



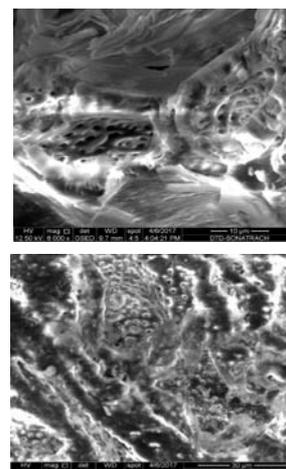
PEACH STONES VALORIZED TO HIGH EFFICIENT BIOSORBENT FOR HEXAVALENT CHROMIUM REMOVAL FROM AQUEOUS SOLUTION: ADSORPTION KINETICS, EQUILIBRIUM AND THERMODYNAMIC STUDIES

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In the last years, much attention has been focused on the use of low-cost adsorbents for the removal of heavy metals from wastewater. Raw biosorbent waste is a cheap and environmentally friendly material that provides good cost-benefit for the industries that use it. The objective of this study is to improve the feasibility of raw local peach stones (RPS) waste for the removal of hexavalent chromium from aqueous solution. The characterization of this raw biomaterial has been performed using various analytical techniques such as FTIR, SEM and XRD. In batch adsorption experiments the adsorption parameters optimized were pH 2, adsorbent dose 4 g/L, equilibrium contact time 240 min, initial Cr (VI) concentration 30 mg/L and temperature 30°C. The removal percentage of Cr(VI) was 97 % at pH 2. The adsorption equilibrium was well explained by the Freundlich isotherm and the process followed the pseudo-second order kinetics. Thermodynamic parameters specify the spontaneous and endothermic nature of biosorption process. Desorption study was carried out with NaOH (0.1, 0.5, and 1M) solutions. Investigations carried out proved that RPS is a good potential and ecofriendly biosorbent for the treatment of toxic hexavalent chromium in aqueous solutions.



INTRODUCTION

Rapid increases in industrial progress consequently resulted in adverse pollution effects on the natural environment.¹ The industrial discharges without any appropriate treatment containing heavy metals represents a significant and long-term environmental hazard.² Heavy metals are nonbiodegradable, and probably may accumulate in microorganisms, aquatic flora and fauna, which in turn may enter into the human food chain and result in significant danger to human health.³

Chromium, one of the most highly toxic heavy metal pollutants in wastewaters, is widely used in a variety of industries, such as pharmacy, electro-

plating, tanning, metallurgy, battery, textile and catalyst synthesis.^{4,5} Chromium exists in two oxidation states, hexavalent Cr(VI), and trivalent Cr(III) and the toxicity of chromium depends upon its oxidation state.⁶ Therefore, due to its high toxicity it is necessary to reduce Cr(VI) to acceptable levels before discharging it into the environments. The maximum concentration limit set by World Health Organization (WHO) for hexavalent chromium for discharge to surface waters is 0.1 mg/L and, in potable water, it is 0.05 mg/L.⁷ Different techniques have been used to reduce the Cr (VI) concentration of the industrial wastewater to the permissible level, such as chemical precipitation, ion exchange, reduction,

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electrochemical precipitation, solvent extraction, electro dialysis and adsorption.^{8,9} However, high chemical and energy requirement, generation of toxic by-products and incomplete removal limits the wide applicability of these treatment techniques.¹⁰ The biosorption technique is the most preferred methods to remove heavy metals due to its high efficiency and low cost,¹¹ it is considered an interesting alternative to operate mainly using economical and eco-friendly biomaterials.¹² In recent years, special attention has been focused towards valorization of many agricultural or industrial wastes for their uses in adsorption treatment. These wastes can be used raw¹³ or treated (physically or chemically).¹⁴ Agricultural by-products exist in large amounts, which represent consequently a solid pollutant to the environment. In recent years, peach stones have been used raw¹⁵ or treated¹⁶ for the removal of heavy metals and organic pollutants from aqueous solution. This study deals with the biosorption ability of raw peach stones for the removal of chromium from synthetic aqueous solutions and the possibility of regenerating the adsorbent and metal recovery.

EXPERIMENTAL

1. Preparation and characterization of biosorbent (RPS)

The adsorbent used in this study was prepared from agricultural waste biomass: peach stones. The collected raw peach stones, were first washed several times with tap water to remove the adhering impurities followed by distilled water, after drying in an oven at 110°C for 24h they were crushed and sieved to desired particle size (0.315–1 mm), finally, the resulting material obtained without any physical or chemical treatment was named as RPS and stored in a desiccator for use in adsorption studies. The characterization of the prepared adsorbent (RPS) is an important factor to explain the mechanism of biosorption process for removal of Cr(VI) from aqueous solutions. Different techniques were used for the adsorbent characterization. The functional groups at the surface of the adsorbent were analysed before and after adsorption using Fourier Transform Infrared spectroscopy (Bruker ALPHA) at wavelengths in the range 400–4000 cm⁻¹. The morphology of the adsorbent was determined by scanning electron microscope (SEM). The crystallinity or amorphous structure of the used adsorbent was determined by X-ray diffractometer (XRD, Philips XPERT PRO) with CuK α radiation ($\lambda=1.54 \text{ \AA}$) generated at (45Kv, 20mA).

