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ORIGINAL ARTICLE

Potentiality of mosambi (*Citrus limetta*) peel dust toward removal of Cr(VI) from aqueous solution: an optimization study

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Abstract

Heavy metal has become a public health concern because of its tendency to accumulate in living organisms. The biosorptive removal of hexavalent chromium (Cr(VI)) from aqueous solution was investigated by using waste mosambi peel dust, and response surface methodology was applied as optimizing technique. The adsorbent was characterized by pH_{ZPC}, scanning electron microscope and Fourier transform infrared spectroscopy. The optimize condition for removal of Cr(VI) was recorded as follows: pH 2; dose: 0.5 g/50 mL; initial concentration: 5 mg/L; contact time: 30 min; agitation speed: 150 mg/L. The significance of independent variables and their interactions were tested by the analysis of variance and t test statistics. The adsorption data are nicely fitted with D–R isotherm and followed pseudo-second-order kinetic model. The monolayer adsorption capacity was recorded as 3.623 mg/g. Finally, thermodynamic results demonstrated that Cr(VI) adsorption is endothermic in nature and spontaneous. Therefore, the present results highlighted that mosambi peel dust is an efficient adsorbent and its versatility represents an eco-friendly alternative that can be implemented as agricultural waste management.

Keywords Biosorption · Hexavalent chromium · Response surface methodology · Isotherm study · Kinetics study · Thermodynamics

Introduction

The existence of heavy metal in the effluent is a tremendous problem for both terrestrial and aquatic community (Wang et al. 2011). There are number of industries such as tannery, leather, chrome plating, ceramics which discharge a significant amount of hexavalent chromium into the environment (Mutongo et al. 2014). When significant amount of chromium enter the human body, it may damage mainly kidney and liver for human being (Achmad et al. 2017). However, low level of chromium may also cause skin irritation, nose bleeding, respiratory track infection, etc. (Zhang 2009). The two main oxidation states of chromium are available in liquid medium; one is Cr(III) and other is Cr(VI). Moreover, out of these two oxidation state, Cr(VI) is thermodynamically more stable and highly mobile than Cr(III) (Mondal and Basu 2019; Ali et al. 2016). Although the form of Cr(VI) is different in different pH medium as chromate (Cr_2O_4), hydrochromate ($HCrO_4^-$) or dichromate (AL-Othman et al. 2012). Many techniques are available for removal of heavy metal an from aqueous solution such as ion exchange, electrodialysis, precipitation, adsorption, ultra-filtration, reverse osmosis; however, only adsorption technique is most suitable one because of its excellent performance and low operating cost (Mondal et al. 2019a; Mondal and Roy 2016).

Many low-cost materials have been used by the earlier researchers for removal of Cr(VI) from aqueous solutions such as *Aspergillus niger* (Mondal et al. 2017); banana peel (Ali et al. 2016); potato peel (Mutongo et al. 2014); human hair (Mondal and Basu 2019); groundnut hull (Owalude and Tella 2016); lychee peel (Rao et al. 2012); chicken feather (Mondal et al. 2019b), etc; however, none of the adsorbent showed high adsorption capacity. Therefore, a new easily available adsorbent should be developed for the fulfillment of the above objective.

In traditional optimization process, one independent variable change while maintaining other variables fixed which

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is time-consuming and laboratories take for a large number of independent variables. To overcome the above problem, response surface methodology (RSM) has been introduced for biosorption of hexavalent chromium from aqueous solution (Mondal et al. 2019b; Bhaumik and Mondal 2016).

In the present study, mosambi peel has been selected as a new low-cost biosorbent for the abatement of Cr(VI) from aqueous medium. Finally, the optimization of Cr(VI) removal was done by response surface methodology (RSM) using Design Expert Version 8.0.7.1. The experimental data were analyzed by fitting to a secondary polynomial model which again validated by analysis of variance (ANOVA) and lack-of-fit test.

Mosambi tree (*Citrus limetta*) is under the category of citrus species of the family *Rutaceae* (Yonis et al. 2015). It is native to the South Asia and Southeast Asia and also cultivated in the Mediterranean Basin. It is a small tree which may reach 8 m in height. It possesses numerous thrones throughout the tree. The skin of the tree is light yellow at maturity. The peels of mosambi have high pectin content which is a good antidote to blood sugar and cholesterol (Baker 1994). Moreover, mosambi peel contains many phytochemicals that are effectively used in pharmaceutical industry for drugs or food supplements (Middleton et al. 2000).

