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Biosorption of Cr(III) from solutions using vineyard pruning waste

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ABSTRACT

The kinetics and biosorption mechanism of Cr(III) ions on vineyard pruning waste (VPW) have been studied using different parameters such as initial concentration, biosorbent dosage, temperature, contact time and solution pH. The results indicated that adsorption was pH-dependent and temperature-dependent. VPW exhibited the highest Cr(III) uptake capacity of 12.453 mg g^{-1} at 303 K and at an initial pH value of 4.2. The kinetic data for the VPW samples support the pseudo-second-order model ($R^2 > 0.99$), but the first-order kinetic model ($R^2 < 0.89$) and intra-particle model ($R^2 < 0.88$) did not adequately correspond to the experimental values. The equilibrium adsorption data were interpreted using Langmuir and Freundlich models, and the adsorption of Cr(III) on VPW was better represented by the Langmuir equation ($R^2 > 0.990$) than Freundlich ($R^2 < 0.980$). In addition, thermodynamic parameters such as ΔG^*, ΔH^* and ΔS^* were found out to be 72.71, −18.77 kJ/mol and −301.93 J/mol K, respectively. The negative value of ΔH^* (−18.77 kJ/mol) showed that the biosorption of Cr(III) on VPW is exothermic. VPW has been characterized by FT-IR, scanning electron microscopy (SEM), BET surface area and energy dispersive X-rays (EDXs). The results have confirmed the applicability of this the VPW as an efficient biosorbent for Cr(III) ions.

1. Introduction

The presence of heavy metals in the aquatic environment has been of great concern because of their toxicity and non-biodegradable nature [1,2]. Chromium (Cr) compounds are widely used by many industries such as electroplating, leather tanning, paint and pigments, metal finishing, resulting in a large quantity of this element being discharged into effluent industrial wastewaters [3,4]. Waters containing a high concentration of Cr can cause serious environmental problems as well as induce toxic and carcinogenic health effects on humans [5–9]. The drinking water guideline recommended by Environmental Protection Agency (EPA) in US is 100 μg/L [10]. The legal discharge limit of Cr(III) varies from 0.5 mg L^{-1} (in surface water) to 2.0 mg L^{-1} (in sewers) depending on the processing, country, and wastewater treatment methods [11]. In this context, the recovery of heavy metals from the wastewater is a major topic in water research and there are several methods which are commonly used for this purpose (chemical precipitation, electrochemical reduction, evaporation, reverse osmosis, membrane filtration, co-precipitation, electro dialysis, adsorption, biosorption, etc.) [12–14]. Precipitation, ion exchange, solvent extraction, and adsorption on oxides are the conventional methods for the removal of heavy metal ions from aqueous solutions, but due to high maintenance cost these methods do not suit the needs of developing countries [15]. Over the last few decades, adsorption has been shown to be an economical and feasible alternative method for the removal of low levels of trace metals from wastewater and water supplies [16]. The adsorption process is used especially in the wastewater treatment field and investigation has been made to determine good, inexpensive adsorbents [17–22]. Natural materials or the wastes/by-products of industries or synthetically prepared materials, which cost less and can be used as such or after some minor treatment as adsorbents are generally called low-cost adsorbents (LCAs) [23]. These low-cost sorbents include industrial or agricultural waste products such as waste slurry, moss, aquatic plants, and algae, sugar beet pulp, lignin, straw and nut shells, sawdust and bark [24–27].

In the present work, the utility of VPW as an biosorbent to remove Cr(III) from wastewater was proposed. VPW produced a significant amount of solid waste vineyard. This material causes a significant disposal problem. These solid waste assessments have been made to use the cheapest unconventional adsorbents to adsorb chromium heavy metal ions from aqueous solution. A series of kinetic and equilibrium experiments have been performed to characterize chromium adsorption onto this biosorbent. Parameters that may affect the adsorption, biosorbent dosage, solution pH, temperature and initial chromium concentration are discussed.

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2. Materials and methods

2.1. Adsorbent preparation

VPW used as an biosorbent was collected from Manisa, Turkey and washed repeatedly with deionized water to remove the water soluble impurities and other surface adhered particles. This VPW was first air-dried and then dried in a pre-heated oven at 373 K for 2.5 h to get rid of the moisture and other volatile impurities. Dried material pieces were crushed in a rotary crusher and sieved with 100 mesh sieve and stored in desiccators.

2.2. Adsorbate preparation

The aqueous solution of trivalent chrome was prepared by dissolving a known quantity of $Cr(NO_3)_3 \cdot 9H_2O$ (Carlo Erba) in double distilled water. It was further diluted to obtain standard solutions. The pH of the solution was arranged using either hydrochloric acid (Riedel, 37%) or NaOH (Merck, 97%). All the reagents used were of analytical grade.