2. Preparation of Cr (VI) solution

A stock synthetic solution of chromium(VI) ions (1000 mg/L) was prepared by dissolving 2.8269 g of potassium dichromate K₂Cr₂O₇ (BIOCHEM chemopharma) in 1000 mL of distilled water. Experimental solutions of the desired concentrations were obtained by dilution of the stock solution. The initial pH of working solutions for biosorption experiments was adjusted to the desired value by adding hydrochloric acid HCl or sodium hydroxide NaOH (0.1M).

2.3. Batch biosorption experiments

The adsorbent prepared from raw peach stones was tested for the removal of Cr(VI) from aqueous solution in batch system. All batch experiments were carried out by mixing a fixed dose of RPS samples with 50 mL of Cr(VI) solution in a 100 mL beakers and agitated on a Heating magnetic-stirrer (IKA R5), for the determination of the optimal conditions on the removal efficiency of Cr(VI) various experimental parameters, such as pH (2–11), temperature (10°C–40°C), adsorbent dose (1–10 g/L), initial Cr(VI) concentration (10–100 mg/L), were investigated. After each experiment of adsorption, the solution was filtered and the residual concentration of Cr(VI) was determined by using spectrophotometer (UV-1800 SHIMADZU) at λ_{max} 540 nm after complexing with 1, 5-diphenylcarbazide in acidic medium.^{17,18}

The removal percentage (R %) and the biosorption capacity q_t (mg/g) of Cr(VI) by RPS were calculated using the following equations:

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 (mg/L) and C_t (mg/L) represent the concentrations initially and at time t respectively.

$$q_t = \frac{C_0 - C_t}{m} \times V \quad (2)$$

where V (L) is the solution volume, m (g) represents the mass of adsorbent, and also C_0 (mg/L) and C_t (mg/L) are the Cr(VI) concentrations initially and at time t respectively.

Furthermore, q_e (mg/g) is the amount of chromium adsorbed at equilibrium and is calculated from equation (2) when t is equal to the equilibrium contact time.

4. Desorption and regeneration of biosorbent

The desorption processes are important from two points of view: first, to recover the metal ion and its subsequent use in industrial field and, secondly, the reuse of the regenerated sorbent.¹⁹ The desorption experiments were carried out using the NaOH desorbing agent at different concentrations (0.1, 0.5, and 1.0 M) with stirring at 200 rpm for 24h. After a desorption process, the filtrates were analyzed to determine the Cr(VI) concentration and the percentage of desorbed Cr(VI) was calculated using the following expression:

$$\% \text{Cr(VI)desorbed} = \frac{\text{amount}_{\text{des}}}{\text{amount}_{\text{ads}}} \times 100 \quad (3)$$

where $\text{amount}_{\text{des}}$ is the amount of Cr(VI) desorbed and $\text{amount}_{\text{ads}}$ is the amount of Cr(VI) adsorbed.

RESULTS AND DISCUSSION

1. Characterization of the RPS biosorbent

In order to understand the adsorption of Cr(VI) onto RPS, physicochemical characterization of the adsorbent was carried out. The morphology of the raw peach stones biosorbent presented in Fig. 1 was observed by using scanning electron microscopy (SEM). The representative SEM figures show that

the external surface of RPS presents irregular porous nature structure. This porosity was formed during the oven-heating step in the preparation of the adsorbent.²⁰ Based on the surface morphology results of the RPS, it is suggested that the raw peach stones can be an effective adsorbent.

The crystalline or amorphous nature of the RPS biosorbent was performed by X-ray diffraction analysis (XRD), the spectrum presented in Fig. 2 shows the presence of major peak at $2\theta = 21.9^\circ$, corresponding to the (200) crystallographic plane. The XRD result shows characteristic wide reflections of cellulose I (card NO.PDF-2 03-0289).¹⁵

The FTIR spectrum of the RPS before and after biosorption of chromium illustrated in Fig. 3 shows a number of major absorption bands indicating the surface functional groups of the adsorbent. The

main absorption bands were observed at 3440, 2925, 1735, 1633, 1261 and 1047 cm^{-1} . The intense absorption band at 3440 cm^{-1} assigned to O-H stretching vibrations of phenol group of cellulose and lignin^{21,2}, the bands at 2854–2925 cm^{-1} are assigned to asymmetric and symmetric stretching vibrations of $-\text{CH}_2$ and $-\text{CH}_3$ cellulose groups.^{22,23} The bands at 1735, 1508, 1457, 1420, and 1047 cm^{-1} are attributed to the stretching vibrations of the aromatic ring stretching (C-C)/(C=C).^{24,25} The band at 1633 cm^{-1} correspond to the C=C stretching vibration of the aromatic ring structures.²³ However, band at 718 cm^{-1} is associated to the torsional vibrations of benzene t(C-H).¹⁵ The FTIR spectrum of the PS biomass after biosorption is very similar to the spectrum before biosorption.