Materials and methods

Collection and preparation of mosambi peel

The mosambi peel was first washed thoroughly with deionized water. The soluble colored components of mosambi peel dust were then removed by washing repeatedly with hot deionized water. The peel was then dried at 70 °C for 24 h. The dried peel was then crushed, passed through a 50–300 sieve and stored in polythene bottles (Fig. 1).

Determination of pH_{ZPC}

The point of zero charge of the adsorbent was determined by the solid addition method. A 50 mL of 0.1 M KNO_3 solution transferred into a series of 100 mL conical flask. The initial pH values of the solution were adjusted from 1.0 to 10.0 by adding either fixed strength of HNO_3 (0.05, 0.1 and 0.5 N) or 0.1 N KOH. Then, 0.15 g of chicken feather, 1.5 g of mosambi peel and 1 g of human hairs were added to each flask which was securely capped immediately (Bhaumik et al. 2017). The flasks were then placed into a constant temperature water bath shaker and shaken for 24 h. The pH values of the supernatant liquid were noted after 24 h.

Fig. 1 Mosambi peel dust

Sample preparation for SEM and FTIR study

After carrying out all the optimum experimental condition, adsorbents were filtered and dried at normal room temperature and finally analyzed their characteristics (Mondal and Kar 2018).

Metal solution preparation

An aqueous stock solution of chromium ions was prepared using potassium dichromate by dissolving 0.2828 g potassium dichromate ($K_2Cr_2O_7$) in 250 mL of deionized water and dilute to 1 L in a volumetric flask with double-distilled water (100 mg/L). pH of the solution was adjusted using 0.1 N HCl or NaOH. Fresh dilutions were used for each sorption study.

Batch experiments for mosambi peel

Batch experiments were carried out in 100 mL conical flask containing 5 mg/L of chromium solution. 1.5 g of mosambi peel dry dust and 5 mg/L of 50 mL chromium solution were taken in each 250 mL conical flask. The desired pH of the respective solutions was maintained by adding 0.5 (N) HNO_3 and/or 0.1 (N) NaOH. The contact time for each solution was maintained for 30 min. The stirring rate of the contact between solution and adsorbent was maintained at 150 mg/L; the particle size is 300 µ, and the temperature for all experiment, except temperature variation, was fixed at 40 °C.

Adsorption experiments were conducted in different batches where the pH, adsorbent dose, stirring rate, contact time, particle size, initial chromium concentration and temperature were changed. In these experiments,

parametric ranges were done by changing pH from pH 1 to 10, adsorbent dose: 0.01 g to 1.5 g, stirring rate 150 mg/L to 350 mg/L, contact time: 1–40 min, particle size 50 µ to 300 µ, initial fluoride concentration: 5–30 mg/L and finally changes in temperature range from 30 to 55 °C. Influence of various operating parameters was studied by varying are parameter at a time and keeping the others constant. This is a serial adsorption process where the best removal of chromium for a parameter can be screening out and fixed the value of that parameter followed the next experiment. Then, the chromium was analyzed by spectrophotometer.

Metal analysis

Hexavalent chromium was form complex with 1–5 diphenyl carbazide, and final purple color was measured by UV spectrophotometer. The percentage of Cr(VI) removal was measured by using the following Eq. (1).

$$\text{Percentage removal of Cr (VI)} = \frac{c_{\text{initial}} - c_{\text{final}}}{c_{\text{initial}}} \times 100 \quad (1)$$

where c_{initial} and c_{final} are the concentrations of Cr(VI) at the beginning and at the end of the adsorption process.

Model study

Various response surface methodologies are central composite; Box–Behnken and Doehlert have been extensively used in experimental design.

In the Box–Behnken design, total number of experiment can be calculated according to the following Eq. 2:

$$N = k^2 + x + c_{\text{p}} \quad (2)$$

where k is the factors numbers, C_{p} is the replicate number of the central point.

This design has been used for fitting in a second-order polynomial Eq. 3:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i \right)^2 + \left(\sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \right) + \varepsilon \quad (3)$$

where Y is the predicted response, b_0 is the constant coefficient, This linear coefficient of the input factors X_i, b_{ii} is the liner interaction coefficient between the input factors X_i and X_j, and b_{ij} is the interaction coefficients of the input factors Xi (Sen et al. 2017).