2.3. Batch adsorption studies

Adsorption capacity experiments were carried out using the batch technique at 303 K. Initial Cr(III) concentrations were prepared in the ranges of 5, 15, 30, 45, 60, 75 and 90 mg L^{-1}. The erlenmeyer flask was shaken using an electric shaker for a prescribed length of time to attain equilibrium at 303 K. Studies of the kinetics of Cr(III) adsorption onto VPW were carried out from its solution. In each adsorption experiment, 50 mL of Cr(III) aqueous solution in desired concentrations and pH was put into a 100 mL erlenmeyer flask. Experiments were conducted with 15 mg L^{-1} Cr(III) concentration and samples with different biosorbent dosages ranging from 2.5 to 10 g L^{-1} in order to determine the effect of solid/liquid ratio on adsorption. Adsorption experiments were carried out in 50 mL of Cr(III) solutions and erlenmeyer flask containing accurately weighed amounts of the biosorbents. The erlenmeyer flask was shaken at 60 min using an electric shaker (Nüve ST 402) for a prescribed length of time to attain equilibrium at 293, 303 and 313 K separately. In all of the experiments, contact time, initial solution concentration, initial pH, biosorbent dose and temperature were selected as experimental parameters. All experiments were run at least twice. A temperature bath was used to keep the temperature constant. At the end of the adsorption period, the solution was centrifuged for 15 min at 5000 rpm [28]. German standard method (DIN DIN 38405-24) was used for the determination of total chromium. Cr(III) ions react with phosphoric acid–sodium peroxodisulphate to oxidize to Cr(VI). Chromium (VI) ions react with 1,5-diphenylcarbazide to form 1,5-diphenylcarbazone, which forms a red complex with chromium (VI). After creating a color chromium complex, the adsorption of the colored solution was measured in 543 nm spectrophotometrically [29].

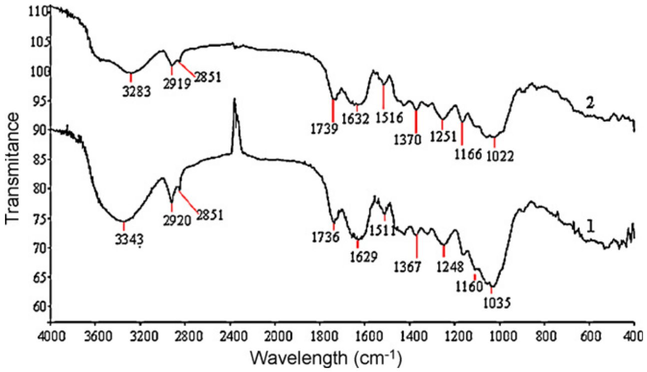

Fig. 1. FT-IR spectra: (1) for the unloaded VPW and (2) for the Cr(III)-loaded VPW.

2.4. Desorption experiment

Initially, in order to determine desorption of the VPW, the experiments were conducted using a 5 g L^{-1} VPW and 15 mg L^{-1} Cr(III) concentration. Results showed that 13.86 mg L^{-1} of Cr(III) was adsorbed onto VPW at the end of 60 min. Then the VPW samples were removed by filtration and dried at room temperature (298 K) until coming to a constant weight. These dried samples were used for desorption experiments. Desorption studies were carried out at different initial pH values (3.0, 4.2 and 8.0). The closed erlenmeyers were shaken using a mechanical shaker at 303 K, and then the adsorbent was removed by filtration. The amount of Cr(III) in the aqueous solution was determined using the method explained in Section 2.3.

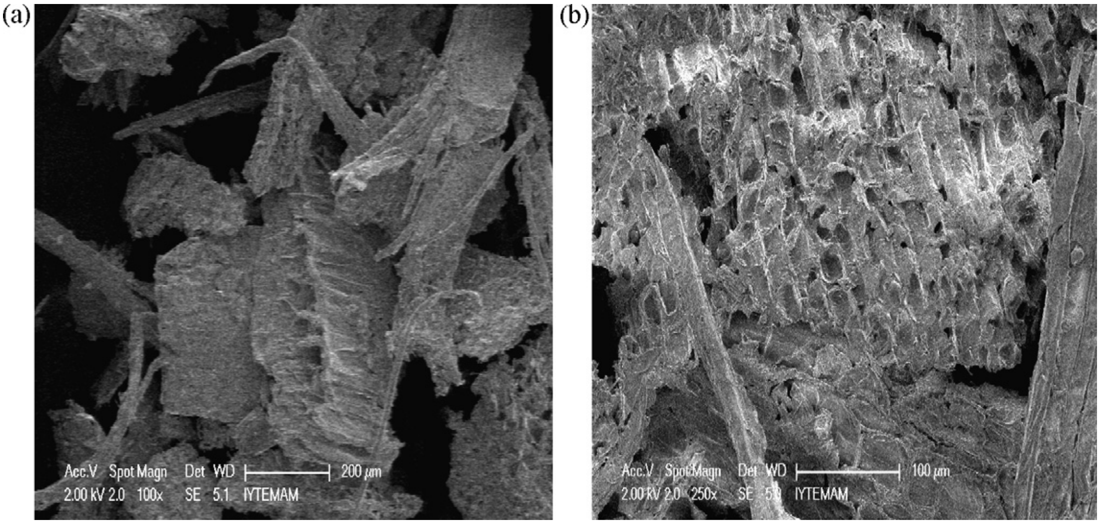

Fig. 2. SEM images: (a) for the unloaded VPW and (b) for the Cr(III)-loaded VPW.

