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Biosorption of chromium(VI) from industrial wastewater onto pistachio hull waste biomass

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ABSTRACT

Raw agricultural waste is an affordable adsorbent for the removal of industrial contaminants. In the present work, pistachio hull powder (PHP) was investigated for the removal of hexavalent chromium (Cr(VI)) from wastewater. The effects of pH (2–8), PHP concentration (0.5–8 g/L), Cr(VI) concentration (50–200 mg/L), temperature (5–50 °C) and contact time (1–60 min) were studied on the removal of Cr(VI) from aqueous solution. The results revealed that PHP adsorbs over 99% of chromium from solutions containing 50–200 mg/L of Cr(VI) at a pH of 2 and an adsorbent concentration of 5 g/L after 60 min of equilibration. The percent chromium adsorbed from solution increased with an increase in temperature from 5 to 40 °C. Kinetic and isotherm modeling studies demonstrated that the experimental data best fit a pseudo-second order and Langmuir model, respectively. The maximum Langmuir adsorption capacity was 116.3 mg/g. In the second part of the study, the efficacy of PHP was examined by analyzing the removal of Cr(VI) from industrial wastewater. Results revealed that 2 g/L of PHP decreased the Cr(VI) concentration from 25 mg/L to less than 0.05 mg/L after 30 min of equilibration. In summary, biosorption onto PHP is an affordable and simple process for treating Cr(VI)-laden industrial wastewaters.

1. Introduction

Heavy metals are toxic compounds that may be generated during manufacturing and processing applications and are often released into the environment through waste effluent. Eliminating toxic metals from contaminated effluent is one of the most important and challenging aspects of pollution control due to the health and economic burdens caused by heavy metal contamination. Hexavalent chromium (Cr(VI)) is widely used in manufacturing and processing plants; Cr(VI) is present in high concentrations in the industrial wastewater of leather tanneries, petroleum refineries and electroplating and metal finishing plants as well as dye production, wood preservation and pulp production facilities [1]. Cr(VI) is included in the CERCLA priority list of hazardous substances because it is toxic to human and environmental health [2]. As established by the US EPA, the concentration of Cr(VI) in wastewater must be less than 0.05 mg/L before the effluent can be discharged into surface waters [3].

Several techniques including adsorption, chemical and electrochemical precipitation, ion exchange, membrane filtration and electrodialysis are available for the removal of heavy metals from wastewaters [4]. The most common method used for removal of Cr(VI) is reduction-precipitation [5,6]. To be conducted on an industrial scale, this removal process requires large amounts of chemicals, a large area of land, a sludge dewatering facility and skilled operators. Furthermore, reduction-precipitation is expensive and does not completely remove Cr(VI) [6]. Thus, this methodology is a technically and economically inefficient technique for the removal of Cr(VI).

An extensively investigated alternative for eliminating contaminants from water and wastewaters is adsorption onto solid adsorbents [7]. Adsorption onto activated carbon is a common technique for the treatment of liquid waste, but it is prohibitively expensive [8,9]. To exploit the high efficacy and simplicity of adsorption for water and wastewater treatment, further research on low- or no-cost adsorbents is necessary. In recent years, materials of biological origin, including agricultural wastes, have been used as adsorbents [e.g., 10]. Adsorption onto raw agricultural waste is a low-cost treatment technique for the removal of contaminants, including heavy metals, from water and wastewater.

The removal of Cr(VI) by adsorption onto raw agricultural waste materials is a relatively rare technique. Adsorption methods found in the literature are summarized in Table 1. Most of the studied adsorbents possess a low capacity for the removal of Cr(VI) and/or consist of a scarce adsorbent, which restricts large scale applications. Thus, further research is necessary to identify widely available and effective agricultural wastes for the adsorption of toxic metals.

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Nomenclature

C_0	initial Cr(VI) concentrations (mg/L)
C_t	Cr(VI) concentrations at a time t (mg/L)
C_e	Cr(VI) concentrations at equilibrium (mg/L)
E	adsorption free energy (kJ/mol)
k_{id}	rate constant for intraparticle diffusion (mg/g min$^{0.5}$)
k_1	pseudo-first order rate constant (min^{-1})
k_2	pseudo-second order rate constant (mg/g min)
K_{DR}	D–R constant (mol^2/kJ^2)
k_L	Langmuir constant (L/mg)
K_F	Freundlich adsorbent capacity (mg/g(L/mg)$^{1/n}$)
M	mass of PHP (g)
n	the reciprocal of the reaction order
q_t	adsorption capacity at time t (mg/g)
q_e	adsorption capacity at equilibrium (mg$_{\mathrm{Cr(VI)}}$/g$_{\mathrm{PHP}}$)
$q_{\max}$	maximum adsorption capacity (mg/g)
R	gas constant (8.314 J/mol K)
T	absolute temperature (K)
V	volume of the Cr(VI) solution (L)
ε	Polanyi potential (J/mol)

An agricultural waste that is widely accessible in Iran is the pistachio hull. Approximately 250 thousand metric tons of green pistachio hulls are generated annually in Iran. Thus, an abundant source of material is available at no-cost. Furthermore, the use of agricultural wastes as adsorbents is an environmentally-friendly technique that can help to reduce waste. Therefore, the purpose of this work was to explore the use of pistachio hull waste in the biosorption of Cr(VI) from industrial wastewater. Initially, the adsorption of Cr(VI) by pistachio hull powder (PHP) was investigated under various experimental conditions, where the solution pH, adsorbent concentration, contact time, chromium concentration and solution temperature were varied. The kinetics, thermodynamics and isotherms of Cr(VI) adsorption onto PHP were also evaluated. Subsequently, the efficiency of PHP was investigated in the removal of Cr(VI) from industrial wastewater under optimized conditions. To the best of our knowledge, the removal of heavy metals from industrial wastewaters by PHP adsorption has not been previously demonstrated. The results of this study indicate that PHP is an efficient, readily available and low-cost adsorbent for the removal of chromium from wastewater.