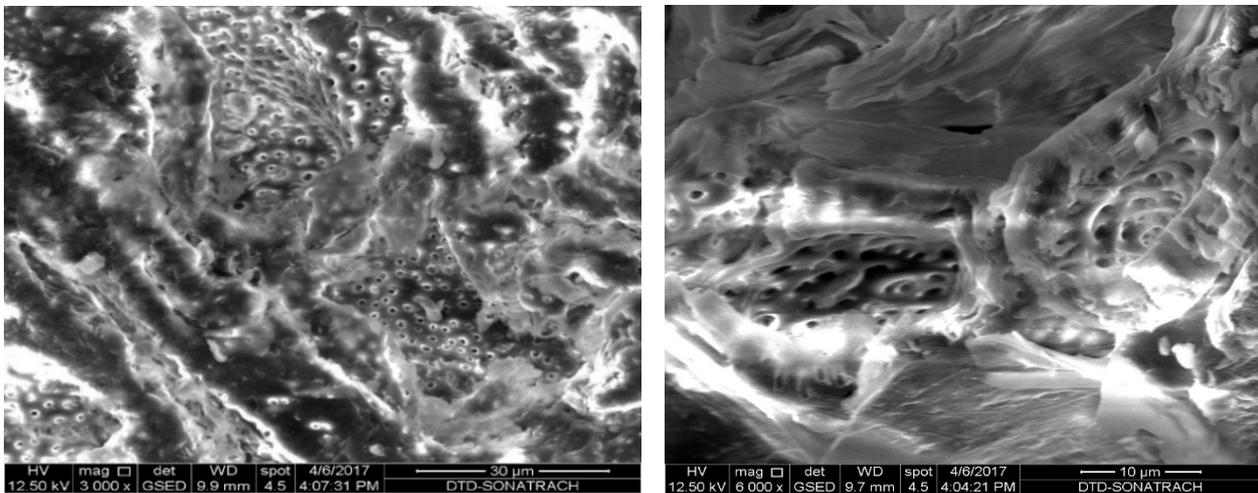


Fig. 1 – SEM images of the raw peach stones adsorbent.

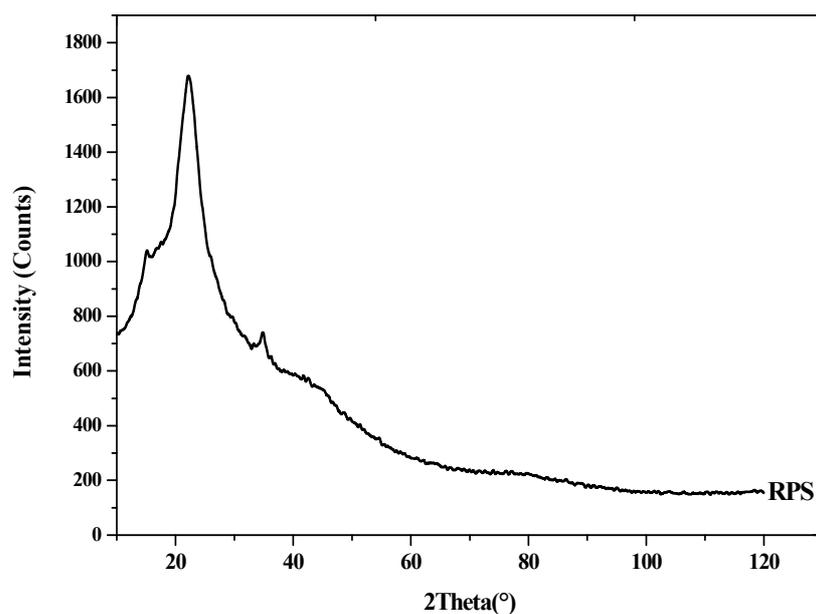


Fig. 2 – XRD pattern of the RPS biosorbent.