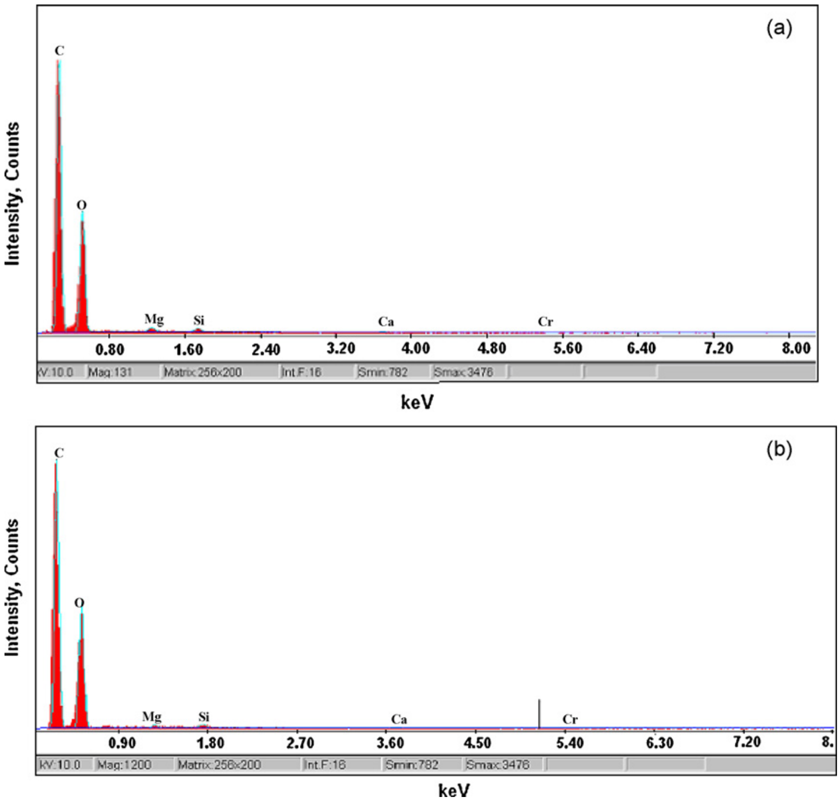

Fig. 3. Energy dispersive X-ray (EDX) analysis of VPW: (a) before and (b) after the sorption of Cr(III).

3. Results and discussion

3.1. Characterization of VPW

FT-IR spectra for VPW in its natural form and loaded with Cr(III) ions are shown in Fig. 1. When these spectra are analyzed, there is a strong peak at 3343 cm^{-1} representing the –OH stretching of the hydroxyl group of cellulose and lignin, and the peak at 2920 cm^{-1} shows the presence of C–H stretching [30]. The appearance of peaks at 1736 and 1629 cm^{-1} indicates the presence of C=O stretching of the aldehyde group, whereas the appearance of peaks at 1511 and 1367 cm^{-1} indicates the presence of secondary amine group and carboxyl groups, respectively. The peaks at 1248 and 1035 cm^{-1} might be due to C–O stretching of the hydroxyl group and ether group of cellulose, respectively. In Fig. 2, the FT-IR spectrum of the VPW laoded with Cr(III) indicates that the peaks regarding the functional groups mentioned above are slightly affected in their position and intensity. It indicates that the adsorption of these ions on the surface of VPW is either through complexation or through physical attractions that are known as weak electrostatic interaction and Van der Waals forces. In addition, no chemical bonding takes place in this process. Thus the FT-IR of the surface functional group remains unchanged. The FT-IR spectra of VPW loaded with Cr(III) show prolongation of these bands after metal adsorption, indicating the role of these groups in adsorption. This might be due to the close affinity of such transition metals in the periodic table [31]. The hydroxyl (R–OH) group can serve as both coordination and electrostatic interaction sites to adsorb heavy metals. The adsorption mechanism can be expressed as following [32]:

$$\text{R–OH} + \text{Cr}^{3+} \leftrightarrow \text{R–O–Cr}^{2+} + \text{H}^{+} \qquad (1)$$

Scanning electron micrographs of the VPW at different magnifications (100 and 250×) are shown in Fig. 2(a) and)b). After 100× magnification, the VPW appears mostly fibrous in shape (Fig. 2(b)). After 250× magnification, it clearly discloses the surface porosity and texture of the VPW with a texture-like activated carbon. In addition, BET surface area of VPW was found 159 $\text{m}^2\,\text{g}^{-1}$, and energy dispersive X-ray (EDX) analysis for both VPW and Cr(III)-VPW were done. The results are shown in Fig. 3. As seen in Fig. 3(a), while it did not show the characteristic signal of Cr(III), the adsorption of Cr(III) on VPW was clearly observed (Fig. 3(b)).

3.2. Effect of different parameters on adsorption

In this section, in order to characterize the adsorption process of Cr(III) on VPW, we investigated the effect of different factors such as biosorbents dosage, initial Cr(III) concentration, solution pH, and temperatures. In addition, a desorption experiment was carried out at pH 3.0, 4.2 and 8.0 under the same conditions.

3.2.1. Effect of adsorbents dosage

To investigate the effect of biosorbent dosage on adsorption, the experiments were conducted with constant concentration (15 $\text{mg}\,\text{L}^{-1}$), and samples with different biosorbent dosages ranging from 2.5 to 10 $\text{g}\,\text{L}^{-1}$ mL (solid/liquid) were used under the constant temperature 303 K and natural pH. The results are given in Fig. 4 and show that the removal percentage of Cr(III) ions increases as the biosorbent amount increases and then becomes constant (30–40 min.). This difference could be explained by the increase in the total surface area of VPW due to the adsorbed amount. Furthermore, because the values of 2.5 and 10 $\text{g}\,\text{L}^{-1}$ are close to each other, the adsorbent dosage was selected as 5 $\text{g}\,\text{L}^{-1}$ in all the experiments.