2. Materials and methods

2.1. Adsorbent preparation and characterization

To prepare PHP, green pistachio hull waste was obtained from a local farm in Kerman, Iran, the location of the major pistachio harvest in the region. Hull waste was air-dried for 3 days and subsequently crushed, powdered and sieved (mesh 200). PHP was stored in a glass bottle and used for experiments as needed.

2.2. Adsorption experiments

The adsorption experiments in this work were divided into two parts. The first part of the study was aimed at investigating the effect of experimental conditions on Cr(VI) adsorption and determining the conditions that achieve the maximum amount of chromium removal. Isotherm and kinetic evaluations were also conducted in this portion of the study. The adsorption tests were conducted in 200 mL flasks with 100 mL of Cr(VI) solution prepared from the dilution of 1 g/L stock solutions. In the tests, 100 mL of a known Cr(VI) solution was poured into each flask, the pH was adjusted and a given mass of PHP was added to the solution. The resultant suspension was paddle-stirred at 100 rpm for a specified amount of time. Upon completion, a sample of the suspension was removed from the flask and filtered through a fiberglass filter (0.2 μm pore size) to remove adsorbent particles. The filtrate was analyzed for residual Cr(VI). The pH of each solution was adjusted to a predetermined value with 0.1 N HCl and NaOH. The effects of pH (2–8), adsorbent concentration (0.5–5 g/L), Cr(VI) concentration (50–200 mg/L) and temperature (5–50 °C) on Cr(VI) adsorption were studied. All experiments were performed in duplicate and average results are reported.

The second part of the study examined the applicability of PHP for the removal of Cr(VI) from industrial wastewater. To this end, wastewater from a chromium electroplating plant was obtained and the concentration of Cr(VI) and the pH of the wastewater were determined. Cr(VI) was removed from 1 L of wastewater at an optimum pH (determined from phase 1 of the study) by adsorption

Table 1
Raw waste materials for the removal of Cr(VI) from aqueous solution.

Adsorbent	pH	Adsorption rate order (degree)	Fitted isotherm model	Adsorption capacity (mg/g)	Reference
Pistachio hull waste	2	2	Langmuir	116.3	Present study
Banana peel	2	1	Langmuir	60.3–131.6	[5]
Saw dust	3	2	Langmuir	20.7	[5]
Neem bark	2	2	Langmuir	19.6	[5]
Walnut hull	1	1	Langmuir	98.1	[11]
Sunflower head	2	2	Langmuir	8.2	[12]
Ocimum americanum L. seed pods	1.5	2	Langmuir	83.3	[13]
Coconut coir	2	NA	Redlich–Peterson	6.3	[14]
Palm flower	7	2	All models	4.9	[15]
Cystoseira indica	3	NA	Dubinin-Radushkevich	17.8–22.7	[16]
Rice straw	2	NA	Langmuir	3.2	[17]
Acorn of *Quercus ithaburensis*	2	2	Langmuir and Freundlich	31.5	[18]
Tamarindus indica seed	4	1	Freundlich	98.1	[19]
Ground nut shell	4	1	Langmuir	5.9	[19]
Walnut shell	4	1	Freundlich	2.3	[19]
Almond shell	2	1	Freundlich	22.1	[19]
Rice bran	1.5–2.0	2	Freundlich	0.15	[20]
Rice husks	3	NA	Freundlich	0.6	[21]
Saw dust	3	NA	Freundlich	1.5	[21]
Coir pith	3	NA	Freundlich	0.2	[21]
Beech sawdust	1	NA	Langmuir and Freundlich	16.1	[22]

NA: not available.

onto varying amounts of PHP (1–2 g/L). The aforementioned experiments were conducted in jar test instrument.

2.3. Kinetic and isotherm experiments

Kinetic experiments were performed using flasks containing 100 mL of Cr(VI) solution at concentrations of 50, 100 and 200 mg/L. The procedure used in kinetic tests was similar to those conducted in the first part of the study. In each test, 100 mL of Cr(VI) solution with the desired concentration was added to each flask and the pH was adjusted to 2 and the salt content was adjusted to 20 g/L. After the adjustments, 0.5 g of PHP was added and the resultant suspension was stirred at 100 rpm for 1–70 min at 25 ± 3 °C. Upon completion, the suspension was filtered, and the filtrate was analyzed for residual Cr(VI). The results were analyzed for fitness with pseudo-first and -second order models [1] to determine the order and rate constant of Cr(VI) biosorption onto PHP.

To evaluate the isotherms of Cr(VI) adsorption onto PHP, a series of experiments were conducted. To this end, 100 mL of a solution containing 50 to 500 mg/L of Cr(VI) with a pH of 2 was poured into seven vessels. Thereafter, 0.25 g of PHP was added to each flask. The flasks were subsequently stirred at a controlled temperature (25 ± 3 °C) for 6 h at 100 rpm to achieve equilibrium. Upon completion, the suspensions were filtered and the filtrates were analyzed for residual Cr(VI). Several isotherm models were evaluated for fitness with experimental data.

