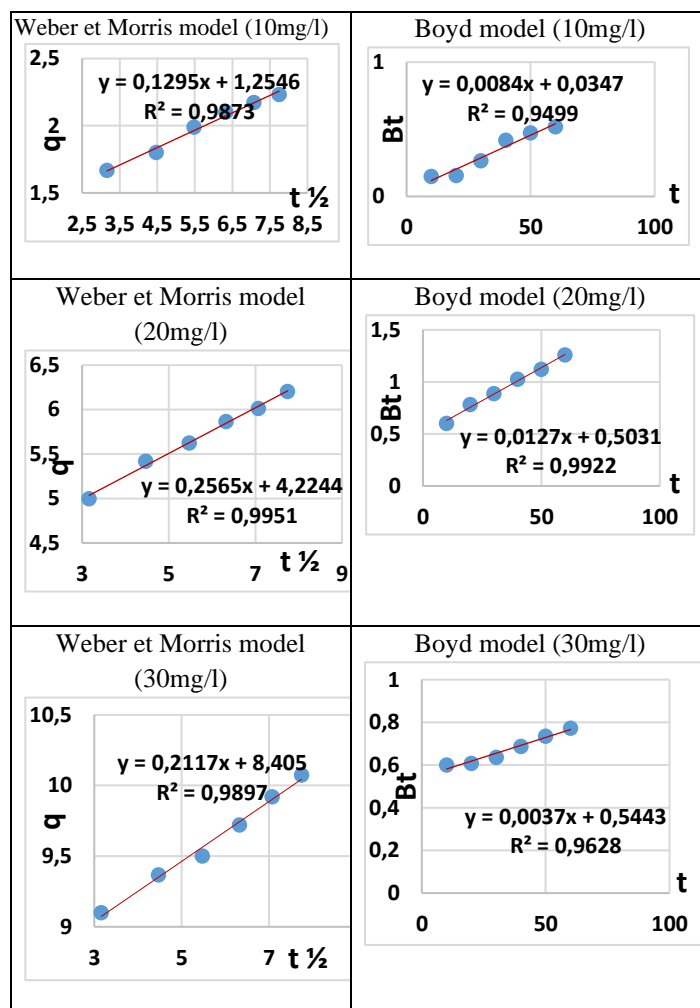


Figure 6 . Pseudo first and pseudo second order curves using PP adsorbent.

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