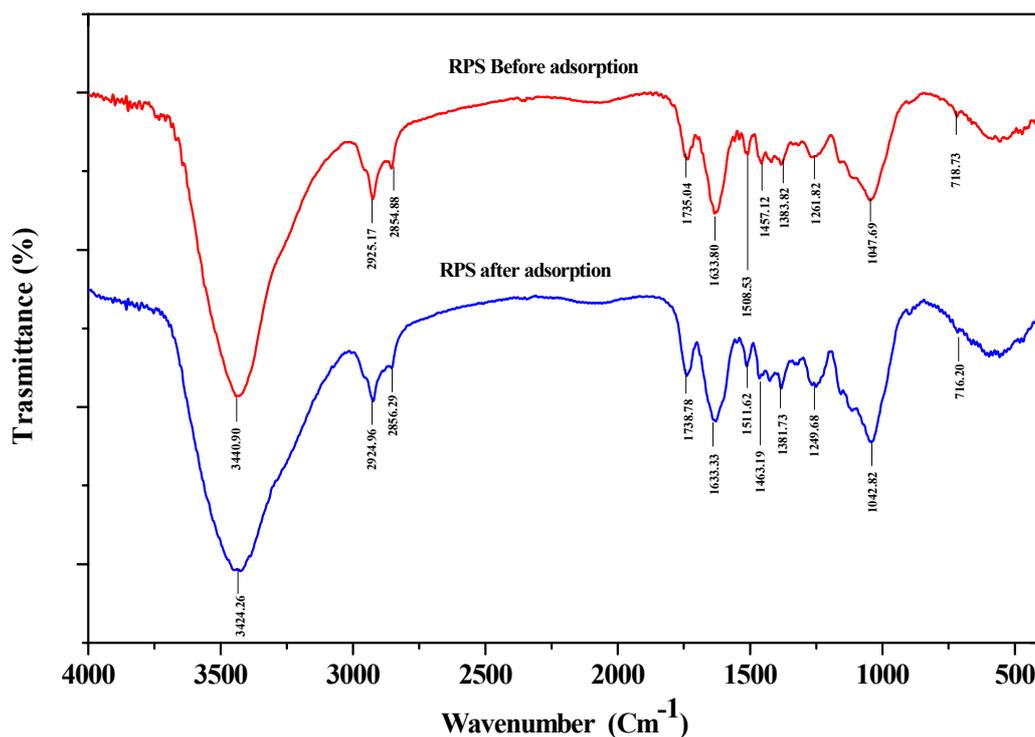


Fig. 3 – FTIR spectra of RPS before and after Cr(VI) adsorption.

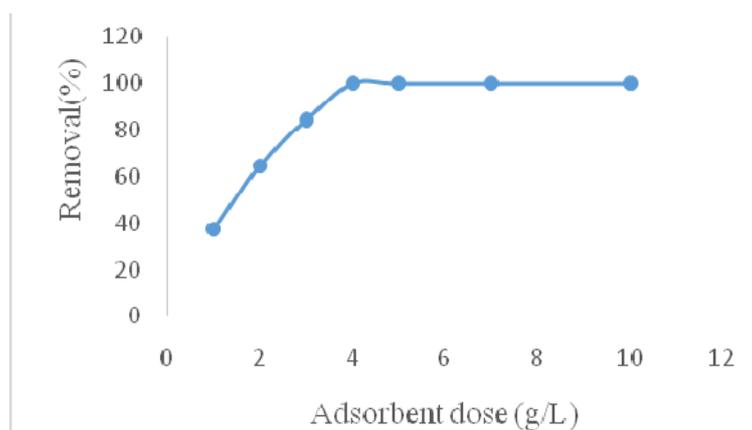


Fig. 4 – Effect of RPS dose on percentage removal of Cr(VI).

2. Biosorption process

Effect of adsorbent dose on Cr(VI) removal

The effect of biosorbent (RPS) dose on Cr(VI) adsorption from aqueous solutions was investigated using 1 to 10 g/L adsorbent dose at initial Cr(VI) concentration of 30 mg/L and pH of 2.0. The effect of adsorbent dose on Cr(VI) removal is shown in Fig. 4. Results show that the removal of Cr(VI) increases with increase in adsorbent (RPS) amounting up to 4 g/L. The increase in Cr(VI) percentage removal at higher adsorbent dose may be due to the fact that higher surface area is available for the adsorption process.²⁷ The optimal adsorbent dose of 4 g/L was

selected for further adsorption experiments in this study.

Effect of contact time and initial Cr(VI) concentration

The effect of contact time and the initial concentration is very important to assess the reaction kinetics. The effect of contact time on Cr(VI) removal by RPS was investigated at different initial Cr(VI) concentrations ranging from 10 to 100 mg/L at pH 2.0, optimal adsorbent dosage and temperature 30°C. The adsorption capacity increased with the increase of contact time for all concentrations. An increase in

adsorption capacity was observed from 2.48 to 17.91 mg/g with an increase in initial Cr(VI) concentration from 10 to 100 mg/L (Fig. 5a). Thus, the adsorption capacity is dependent on contact time and the initial Cr(VI) concentration. The increase in adsorption capacity of the RPS biosorbent with increasing Cr(VI) concentration was due to higher probability of collision between Cr(VI) ions and RPS biosorbent, increased driving force of the concentration gradient.^{28,29} As is seen in Fig. 5b, the percentage removal then depended upon the initial concentration. At contact time of 240 min (Equilibrium time), the percentage removal of Cr(VI) decreased from 100% to 71.65% with an increase of Cr(VI) concentration from 10 to 100 mg/L. The decline in the Cr(VI) percentage removal could be explained by the fact that with the increasing concentration, the binding sites of biosorbent are becoming saturated and no additional ions can be adsorbed.

Effect of initial pH solution on Cr (VI) adsorption

The pH of the aqueous solution is one of the most important controlling parameter in the

chromium biosorption process. It controls the surface properties of the biosorbent and adsorbate speciation. The plot of percentage removal of Cr(VI) represented in Fig. 6 shown that the Cr(VI) adsorption on RPS was strongly dependent on the initial solution pH. The maximum percentage chromium removal was 97 % at pH 2.0. This could be explained by the fact that Cr(VI) exists in HCrO_4^- predominant form at pH 2.0 and the adsorbent surface is also protonated and there is a strong electrostatic attraction between positively charged adsorbent surface and negatively charged HCrO_4^- . Thereafter, it was observed a drastic decrease in Cr (VI) adsorption percentage with an increase in pH solution. At higher pH the surface of adsorbent becomes negatively charged and also there is abundance of hydroxyl ions in aqueous solution^{11,6} resulting in the repulsive force between Cr(VI) anions and negatively charged biosorbent surface. Additionally, higher pH decreasing the removal may be explained by the competitive adsorption between chromate and hydroxyl ions. Therefore, a pH of 2.0 was taken as the optimum value for the rest of the experiments study and was in accordance with other work in the literature.^{30,31}