2.4. Analytical methods

The surface morphology, specific surface area, pore volume and size, pH of zero point charge (pHzpc) and surface functional groups of PHP were characterized. The morphology of the surface of PHP was observed with a scanning electron microscope (SEM, Philips-XL30) equipped with energy dispersive X-ray microanalysis (EDX), and the specific surface area and total pore volume of PHP were measured using a nitrogen adsorption technique (Micromeretics/Gemini-2372). The pHzpc of PHP was determined by the procedure described by Moussavi and Mahmoudi [7]. The functional groups on the surface of PHP were analyzed using Fourier transform infrared (FTIR) spectroscopy at a wave number between 400 and 4000 cm^{-1}. The oxidation state of chromium adsorbed onto PHP particles at an optimum pH was examined using X-ray photoelectron spectroscopy (XPS) (Nicolet spectrometer).

The concentration of Cr(VI) was determined colorimetrically according to the standard method of APHA [23]. The procedure was based on measuring the color of the solution after reaction with 1,5-diphenylcarbazide under acidic conditions. Based on the measurements, the adsorption efficiency and equilibrium adsorption capacity, q_e ($\mathrm{mg}_{\mathrm{Cr(VI)}}/\mathrm{g}_{\mathrm{PHP}}$), were calculated according to Eqs. (1) and (2).

$$\mathrm{Cr(VI)\ \ removal\ \ (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{V(C_0 - C_e)}{M} \tag{2}$$

3. Results and discussion

3.1. Characteristics of PHP before and after biosorption

Analysis indicated that PHP particles had a BET multipoint surface area of 1.04 m^2/g and a total pore volume at $0.9925P/P_0$ of 0.0002 cm^3/g. According to the calculations, the average size of pores was 0.77 nm, indicating that PHP was a microporous adsorbent. The surface structures of the original and Cr-loaded PHP particles imaged at various magnifications are depicted in Fig. 1. As shown in Fig. 1a and b, the original adsorbent was a porous material with a smooth surface. Fig. 1c depicts PHP after adsorption, indicating that chromium molecules adsorbed evenly on the surface of PHP. EDX analysis of adsorbent before and after Cr(VI) adsorption (data not shown) confirmed this observation. The presence of chromium on PHP (~83 wt%) proved that the chromium removed from solution had been adsorbed onto PHP.

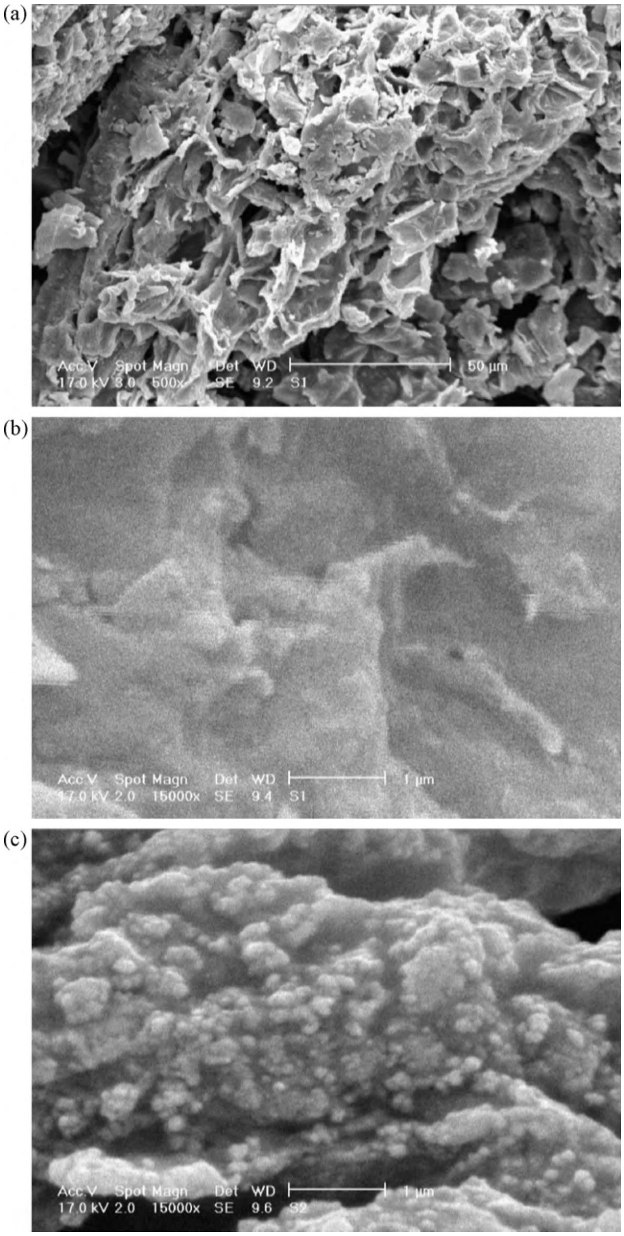

Fig. 1. SEM images of PHP (a, b) before and (c) after Cr(VI) biosorption.