Results and discussion

Adsorbent characterization

Mosambi peel dust showed very sharp bands at 3338 cm^{-1}, 2918 cm^{-1}, 2360 cm^{-1}, 1604 cm^{-1}. These bands attributed the functional groups such as alcoholic –O–H, –C–H, –P–H and –C=O stretching vibration (Fig. 2a). But after Cr(VI) adsorption, the active functional groups of the mosambi peel dust showed very nominal changes at 2360 cm^{-1}, 1604 cm^{-1} and 1051 cm^{-1} and the changes in stretching frequency are 2362 cm^{-1}, 1641 cm^{-1} and 1016 cm^{-1}, respectively (Fig. 2b). This information clearly suggests that the functional groups –O–H, phosphoric –P–H and –C=O definitely form some kind covalent bonding with Cr(VI) ions (Saha et al. 2013).

SEM study

Scanning electron microscopy is a valuable technique to understand the surface morphology of the adsorbent. The present study results depicted that mosambi peel dust has

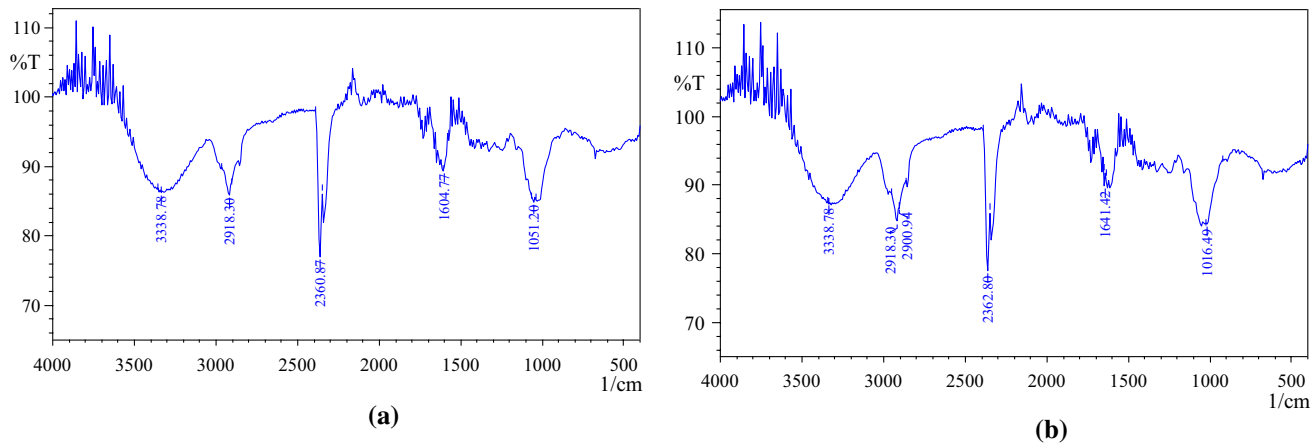

Fig. 2 a FTIR of mosambi peel dust before Cr(VI) adsorption **b** FTIR of mosambi peel dust after Cr(VI) adsorption