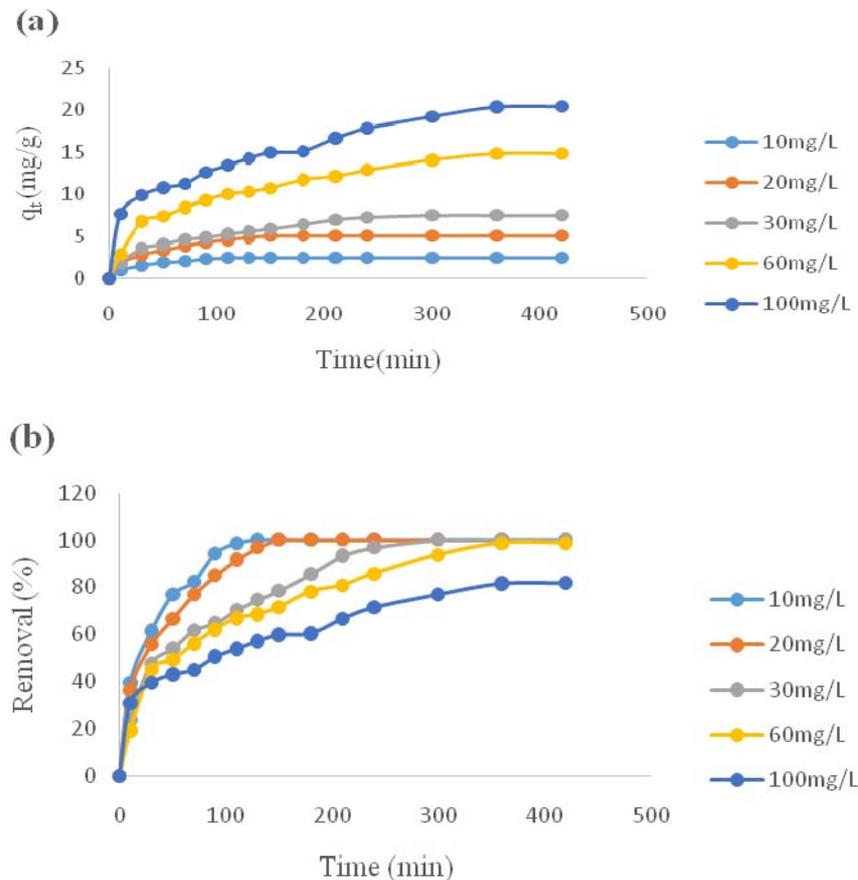


Fig. 5 – Effect of contact time and initial Cr(VI) concentration on adsorption capacity (a) and percentage removal (b) of Cr(VI) by RPS.

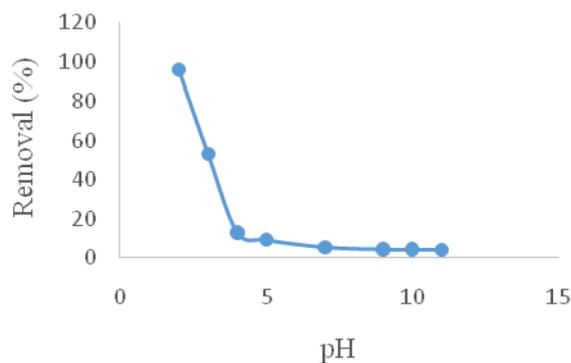


Fig. 6 – Effect of pH on the percentage removal of Cr(VI) by RPS.

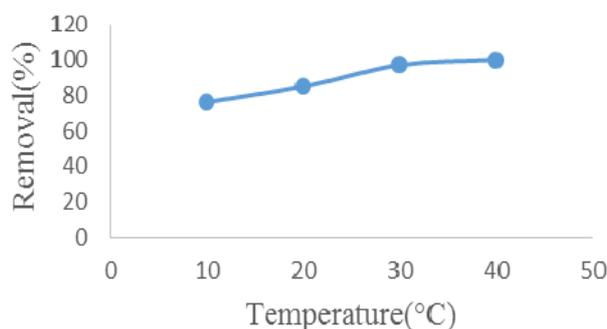


Fig. 7 – Effect of temperature on the removal of Cr(VI) on RPS.

Effect of temperature

The effect of temperature on the removal of Cr(VI) by RPS was studied at four different temperatures 10, 20, 30 and 40°C at pH 2.0 with initial Cr(VI) concentration (30mg/L). As shown in Fig. 7, chromium sorption percentage increased from 76.15 to 99.93% for increasing temperatures from 10 to 40°C. The increase in metal sorption with increase in solution temperature may be due to the increase in diffusion rate of Cr(VI) ions in the external mass transport process with temperature,^{32,33} and the increase in the number of the adsorption sites generated due to the internal bond breakage near the edge of the adsorbents' active surface sites.^{34,35} The increase in the adsorption with temperature may also explained by the relationship between the kinetic energies of the chromium ion and the active sites of the biosorbent.^{36,5} There is no significant change in adsorption percentage at 30 and 40 °C and hence, 30 °C is considered as optimum.

3. Kinetics of Cr(VI) adsorption

The kinetics of adsorption shows the relationship between rates of adsorption with its contact time. Several kinetic models can be used to

explain it. In this work the adsorption kinetics of Cr(VI) on RPS was evaluated using pseudo first-order (Eq 4)³⁷ and pseudo second-order (Eq 5)³⁸ models.