The functional groups present on the surface of fresh adsorbent, as well as the changes in vibrational frequency of functional groups, were investigated by examining FTIR spectra of fresh and adsorbed PHP. The FTIR spectra are shown in Fig. 2 and demonstrate the presence of various functional groups on the surface of PHP (Fig. 2a). As seen in Fig. 2a, the peaks at 3400, 2925, 1607 and 1072 cm^{-1} were assigned to the stretching vibrations of –OH, –CH, C=O, and –CO groups, respectively [24]. The additional peak at 608 cm^{-1} corresponded to bending modes of aromatic compounds [24]. The FTIR results indicated that PHP contains complex functional groups that are capable of participating in the adsorption of chromium ions. The predominant group involved in the adsorption of metal ions depends on the pH of the solution, which affects the surface chemistry of the adsorbent; this will be discussed in the following section.

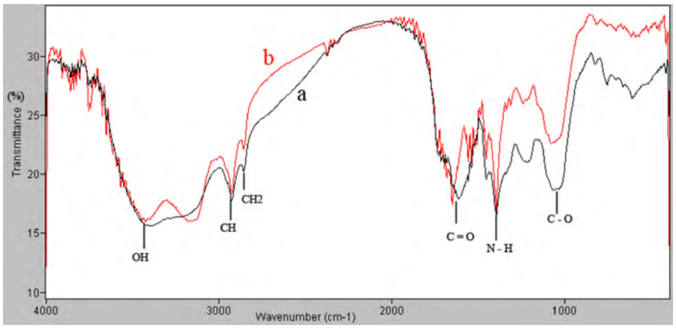

Fig. 2. FTIR spectra of (a) fresh and (b) Cr(VI)-loaded PHP.

3.2. Effect of pH and mechanism of Cr(VI) biosorption

Fig. 3 shows the removal of Cr(VI) versus the pH at a constant Cr(VI) concentration of 50 mg/L, a PHP concentration of 2.5 g/L and a contact time of 60 min. The results displayed in Fig. 3 demonstrate that Cr(VI) biosorption onto PHP is a pH-dependent process. The average Cr(VI) removal under the selected conditions decreased from 99.6 to 52% when the pH of solution increased from 2 to 8. Maximum biosorption of Cr(VI) was attained at pH 2 in accordance with previous reports (Table 1). Because wastewater generated in chromium-plating plants is typically acidic, attaining maximum Cr(VI) adsorption at a low pH is advantageous because the pH of wastewater does not need to be adjusted for efficient adsorption. Furthermore, the final pH of the solution at the end of each experiment was similar to the initial value (Fig. 3). Control of the pH at an optimal value is critical to attaining maximum performance. However, the results indicate that the adjustment of pH during adsorption onto PHP is unnecessary, which reduces the overall cost of treatment.

The pH-dependency of Cr(VI) removal by PHP is a direct result of the dominant form of chromium present at different pHs and by the pHzpc of PHP. According to the solubility equilibrium of chromium [1], $HCrO_4^-$ is the dominant species of Cr(VI) at a pH between 2 and 3. As the pH increases, the dominant form of chromium becomes CrO_4^{2-}. Furthermore, the surface of PHP particles is positively charged at a pH below 4.9 (pHzpc). Therefore, at a pH below the pHzpc of PHP, Cr(VI) is likely adsorbed onto PHP through electrostatic attraction and/or by the binding of $HCrO_4^-$ to acidic functional groups on the surface [5,11,25]. As the pH of the solution decreases below 4.9 (pHzpc), the number of protons available on the surface of the adsorbate increases, which increases the attraction between $HCrO_4^-$ and PHP and causes the percent adsorption to increase. As the pH of the solution increases past the pHzpc, charges on the surface of PHP become negative; this leads to repulsion forces between chromium ions and PHP and inhibits adsorption, reducing the percent of chromium removed from solution. To determine the functional groups involved in Cr(VI) biosorption, the FTIR spectrum of Cr(VI)-loaded PHP was obtained (Fig. 2b). A comparison of spectrum *a* and *b* in Fig. 2 illustrates the changes in the vibrational frequency of functional groups present on PHP upon adsorption of Cr(VI) from a solution with a pH of 2. Most of the changes in vibrational frequency occurred in bands between 3350–3450, 2890–2960, and 600–1700 cm^{-1}, which correspond to –OH, –CH, C=O, C–O, and N–H functional groups, suggesting that –OH, –CH, C=O, C–O, and N–H groups were the most active groups involved in biosorption. Thus, the reduction in bands at 3400 and 2925 cm^{-1} indicate that the dominant complexation mechanism [24] consists of electrostatic attraction between protons of symmetric and asymmetric C–H and O–H functional groups on the surface [9] of PHP with anionic chromium in solution. Thus, FTIR results confirm the aforementioned mechanism of Cr(VI) biosorption onto PHP.

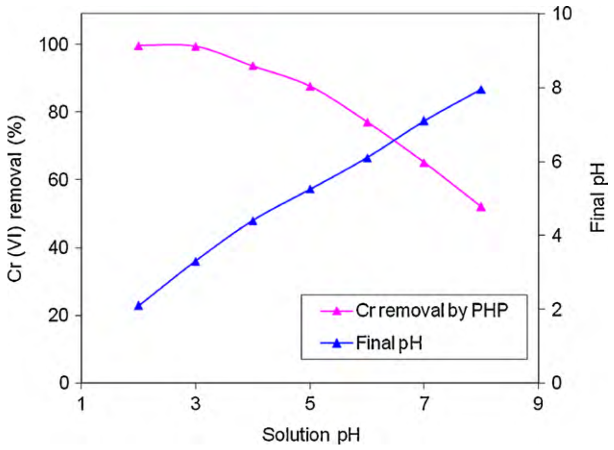

Fig. 3. Effect of solution pH on Cr(VI) removal by adsorption onto PHP (conditions: Cr(VI) = 50 mg/L; PHP concentration = 2.5 g/L; stirring speed and time = 100 rpm and 60 min; NaCl concentration = 20 g/L; temperature = 25 ± 3 °C).