3.2.2. Effect of initial concentration

Initial concentrations of Cr(III) ions varied from 15 to 60 $\text{mg}\,\text{L}^{-1}$ at a constant pH, temperature and biosorbent dose (303 K; pH: 4.2 and 5.0 $\text{g}\,\text{L}^{-1}$). The adsorption reached equilibrium within 10–15 min for all initial concentrations; thereafter, it became nearly

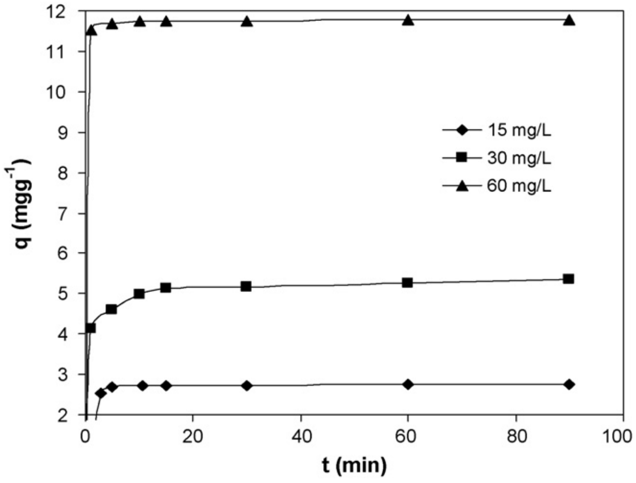

Fig. 4. Effect of adsorbents dosage for removal of Cr(III) (303 K; pH: 4.2, Cr(III): 15 mg L^{-1}).

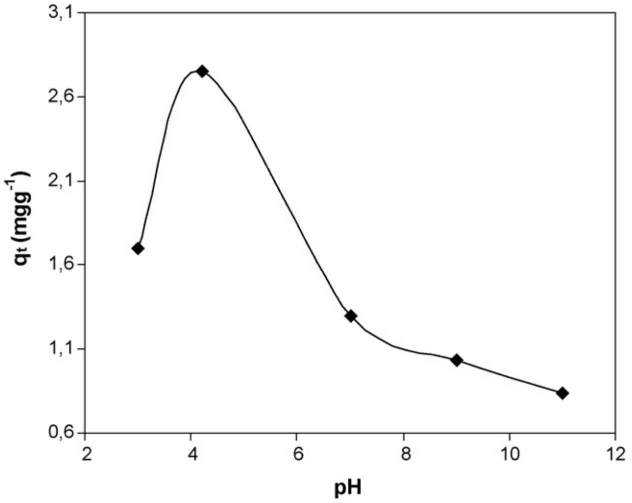

Fig. 6. Effect of pH on adsorption Cr(III) onto VPW (solid/liquid: 5 g L^{-1}, 303 K, time: 1 h).

constant (Fig. 5). In addition, in changing the concentration of the solution from 15 to 60 mg L^{-1}, the amount of Cr(III) ions adsorbed per unit of adsorbent increased from 2.07 to 11.50 mg g^{-1}.

3.2.3. *Effect of pH on adsorption process*

The removal of metal ions from an aqueous solution by adsorption is highly dependent on the pH of the solution which affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate [12,33]. Hence the adsorption of chromium on VPW was examined from solutions with different pH values of 3.0–9.0. The results were shown in Fig. 6, which reveals that the adsorption of the Cr(III) increases from 1.69 to 2.73 mg g^{-1} with an increase in pH of the solution from 3.0 to 4.2 and then decreases to 0.84 mg g^{-1} at pH 9.0.

The behaviour of metal ions in an aqueous solution is complex in the sense that it may be present as ions of different compositions and shows a different degree of activity (Fig. 7, Eh–pH diagrams) [34]. Therefore, it is necessary to ascertain the nature of Cr ions in a solution of various hydrolyzed Cr species as a function of pH Cr(III) predominates at pH < 3.0. At very lower pH values, adsorption was very low, which suggests that a weak attraction between the VPW surface and the positive ions took place. The fact that the amount of removal at a low pH is considerably lower may be due to competition between Cr(III) and H$^+$ ions on the active sites of the adsorbent surface. Similar results have been reported by other researchers [12,35–39]. At pH > 3.5, hydrolysis of aqueous Cr(III) yields trivalent chromium hydroxy species [CrOH^{2+}, Cr(OH)$^{2+}$, Cr(OH)$_3{}^0$ and Cr(OH)$_4{}^-$·Cr(OH)$_3{}^0$] is the only solid species existing as an amorphous precipitate [34]. The highest metal removal percentage took place in pH around 4.2. But, after this pH, it was seen that the adsorption of Cr(III) decrease. In literature study, it was reported that Cr(OH)$_4{}^-$ and Cr(OH)$_3$(s) are most likely to be found in alkaline medium [34]. Therefore, it is expected that the adsorption with increasing pH will decrease because the negative charge on both Cr(III) spices and VPW surface increases, which results in an electrostatic repulsion.