3.1. Pseudo-first order model

The pseudo-first order kinetic equation is expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

In this equation, q_t is adsorption quantity (mg/g) at time t , q_e is sorption capacity at equilibrium (mg/g), k_1 is kinetic rate constant for pseudo-first order (min^{-1}) and it was calculated from the plot of $\log (q_e - q_t)$ against t .

3.2. Pseudo-second order model

The linear form of pseudo-second order kinetic model equation is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t \quad (5)$$

where q_e and q_t are the amount of Cr(VI) that was adsorbed (mg/g) at equilibrium and at time t (min) respectively, and k_2 is the pseudo-second-order

rate constant of adsorption (g/mg min). The pseudo-second-order rate constants q_e and k_2 were calculated by plotting t/q_t versus t at different concentrations of Cr(VI).

The kinetic modeling of the experimental is shown in Fig. 8. All the obtained kinetic parameters calculated from linear plots and correlation

coefficient (R^2) values were represented in Table 1. Straight lines were achieved for all the initial concentrations based on the pseudo-first-order and pseudo-second-order models (Fig. 8(a) (b)). On comparison of R^2 values, it can be concluded that the adsorption of Cr(VI) ions onto the RPS followed the pseudo second order kinetic model.

Table 1

Adsorption kinetics parameters of Cr(VI) on RPS

C_0 (mg/L)	$q_{e e}$ (mg/g)	Pseudo-first order parameters			Pseudo-second order parameters		
		$q_{e c}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e c}$ (mg/g)	K_2 (g/mg.min)	R^2
10	2.482	3.001	0.0387	0.9083	2.9620	0.0134	0.9928
20	4.919	5.300	0.0272	0.9327	5.8893	0.0053	0.9890
30	7.27	6.778	0.0127	0.9236	8.4175	0.0022	0.9757
60	13.941	11.447	0.0094	0.9751	15.7233	0.0011	0.9863
100	21.457	16.248	2.3092	0.9570	22.8310	0.0007	0.9581

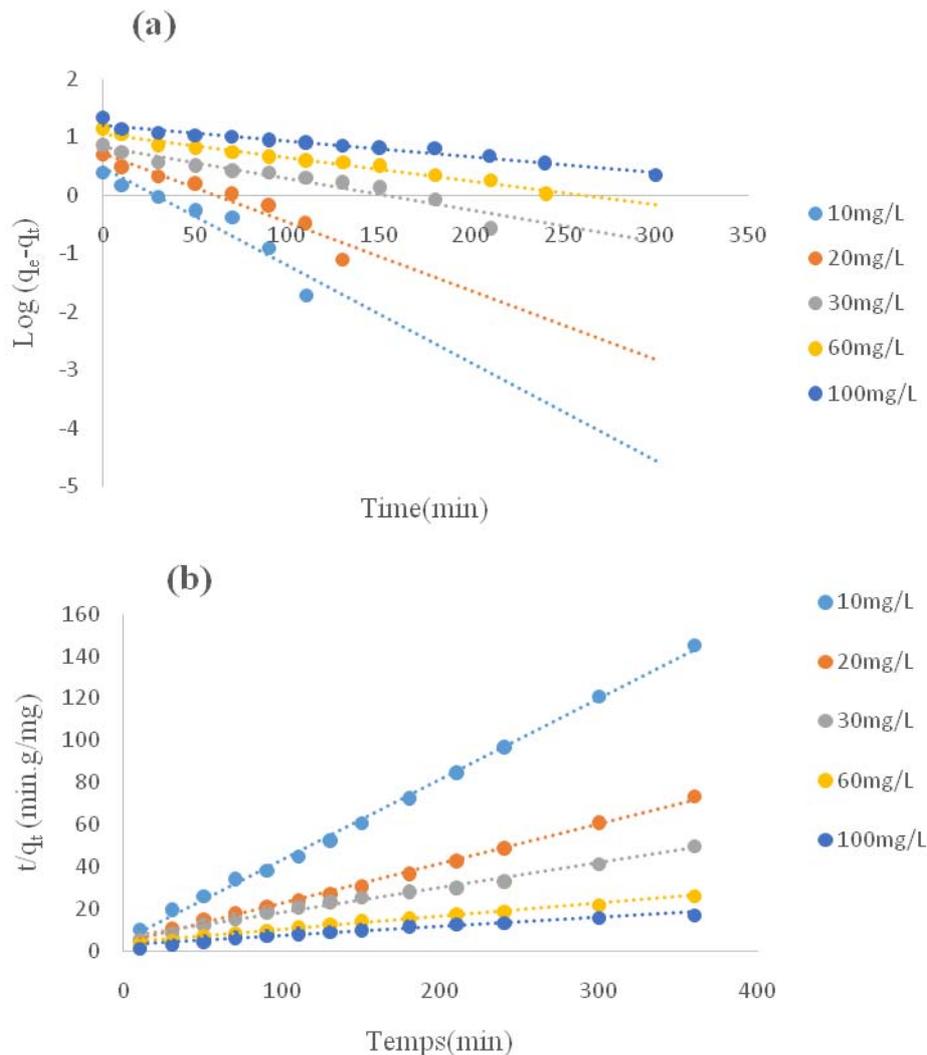


Fig. 8 – Kinetic models for Cr(VI) adsorption (a) pseudo first order, (b) pseudo second order.