To determine the oxidation state of Cr(VI) adsorbed onto PHP, chromium-loaded PHP was analyzed by XPS. The XPS spectrum of PHP after chromium adsorption from a solution with a pH of 2 displayed a sharp peak at a binding energy of 578.5 eV. The binding energies of Cr(III) and Cr(VI) are approximately 577 and 578.5 eV, respectively [26]; thus, Cr(VI) is the dominant oxidation state of chromium adsorbed onto PHP particles. Chromium adsorbed on the surface of PHP does not become reduced, reconfirming that chromium removed from solution was adsorbed onto PHP particles as Cr(VI) through a mechanism based on electrostatic interactions. In contrast, Park et al. [27] found that banana skins completely reduced Cr(VI) to Cr(III). This discrepancy may be due to the difference in the nature of the adsorbent, as well as the selected experimental conditions.

3.3. Effect of PHP dose

The effect of PHP concentration, ranging from 0.5 to 8 g/L, on the removal of different concentrations of Cr(VI) was evaluated at a pH of 2 and a contact time of 60 min. Fig. 4 displays the average Cr(VI) removal versus PHP dose at concentrations between 50 and 200 mg/L, indicating an increase in the removal of Cr(VI) with an increase in adsorbent concentration until a maximum value is obtained. Improved adsorption with an increase in PHP for each concentration of Cr(VI) is related to an increase in the ratio of adsorbent to adsorbate, which increase the surface area and the number of sites available for adsorption [8]. This result is in accordance with other studies [e.g., 11,24,28,29], where an increase in Cr(VI) adsorption was observed with an increase in the concentration of adsorbent.

As shown in Fig. 4, the concentration of PHP at which 99% of 50, 100, 150 and 200 mg/L of Cr(VI) was removed under the experimental conditions was 1, 2.5, 4 and 5 g/L, respectively. Therefore, the optimal concentration of PHP depends directly on the concentration of chromium in solution; a higher Cr(VI) concentration requires a greater dose of PHP. Rao et al. [28] observed a chromium removal of 85% from a solution containing 100 mg/L of Cr(VI) after 90 min of contact time with 4 g/L of bagasse. Bhattacharya et al. [29], observed a chromium removal of 80.7 and 84.3% using 5 g/L of sawdust and

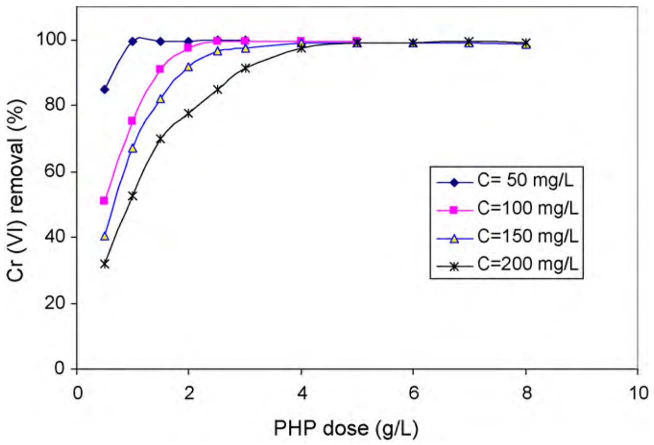

Fig. 4. Cr(VI) removal as a function of adsorbent concentration (conditions: Cr(VI) = 50–200 mg/L; pH 2; stirring speed and time = 100 rpm and 60 min; NaCl concentration = 20 g/L; temperature = 25 ± 3 °C).

10 g/L neem bark, respectively, from a 50 mg/L solution after 4 h of contact time. Bonsal et al. [24] reported 76.5% Cr(VI) removal from a 100 mg/L solution with 20 g/L of formaldehyde-treated rice husk. In this study, PHP possessed a higher adsorption capacity compared to most of the tested agricultural wastes, indicating that PHP is a promising low-cost adsorbent for Cr(VI) removal.

3.4. *Effect of Cr(VI) concentration and contact time*

The percent biosorption of 50, 100 and 200 mg/L of Cr(VI) from aqueous solution (containing 20 g NaCl/L) onto PHP versus contact time at a pH of 2 and an adsorbent (1–70 min) was investigated. The pH was adjusted to 2 and the concentration of PHP was adjusted to 5 g/L. Fig. 5 shows the average Cr(VI) removal obtained from duplicate experiments and reveals an increase in percent adsorption with an increase in contact time at each concentration. The equilibrium adsorption times of Cr(VI) at concentrations of 50, 100 and 200 mg/L under optimal conditions were 2, 40 and 70 min, respectively, with corresponding removals of approximately 100, 99.6 and 99%. The high removal rates indicate a high affinity of PHP for Cr(VI) molecules.

As shown in Fig. 5, before establishing equilibrium at each concentration, the removal efficiency at each contact time decreased with an increase in initial concentration of chromium with a constant concentration of adsorbent. Considering the identical adsorbent concentration used in the experiments, a decrease in Cr(VI) removal with an increase in initial concentration was attributed to limited adsorption sites [8,12] and a decrease in intraparticle diffusion. Thus, the removal of Cr(VI) by adsorption onto PHP depends on the initial chromium concentration and contact time.