3.2.4. *Effect of temperature*

To investigate the effect of the temperature (293, 303 and 313 K) on the Cr(III) adsorption, the experiments were conducted using constant concentrations of Cr(III) (15 mg L^{-1}) at different times. The results are given in Fig. 8. As can be seen from these figures, the adsorption of Cr(III) onto the surface of VPW occurred quickly for three temperatures during the first 30 min. It was then observed that the adsorption rate was constant in 60 min by increasing times at all temperatures. The adsorbed amount of Cr(III) ions decreases

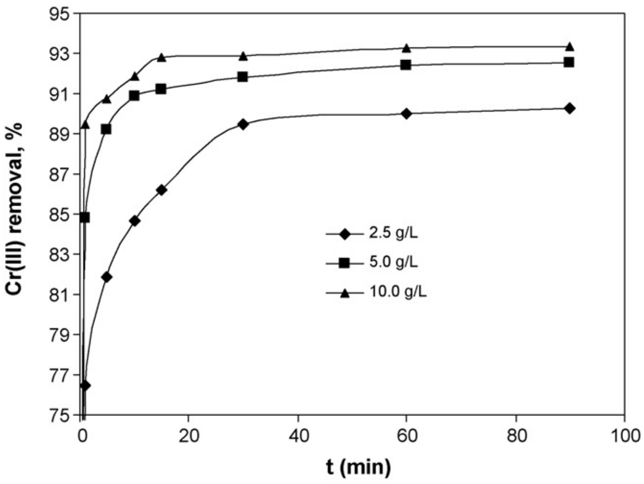

Fig. 5. The effect of initial concentration on the adsorption of Cr(III) (solid/liquid: 5 g L^{-1}, 303 K, pH: 4.2).

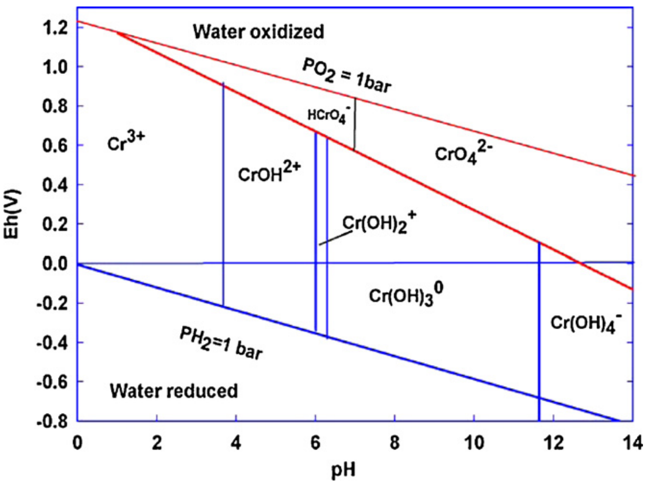

Fig. 7. Eh–pH diagram for chromium [34].

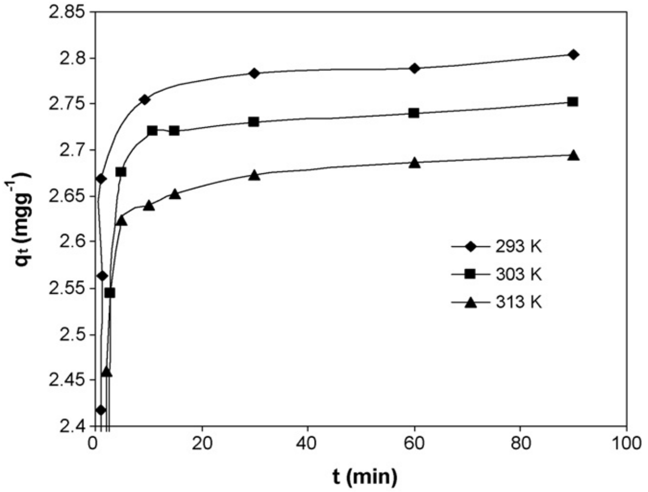

Fig. 8. The effect of the different temperatures on the adsorption of Cr(III) (cons.:15 mg L^{-1}, solid/liquid: 5.0 g L^{-1}, pH: 4.2).

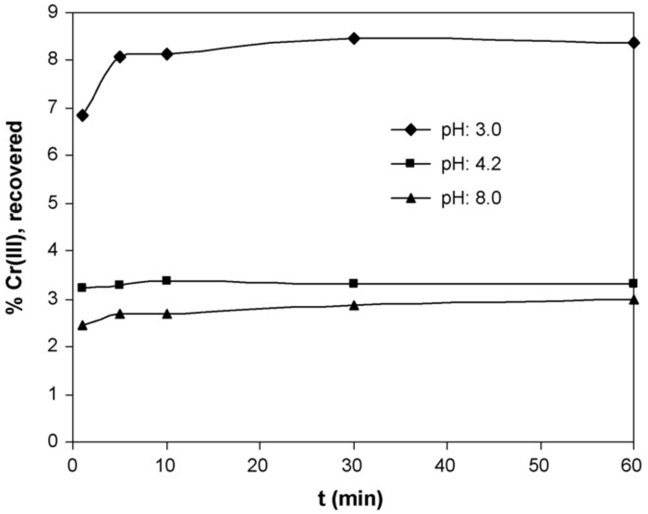

Fig. 9. Effect of different initial pH on the desorption of Cr(III) onto vineyard pruning waste (Solid/liquid: 5 g L^{-1}; 60 min; Cr(III): 15 mg L^{-1}).

with increasing temperatures from 293 to 313 K. The observed decrease in the adsorption capacity with an increase of temperature from 293 to 313 K indicated that low temperatures favor Cr(III) ions removal by adsorption onto the VPW. These results indicate that the adsorption process is exothermic in nature. This may be due to a tendency for the Cr(III) to escape from the solid phase of biomass to the liquid phase of Cr(III) solution with increasing temperature. Similar results have also been reported for the biosorption of Pb(II) and Cr(III) of lichen biomass, biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (*Cladonia furcata*) biomass and biosorptive removal of mercury(II) from aqueous solution using lichen (*Xanthoparmelia conspersa*) biomass [40–42].