4. Biosorption isotherm

Biosorption isotherm represents the relationship between adsorbed metal ion per unit weight of adsorbent (q_e) and residual concentration of metal ion in solution (C_e) at equilibrium.

Langmuir and Freundlich isotherm models were applied to investigate the biosorption process of Cr(VI) on RPS adsorbent at a constant temperature and the different isotherm constants and regression values determined were presented in Table 2.

4.1. Langmuir isotherm model

Langmuir adsorption isotherm model assumed that the uptake of adsorbate molecules occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed molecules.^{39,40}

The Langmuir isotherm model is given by the following equation:^{41,42}

$$\frac{C_e}{q_e} = \frac{1}{q_m \cdot K_L} + \frac{C_e}{q_m} \quad (6)$$

where, C_e (mg/L) is the equilibrium Cr(VI) concentration, q_e (mg/g) is the amount of Cr(VI) adsorbed at equilibrium, q_m (mg/g) is the maximum Cr(VI) adsorption capacity by the biomaterial and K_L (L/mg) is the Langmuir isotherm constant related to energy of adsorption. A plot of C_e/q_e versus C_e gives a straight line of slope $1/q_m$ and intercepts $1/(q_m \cdot K_L)$. The essential characteristics of the Langmuir isotherm, dimensionless separation factor R_L , defined by Weber and Chackravorti,⁴³ is expressed by the following equation:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (7)$$

The value of separation factor R_L indicate the type of isotherm: favorable ($0 < R_L < 1$, linear ($R_L = 1$) and irreversible ($R_L = 0$).

4.2. Freundlich isotherm model

The Freundlich model is an empirical equation based on the adsorption of adsorbate onto heterogeneous surface.^{44,42}

The linear logarithmic form of the Freundlich equation is expressed by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

where K_F ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) and n are the Freundlich constants indicating adsorption capacity and intensity.

The graph of $\log q_e$ versus $\log C_e$ was drawn to determine Freundlich constants K_F and n .

The plots of isotherms linearized of the Langmuir (a) and Freundlich (b) of Cr(VI) adsorption on RPS are presented in Fig. 9. From Table 2, the calculated value for R_L was found less than one confirmed favorability of Cr(VI) biosorption onto RPS under the conditions used in this study. The value of constant n obtained from the Freundlich isotherm model for RPS was greater than unity, indicated favorable nature of adsorption. The results showed that Freundlich isotherm gave the best fit for the chromium (VI) adsorption by RPS and was confirmed by high R^2 value (0.998).

3.5. Thermodynamic parameters of Cr(VI) adsorption

The thermodynamic parameters such as entropy change (ΔS), enthalpy change (ΔH) and Gibb's energy (ΔG) were determined to evaluate the feasibility and nature of Cr(VI) adsorption by adsorbent, using the following expressions.⁴⁵

$$\Delta G = -RT \ln K_c \quad (9)$$

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (10)$$

where R (8.314 J/mol K) is the gas constant, T (K), absolute temperature and K_c is the equilibrium constant defined by

$$K_c = \frac{C_0 - C_e}{C_e} \quad (11)$$

The values of ΔH and ΔS were calculated from the plot of K_c vs $1/T$ as shown in Fig. 10. The values of ΔH , ΔS and ΔG for the biosorption of Cr(VI) onto RPS at various temperatures are listed in Table 3. The positive value of ΔH confirmed the endothermic process of adsorption and that an increase in temperature favored the biosorption process. The negative values of ΔG show that the adsorption process is feasible and spontaneous. The ΔS value is positive, which suggested that the randomness increased at solid- solution interface during the adsorption of Cr(VI) on the RPS.

Desorption study

Desorption experiments was carried out using different concentrations of NaOH desorbing agent. The percentage of Cr(VI) desorbed with 0.1,0.5, and 1M NaOH were:11.91 %, 45.83% and 57.89 respectively. The desorption results indicated that a higher concentration of NaOH is more favorable for attaining the better desorption percentage.

CONCLUSION

RPS was found to be an effective low-cost biosorbent for the removal of toxic hexavalent

chromium from aqueous solution. Utilization of the biomaterial without any physical or chemical treatment is important from both environmental and economical viewpoints and is one of the important features of this study.

The main conclusions of the results obtained of Cr(VI) adsorption on RPS are summarized as follows:

The FTIR analyses showed presence of significantly functional groups on the RPS surface.

The optimum pH for maximum Cr(VI) removal was 2, and the percentage removal of Cr(VI) at higher pH decreases dramatically.