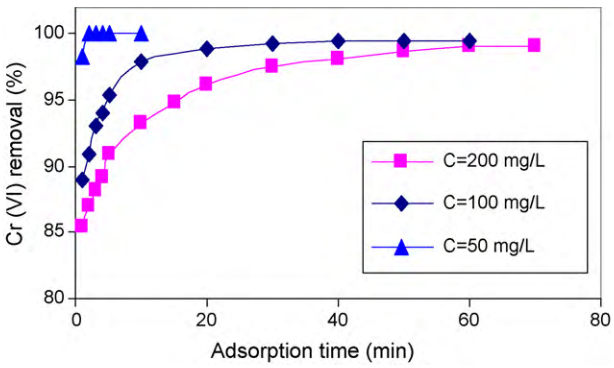

Fig. 5. Cr(VI) removal as a function of initial Cr(VI) concentration and contact time (conditions: Cr(VI) = 50–200 mg/L; pH 2; PHP dose = 5 g/L; stirring speed = 100 rpm; contact time = 1–70 min; NaCl concentration = 20 g/L; temperature = 25 ± 3 °C).

In contrast, the adsorption capacity of Cr(VI) increased with an increase in initial ion concentration and contact time. For each equilibrium time, adsorption capacities reached 10.5, 21.1 and 39.6 mg/g, respectively. An increase in adsorption capacity may be due to improved collisions between Cr(VI) molecules and PHP particles, as well as the increased concentration gradient and rate of mass transfer [8,30]. Overall, these forces lead to the enhancement of Cr(VI) uptake by PHP particles.

3.5. *Effect of solution temperature*

The effect of temperature (5–50 °C) was evaluated on the adsorption of 100 mg/L of Cr(VI) onto 2.5 g/L of PHP at a pH of 2 and contact time of 20 min. The experimental results indicated that the percent adsorption increased from 95.7 to 100% with an increase in temperature from 5 to 40 °C, illustrating that Cr(VI) adsorption onto PHP is an endothermic process. The increase in adsorption efficiency with an increase in temperature may be due to the development of new adsorption sites on adsorbent particles or to the increased kinetic energy of the $Cr_2O_7^{2-}$ ion, which is the dominant form of chromium under acidic conditions [1]. Other researchers [e.g., 1,31] also observed a similar temperature effect for adsorption of Cr(VI). While temperature had the same effect in previous studies, the magnitude of temperature-dependence was different, which may be due to differences in experimental conditions and nature of the adsorbent.

3.6. *Thermodynamics of Cr(VI) biosorption*

Thermodynamic analysis provides valuable information on the mechanism of adsorption. The thermodynamics of Cr(VI) adsorption onto PHP were studied using the free energy change, ΔG°, according to Eq. (3):

$$\Delta G^\circ = RT \ln k_L \tag{3}$$

The calculated values of ΔG ranged from 4 to 9 kJ/mol for temperatures of 5–50 °C. Positive values of ΔG imply that Cr(VI) adsorption by PHP is an endothermic process [32] at all temperatures. Values of ΔG were between 4 and 9 kJ/mol, indicating that a chemical sorption process occurred under the experimental conditions [33]. Thus, the results of thermodynamic evaluation demonstrate that adsorption is endothermic and that chemisorption is the dominant mechanism of Cr(VI) adsorption onto PHP.

3.7. *Kinetic modeling*

Kinetic information is required for modeling and the design of adsorption processes [34]. The fitness of experimental data to pseudo-first order and pseudo-second order models was tested. The kinetic information obtained from the models is summarized in Table 2. The pseudo-second order model had a higher correlation ($R^2 > 0.99$) with experimental data for moderate (100 mg/L) and high (200 mg/L) concentrations of Cr(VI). As indicated in Fig. 5, the adsorption rate for 50 mg/L of Cr(VI) was complete within only 2 min, making it impossible to calculate the data needed for kinetic evaluation. The fitness of experimental data to a pseudo-second order model implies that adsorption is likely controlled by chemisorption [1], including the sharing or exchanging of electrons between metal ion and adsorbent. Moreover, the results demonstrated that the concentration of metal ions and PHP both influence the adsorption of Cr(VI). A review of the available literature on the adsorption of Cr(VI) onto waste materials (Table 1) revealed that

Table 2
Results of Cr(VI) biosorption kinetic modeling.

Model	Pseudo-first order equation		Pseudo-second order equation		Weber and Morris's model	
Equation	$\ln(q_e - q_t) = \ln q_e - k_1 t$		$t/q_t = (1/k_2 q_e^2) + t/q_e$		$q_t = k_{id} t^{0.5} + C$	
Plot	$\ln(q_e - q_t)$ vs. t		(t/q_t) vs. t		q_t vs. $t^{0.5}$	
Concentration	100	200	100	200	100	200
Fitted model	$\ln(q_e - q_t) = 0.309 - 0.055t$	$\ln(q_e - q_t) = 1.514 - 0.044t$	$t/q_t = 0.028 + 0.046t$	$t/q_t = 0.017 + 0.025t$	$q_t = 0.29t^{0.5} + 19.16$	$q_t = 0.74t^{0.5} + 34.36$
R^2	0.865	0.903	0.9985	0.9986	0.975	0.943
Constant	$k_1 = -0.055\ \text{min}^{-1}$	$k_1 = -0.044\ \text{min}^{-1}$	$k_2 = 0.076$ mg/(g min)	$k_2 = 0.036$ mg/(g min)	$k_{id} = 0.29$	$k_{id} = 0.74$
Calculated q_e, $(q_{e,cal})$	1.36 mg/g	4.55 mg/g	21.7 mg/g	40.3 mg/g	–	–
Experimental q_e, $(q_{e,exp})$	21.1 mg/g	40 mg/g	21.1 mg/g	40 mg/g	–	–
Δq	54.10%	25.40%	4.60%	3.80%	–	–

most researchers also reported that pseudo-second order models best fit experimental data.