3.2.5. Desorption experiment

Desorption studies are helpful in exploring the possibility of recycling the adsorbents and recovering metal resources [43]. Initially, in order to determine desorption of the VPW, the experiments were conducted using a 5 g L^{-1} VPW and 15 mg L^{-1} Cr(III) concentration. Results showed that 13.86 mg L^{-1} of Cr(III) was adsorbed onto VPW at the end of 60 min. Then the VPW samples were removed by filtration and dried at room temperature (298 K) until coming to a constant weight. These dried samples were used for desorption experiments. Desorption studies were carried out at different initial pH values (3.0, 4.2 and 8.0). The closed erlenmeyers were shaken using a mechanical shaker at 303 K, and then the adsorbent was removed by filtration. The amount of Cr(III) in the aqueous solution was determined using the method explained in Section 2.3. The results of desorption shown in Fig. 9 indicate that the desorption percentage also somewhat increased as the time increased, and after 10 min, the desorption rate stabilized. The percentages of desorption for pH 3.0, 4.2 and 8.0 were found to be 8.0%, 3.5% and 2.8%, respectively, at the end of the first 10 min. The explanation for this is that when the solution pH is reduced, hydrogen ion (H^+) in the solution displaces the biosorbed Cr(III) ions onto the VPW.

3.3. Sorption isotherms

The adsorption capacity and affinity of VPW for Cr(III) were determined with two isotherms models (Langmuir and Freundlich), using Cr(III) solutions at 5, 15, 30, 45, 60, 75 and 90 mg L^{-1}. The Langmuir isotherm equation has been widely applied to describe experimental adsorption data [44]. The Langmuir equation assumes that there is no interaction between the sorbate molecules and that the sorption is localized in a monolayer. It is then assumed that once a Cr(III) occupies a site, no further sorption can take place at that site. The well known expression of the Langmuir model is represented by Eqs. (2) or (3):

$$q_e = \frac{q_m K C_e}{1 + K C_e} \tag{2}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \tag{3}$$

where q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amount of adsorbed Cr(III) per unit weight of adsorbent and un-adsorbed Cr(III) concentration in solution at equilibrium, respectively, q_m is the maximum amount of the Cr(III) bound per unit weight of adsorbent to form a complete monolayer on the surface at high C_e, and K is the equilibrium constant or Langmuir constant related to the affinity of binding sites (L mg^{-1}). q_m and K were calculated from the slope and intercept of the straight lines of the plot C_e/q_e versus C_e [45–47].

The Freundlich isotherm is a nonlinear sorption model. This model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The general form of this model is:

$$q_e = K_F C_e^{1/n} \tag{4}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

where K_F is a Freundlich constant that shows both the adsorption capacity of an adsorbent and the strength of the relationship between adsorbate and adsorbent. The slope $1/n$, ranging between

Table 1
The characteristic parameters of sorption process of Cr(III) on vineyard pruning waste.

Temp. (K)	Langmuir isotherm				Freundlich isotherm
	q_m (mg g^{-1})	K (L mg^{-1})	R^2	R_L	R^2
303	12,453	0.184	0.990	0.136–0.874	0.971

Table 2
First, pseudo-second-order kinetics and intra-particle diffusion model parameters for the adsorption systems in the study.

Temp.	Initial con.	First-order	Second-order				$t_{1/2}$ (min)	Intra-particle diffusion	
T (K)	$[C_0]$ (mg L^{-1})	R^2	$q_{e(calc.)}$ (mg g^{-1})	$q_{e(exp)}$ (mg g^{-1})	k_2 (g/mg min)	R^2		R^2	D (cm^2 s^{-1}) × 10^6
293	15	0.887	2.79	2.80	2.341	0.999	0.152	0.800	8.19
303	15	0.890	2.73	2.75	1.760	0.999	0.206	0.883	6.05
313	15	0.853	2.69	2.70	1.555	0.999	0.238	0.627	5.25
303	30	0.890	5.35	5.37	0.237	0.999	0.785	0.726	1.59
303	60	0.603	11.77	11.77	1.71	0.999	0.049	0.627	2.52

0 and 1, is a measure of adsorption intensity or surface heterogenity, becoming more heterogeneous as its value gets closer to zero. In general, as K_F increases the adsorption capacity of an adsorbent for a given adsorbate increases. K_F and $(1/n)$ can be determined from the linear plot of ln q_e versus ln C_e [48,49]. Values of q_m, K, K_F, and n were calculated from the intercept and slope of the plots. The values for q_m, K, are shown in Table 1. The isotherm data were calculated from the least square method and the related correlation coefficients (R^2 values) are given in the same table.