Table 2

Constants of Langmuir and Freundlich for Cr(VI) adsorption on RPS

Langmuir isotherm			Freundlich isotherm			
q_m (mg/g)	K_L	R_L	R^2	n	K_F (mg/g)	R^2
23.256	0.636	0.0498	0.979	2.445	7.501	0.998

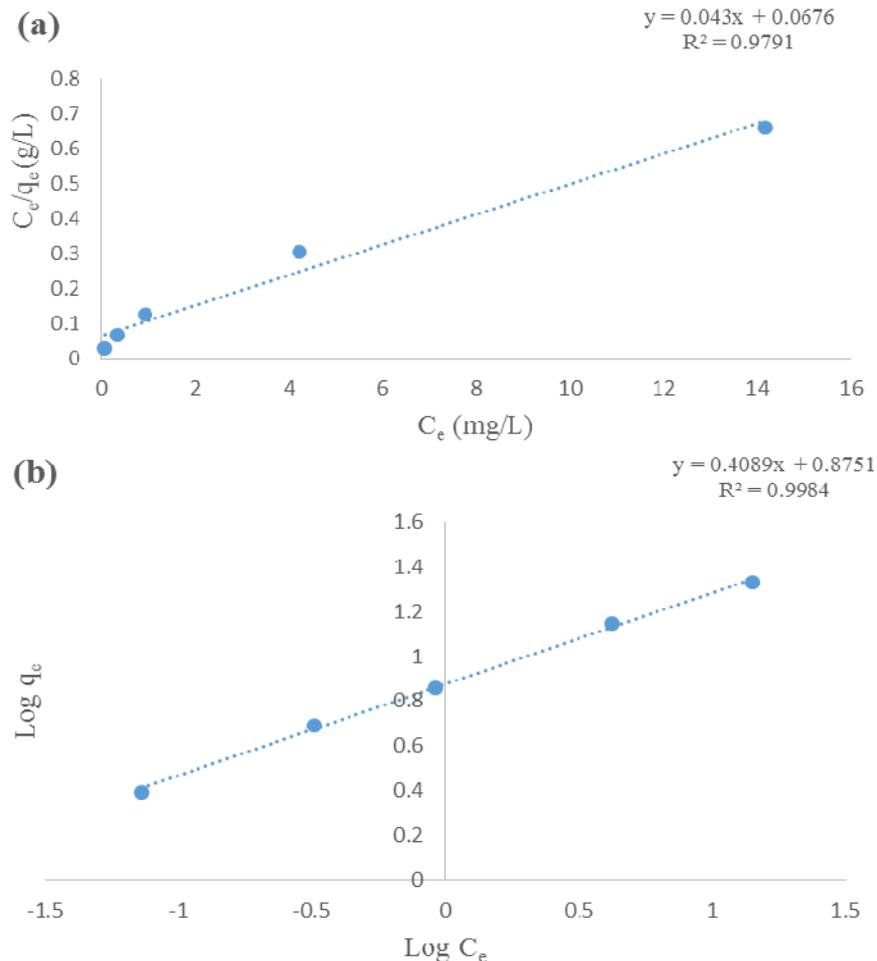


Fig. 9 – Plots of adsorption isotherms (a) Langmuir and (b) Freundlich.

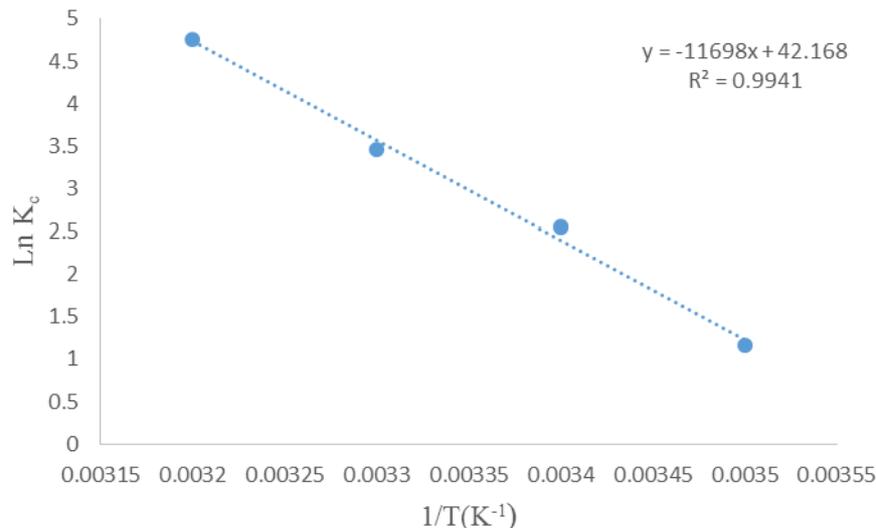


Fig. 10 – Plot of $\ln K_c$ versus $1/T$ for Cr(VI) adsorption on RPS.

Table 3

Thermodynamic parameter values for Cr(VI) adsorption on RPS

T(K)	283	293	303	313	ΔH (kJmol ⁻¹) = 97.257
ΔG (kJmol ⁻¹)	-1.793	-5.293	-8.793	-12.293	ΔS (kJmol ⁻¹ K ⁻¹) = 0.350

The adsorption equilibrium was well explained by the Freundlich isotherm and the pseudo second order kinetics with satisfactory values of R^2 .

The negative ΔG and the positive ΔH indicated the spontaneous and endothermic nature of the Cr(VI) adsorption process onto investigated biosorbent.

The highest chemical regeneration percentage was obtained in alkaline conditions (1 M NaOH) and the RPS was recycled successfully.

Further, it can be concluded that RPS is a good potential, inexpensive and eco-friendly biosorbent for the removal of Cr(VI) from aqueous solution.

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