As shown in Table 2, the pseudo-second order rate constant (k_2) of adsorption for 100 mg/L of Cr(VI) was more than two times the adsorption of a solution of 200 mg/L of Cr(VI) under similar experimental conditions. This result confirms that a rate enhancement due to mass transfer occurs with an increase in the concentration gradient [34]. Furthermore, the experimental adsorption capacity is close to the calculated capacity for both concentrations of Cr(VI). This result validates the pseudo-second order model for the adsorption of chromium onto PHP. The pseudo-second order model was further evaluated by determining the standard deviation between experimental and calculated adsorption capacities, which are included in Table 2. The values of Δq in Table 2 are very low for the pseudo-second order model compared to the pseudo-first order model, confirming the superior fitness of the pseudo-second order model with experimental results.

As shown in Table 2, the experimental data were fitted to Weber and Morris's model to evaluate whether intraparticle diffusion controlled the rate of Cr(VI) adsorption onto PHP. High values of R^2 were obtained for both concentrations of Cr(VI) (100 and 200 mg/L), suggesting that intraparticle diffusion was involved in the adsorption of chromium ions by PHP under the experimental conditions. However, the regression lines did not pass through the origin of the plot and a positive intercept was observed at both concentrations, indicating that another process was also involved in adsorption [34] of Cr(VI) onto PHP. Considering the concentration of Cr(VI) in solution, mass transfer of ions from boundary layer to adsorbate was not likely limiting the rate of adsorption. Therefore, both intraparticle diffusion and chemical sorption were assumed to control the adsorption of Cr(VI) onto PHP particles under the experimental conditions. The low slope of the plots (Table 2) indicated that adsorption approaches equilibrium in 60 min, illustrating a high rate of Cr(VI) adsorption onto PHP. The rate constants for intraparticle diffusion, k_{id}, obtained from the plots [29] are included in Table 2. The k_{id} increased with an increase in Cr(VI) concentration, which validated the observed reduction in the pseudo-second order constant and the increase in the rate of adsorption as a function of ion concentration. Moreover, the value of the constant C (intercept) was higher for a chromium concentration of 200 mg/L than 100 mg/L (Table 2), indicating that chemisorption effects were more significant at higher ion concentrations.

3.8. *Isotherm modeling*

To gain more insight on the adsorption of Cr(VI) onto PHP, the results of equilibrium experiments were evaluated with the models of Langmuir, Freundlich, and Dubinin–Radushkevich. The information obtained from isotherm modeling is summarized in Table 3. The results revealed that the R^2 of the Langmuir isotherm was greater than the other models, indicating that the Langmuir isotherm better represented the adsorption of Cr(VI) onto PHP. This result suggested that the adsorption of metal ions occurred on a monolayer of the PHP surface. Conformity of the experimental data to the Langmuir model is in agreement with most previously published experiments (Table 1). The maximum adsorption capacity of Cr(VI) onto PHP, obtained from the fitted Langmuir model, was 116.3 mg/g (Table 3), which is greater than most of the raw agricultural wastes reported for adsorption of chromium (Table 1). Although Memon et al. [5] reported a comparable adsorption capacity for banana peels, pistachio hulls are a superior adsorbent for industrial applications due to its availability in high quantities, as well as its accessibility in no-cost stacked bulks. In contrast, banana peels are typically generated when the banana is consumed and is a by-product that is consumer-dependent. Thus, the dispersion and lack of access to bulk sources of banana peels makes them an

Table 3
Results of Cr(VI) biosorption isotherm modeling.

Isotherm	Unit	Information
Langmuir model		$C_e/q_e = 1/k_L q_{\max} + C_e/q_{\max}$
Plot	–	(C_e/q_e) vs. C_e
Fitted model	–	$C_e/q_e = 0.1142 + 0.0086C_e$
$q_{\max}$	mg/g	116.3
k_L	L/mg	0.075
R^2	–	0.996
$R_L = 1/1 + k_L C_i$		
Freundlich model		$\ln q_e = \ln K_F + 1/n \ln C_e$
Plot	–	$\ln q_e$ vs. $\ln C_e$
Fitted model	–	$\ln q_e = 3.444 + 0.2557 \ln C_e$
K_F		31.3
n	$(\text{mg/g}(\text{L/mg})^{1/n})$	3.91
R^2	–	0.8522
Dubinin–Radushkevich model		$\ln q_e = \ln q_m - K_{DR}\varepsilon^2$
Plot	–	$\ln q_e$ vs. ε^2
Fitted model	–	$\ln q_e = 4.46 - 0.0025\,\varepsilon^2$
K_{DR}	mol^2/kJ^2	0.0025
$E = 1/\sqrt{2K_{DR}}$	kJ/mol	14
R^2	–	0.851