As seen from Table 1, the Langmuir equation represents the adsorption process very well; the R^2 value was found to be 0.99, indicating a very good mathematical fit. Still, it was seen that the Freundlich isotherm was not suitable ($R^2 < 0.98$). The fact that the Langmuir isotherm fits the experimental data very well may be due to the homogeneous distribution of active sites onto the biosorbent surface, since the Langmuir equation assumes that the surface is homogenous [50,51]. As seen in Table 1, the maximum adsorption capacities for Cr(III) onto the biosorbent surface was found to be in the range of 12,453 mg g^{-1}. In addition, the essential characteristics of the Langmuir isotherm can be expressed by a separation or equilibrium parameter, a dimensionless constant, which is defined by Eq. (6) [52,53]:

$$R_L = \frac{1}{1 + KC_e} \tag{6}$$

The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values were reported in Table 1 which shows the adsorption behaviour of vineyard pruning waste. The value of RL was found to be in the range of 0–1, indicating that the adsorption process is favorable for Cr(III) (Table 1).

3.4. Kinetics analysis

In order to determine the adsorption kinetics of Cr(III) ions, the first-order and second-order kinetics models were checked. The Lagergren pseudo-first-order equation was used to fit the experimental results:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

The straight line of the plot of ln $(q_e - q_t)$ versus time suggests the applicability of the Lagergren equation for the present system. The values of R^2 were determined from the slope of the plots and are given in Table 2. Recently, Ho and McKay [54] have reported that most of the sorption systems followed a second-order kinetic model which can be expressed as:

$$\frac{t}{q_t} = \left[\frac{1}{k_2 q_e^2}\right] + \frac{t}{q_e} \tag{8}$$

where k_2 is the adsorption rate constant (g mg^{-1} min^{-1}). According to Eq. (8), a plot of t/qt versus t should be a straight line with a slope $1/q_e$. The values of k_2 were determined by the slope of the plot and are given in Table 2. Lagergren's first-order model showed a correlation coefficient (R^2) of 0.60–0.90 (Table 2), whereas that of the second-order kinetic model was 0.99. As a result, the kinetic adsorption data were further fitted the pseudo-second-order kinetic model.

The half-adsorption time, $t_{1/2}$, is another parameter which can be calculated from the equilibrium concentration and the diffusion coefficient rate values. Half-adsorption time, $t_{1/2}$, is defined as the time required for the adsorption to take up half as much VPW as its equilibrium value. This time is often used as a measure of the adsorption rate. This was calculated by using the following equation:

$$t_{1/2} = \frac{1}{k_2 q_e} \tag{9}$$

The diffusion coefficient largely depends on the surface properties of adsorbents. The diffusion coefficient for the intra-particle transport of Cr(III) under different initial concentration and temperature were also calculated by using the following relationship [55]:

$$q_t = k_{dif}\sqrt{t} + C \tag{10}$$

where q_t is the amount of Cr(III) adsorbed at time t (mg g^{-1}), C is the intercept and k_{dif} is the intra-particle diffusion rate constant (mg s$^{-1/2}$ g^{-1}). According to Eq. (10), a plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{dif} and intercept C when the adsorption mechanism follows the intra-particle diffusion process. The intra-particle diffusion process model showed a correlation coefficient (R^2) of 0.62–0.88 (Table 2). Therefore, the intra-particle diffusion process model is not a good fit for Cr(III) adsorption on VPW.

The diffusion coefficient largely depends on the surface properties of biosorbents. The diffusion coefficient for the intra-particle transport of Cr(III) under different conditions were also calculated by using the following relationship [55]:

$$t_{1/2} = \frac{0.030 r_0^2}{D} \tag{11}$$

where $t_{1/2}$ is the half life in seconds as calculated from Eq. (11), r_0 is the radius of the adsorbent particle in centimetres and D is the diffusion coefficient value in cm^2 s^{-1}. In these calculations, it has been assumed that the solid phase consists of spherical particles with an average radius between the radius corresponding to upper- and lower-size fractions. The value of r_0 was calculated as 2.5 × 10^{-3} cm for VPW samples. Calculated values of $t_{1/2}$ and D are given in Table 2. D values for the adsorption of Cr(III) on VPW under different conditions are in the range of 1.59 × 10^{-6} to 8.19 × 10^{-6} cm^2 s^{-1}.

Table 3
Adsorption capacity of Cr(III) by various adsorbents.

Adsorbents	$q_{max.}$ (mg g^{-1})	Refs.
Sawdust	5.52	[56]
Cork powder	3.40	[57]
Rhizoclonium heiroglyphicum	11.81	[16]
Reed mat	7.18	[58]
Modified peanut husk	7.67	[56]
Mangrove leaves	6.54	[58]
Moss-tannery waste	13.10	[59]
Algal biomass	28.16	[60]
Vineyard pruning waste	12,453	In this study

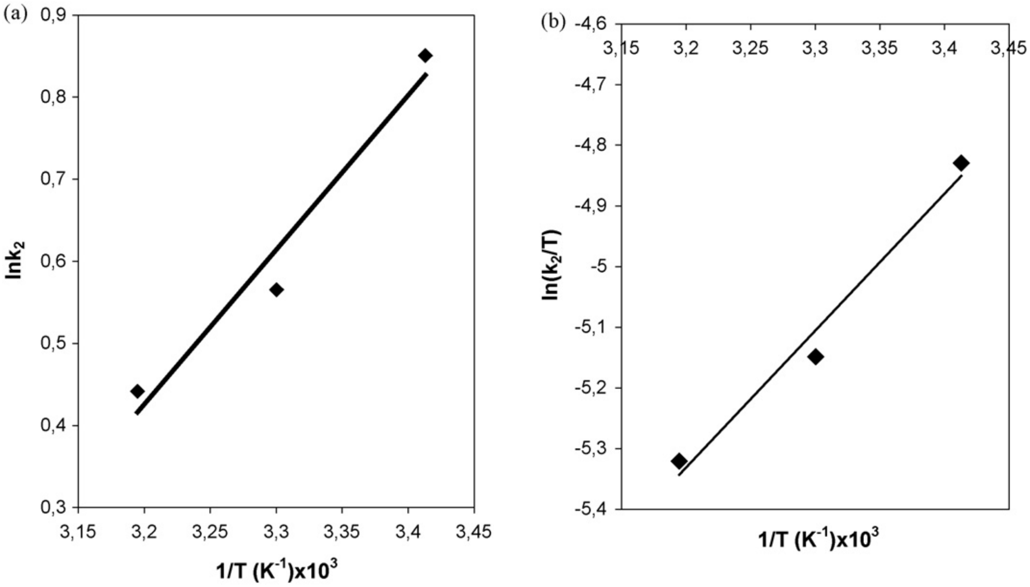

Fig. 10. (a) Arrhenius plot for the adsorption and (b) plot of ln(k_2/T) versus 1/T for adsorption of Cr(III) on VPW.

3.5. *Comparison of VPW with other adsorbents*

For further demonstrating the application of VPW in removing Cr(III) from wastewater, a comparison of the maximum capacity of various adsorbents for Cr(III) reported in literatures is given in Table 3. As can be seen from Table 3, VPW has good adsorption capacity when compared with other adsorbents. The values of Cr(III) specific uptake found in this work were significantly higher, with two exceptions [59,60], than reported elsewhere.

3.6. *Thermodynamic study*

The temperature is an important parameter in a thermodynamic study. The several thermodynamic parameters including the Arrhenius activation energy, free energy change (ΔG^*), activation enthalpy change (ΔH^*), and activation entropy change (ΔS^*) can be calculated by using different equations [61]:

$$\ln k_2 = \ln k_0 - \frac{E_a}{R_g T} \tag{12}$$

where E_a is the Arrhenius activation energy, and k_0 is the Arrhenius factor. To extract k_0 and E_a from kinetic data, we plot the series of rate constants measured at different temperatures in a graph of ln k versus 1/T. As shown in Fig. 10(a), the corresponding activation energy was determined from the slope of the linear plot. The result obtained is −15.65 kJ/mol for adsorption from its solution. The magnitude of activation energy gives an idea about the type of adsorption which is mainly the nature of adsorption. Since the values of the activation energy are lower than 40 kJ/mol [55], this shows that the adsorption has a potential barrier corresponding to a physisorption. In a similar study, Padmavathy (2008) observed activation energy of −13.9 kJ/mol for the biosorption of nickel(II) ion onto deactivated protonated yeast [62]. In another study, Aksu [63] also observed activation energy of −8.0 kJ/mol for the biosorption of cadmium(III) ion onto dried *C. vulgaris*.

Free energy (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) of activation can be calculated by Eyring equation [61]:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S*}{R_g} - \frac{\Delta H*}{R_g T} \tag{13}$$

where k_b and h are Boltzmann's and Planck's constants, respectively. According to Eq. (13), a plot of ln (k/T) versus 1/T should be a straight line with a slope $-(\Delta H^*/R_g)$ and intercept [ln $(k_b/h)+(\Delta S^*/R_g)$]. ΔH^* and ΔS^* were calculated from the slope and intercept of line (Fig. 10(b)). Gibbs energy of activation may be written in terms of entropy and enthalpy of activation:

$$\Delta G^* = \Delta H * - T\Delta S* \tag{14}$$

ΔG^* was calculated at 303 K from Eq. (14). It was determined that the values of the free energy ΔG^*, enthalpy (ΔH^*) and entropy (ΔS^*) of activation were 72.71, −18.77 kJ/mol and −301.93 J/mol K, respectively. The negative value of ΔH^* (−18.77 kJ/mol) showed that the biosorption of Cr(III) on VPW is exothermic. Similar negative values of the same order of magnitude have been already reported by Gupta et al. [64,65] for the biosorption of hexavalent chromium and cadmium(II) from aqueous solution using a low-cost biosorbents. The negative entropy (ΔS^*) value suggests a decrease in the randomness at the solid/solution interface during the biosorption process [66]. In addition, this can be explained by the fact that Cr(III) ions are bound to the active areas of VPW surface, such as hydroxyl, carboxyl, methoxyl and hydroxyl groups via Van der Waals binding [12,67].

4. Conclusions

The results showed that VPW can be used as an adsorbent for the effective removal of Cr(III) from aqueous solutions. The amount of Cr(III) ions adsorbed into the VPW increased with an increase in dosage of biosorbent. It was observed the highest Cr(III) uptake capacity of 12.453 mg g^{-1} at 303 K and at an initial pH value of 4.2. The reaction rate for the adsorption of Cr(III)) ions decreased with an increase in temperature. The kinetic studies indicated that equilibrium in the adsorption of Cr(III) ions on VPW was reached in 30 min of contact between the VPW and the solution. As a result of thermodynamic parameters calculations, Cr(III) sorption on VPW was an exothermic process. The kinetic sorption data fit well to the second-order kinetic model. The adsorption isotherms followed the Langmuir model of isotherms (R^2 > 0.99). Taking into consideration the above results, it can be concluded that the VPW is a suitable biosorbent for the removal of Cr(III) ions from aqueous solutions in terms of low-cost and its natural and abundant availability.

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