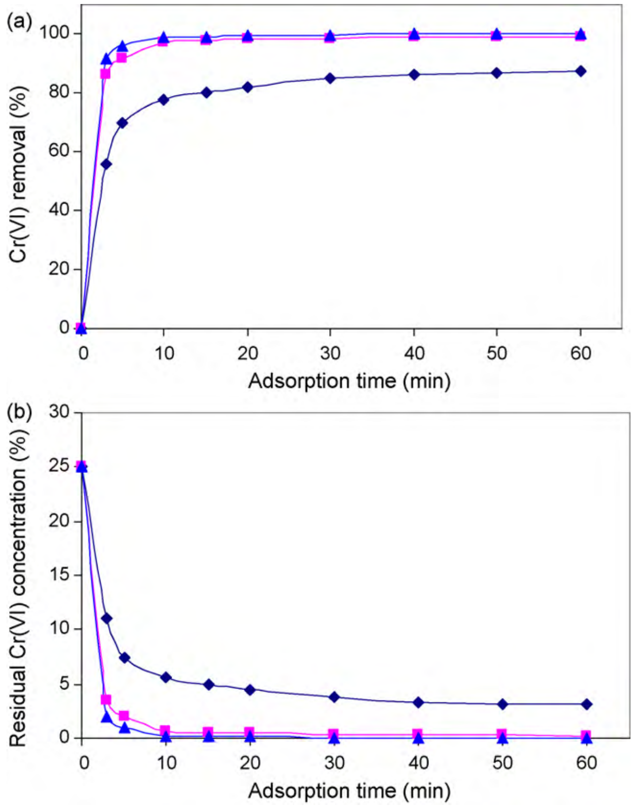

Fig. 6. Cr(VI) removal from industrial wastewater expressed as percent adsorption (a) and residual Cr(VI) concentration (b), (conditions: Cr(VI) = 25 mg/L; pH 2; PHP dose = 1–2 g/L; stirring speed = 100 rpm; contact time = 3–60 min; NaCl concentration = 20 g/L; temperature = 25 ± 3 °C).

unattractive adsorbent for large scale applications. It is evident that pistachio hull wastes are a promising and efficient material with a high capacity for adsorption. Furthermore, pistachio hulls are available in large amounts at no-cost and can be used as an adsorbent without modifications. According to the data provided in Table 3, the value of the constant n in the Freundlich model is greater than one, which confirms the suitability of PHP as an adsorbent for Cr(VI) adsorption from wastewater. The favorability of Cr(VI) adsorption onto PHP was further evaluated by the dimensionless parameter, R_L, which was derived from the Langmuir model. As shown in Table 3, the values of R_L for Cr(VI) adsorption onto PHP are between 0 and 1, indicating that the process is favorable.

Based on the results of the Dubinin–Radushkevich (D–R) model (Table 3), the amount of free energy in Cr(VI) adsorption by PHP is 15 kJ/mol. A value of E between 8 and 16 kJ/mol indicates that chemical adsorption is the dominant process under the experimental conditions [35]; thus, the adsorption of Cr(VI) by PHP occurs by a mechanism of chemisorption.

3.9. *Removal of Cr(VI) from real wastewater by PHP*

Upon completion of basic adsorption experiments, the efficacy of PHP in the removal of Cr(VI) from industrial wastewater was evaluated. To this end, a bulk wastewater sample was obtained from a local electroplating plant. The pH, electrical conductivity, color and Cr(VI) concentration of collected wastewater was determined at the beginning of adsorption experiments, where values of 2.1, 2.4 ms/cm, yellowish, and 25 mg/L, respectively, were obtained. The pH of the wastewater and the optimal pH obtained from basic adsorption experiments were identical; thus, chemical adjustment of the pH was unnecessary. Adsorption was performed on 0.5 L of wastewater with PHP concentrations of 1, 1.5 and 2 g/L. The suspensions were stirred at room temperature (25 ± 2 °C) and 100 rpm for various amounts of time (3–60 min). Fig. 6a and b illustrates Cr(VI) removal from wastewater in terms of residual concentration and percent removal, respectively. As shown in Fig. 6a, upon addition of 1, 1.5 and 2 g/L of PHP, the removal of Cr(VI) increased as a function of time and reached 87.5, 99.1 and 100%, respectively, after 60 min of contact time. Thus, the equilibration of wastewater with 2 g/L of PHP for 30 min reduced the Cr(VI) concentration from 25 to 0.025 mg/L (Fig. 6b), a value well below the level established by the US EPA for the discharge of wastewater into surface waters [3]. Thus, PHP is an efficient and cost-effective adsorbent for the removal of Cr(VI) from industrial wastewaters. The main advantages of raw pistachio hull biomass for the removal of chromium from water and wastewater include a high adsorption rate, capacity, and efficacy, as well as a short equilibration time. Furthermore, pistachio hulls are available as a no-cost waste and can be used without modifications. Thus, PHP adsorption is environmentally friendly and achieves treatment goals in a simple and low-cost manner.

4. Conclusion

In the present work, PHP, a no-cost and efficient biosorbent, was investigated for the removal of Cr(VI) from wastewater. Basic adsorption experiments indicated that the adsorption of Cr(VI) by PHP was an adsorbate, adsorbent and temperature dependent process that was favorable under acidic conditions. Pseudo-second order and Langmuir models fit the kinetic and equilibrium experimental data, respectively. The maximum adsorption capacity was found to be 116.3 mg Cr(VI) per g PHP. Results revealed that the rate of adsorption was controlled by interparticle diffusion and chemisorption. Furthermore, PHP reduced the concentration of Cr(VI) in industrial wastewater to levels below the designated standards for effluent discharge. Thus, PHP is an efficient and economical adsorbent for industrial applications.

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