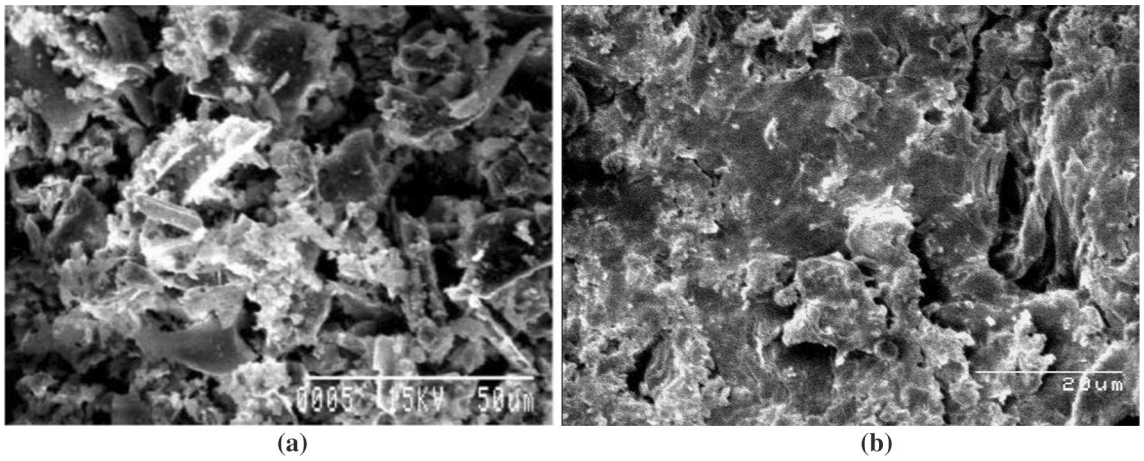

Fig. 3 **a** SEM of mosambi peel dust before Cr(VI) adsorption (1500×) **b** SEM of mosambi peel dust after Cr(VI) adsorption (1500×)

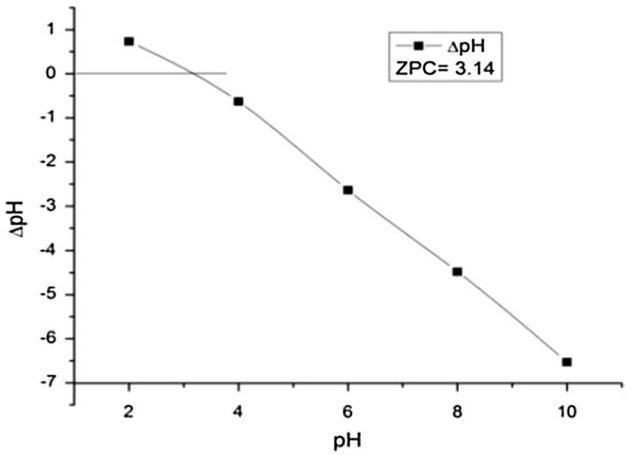

Fig. 4 pH_{ZPC} of mosambi peel dust

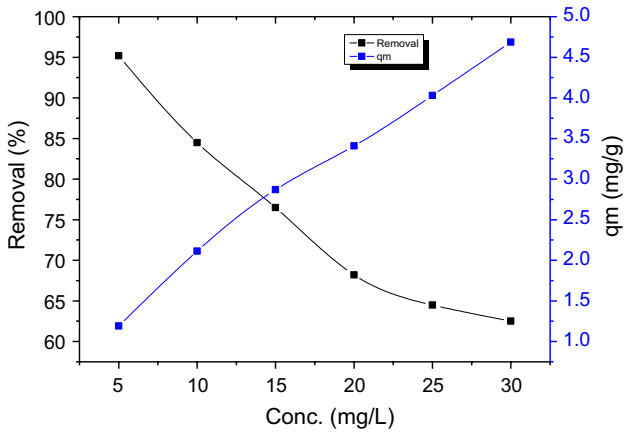

Fig. 5 Effect of initial concentration of Cr(VI)

numerous rough surface morphology (Fig. 3a) (Mondal and Roy 2018). However, after removal of Cr(VI), the surface of the mosambi peel dust is smooth enough which perhaps due to accumulation of Cr(VI) onto the surface of mosambi peel dust (Fig. 3b).

pH_{ZPC} study

Point of zero charge (pH_{ZPC}) is valuable parameter which helps to identify the availability of H^+ or OH^- ions on the surface of the adsorbent (Mushtaq et al. 2014). The present result depicted that mosambi peel has zero charge at pH 3.14 (Fig. 4). Therefore, removal of Cr(VI) is favorable below 3.14 pH, and the results of the present study also indicate that maximum Cr(VI) removal occurred at pH 1.0. This can be attributed by the fact that under such acidic condition chromium may exist as $HCrO_4^-$ (Siboni et al. 2011). However, at alkaline pH, the dominant species is CrO_4^{2-} and $Cr_2O_7^{2-}$ which may repel by the negative surface. Almost similar observation was reported by Mondal et al. (2018).

Effect of initial concentration

In order to find out the best removal of Cr(VI) under the influence of different initial concentration of Cr(VI) fixed pH (2), dose (0.2 g), contact time (30 min), stirring rate (150 mg/L) and temperature (40 °C) was studied and it is presented in Fig. 1. Results revealed that percentage of Cr(VI) removal decreased from 94.6 to 22.11%, when initial concentration increased from 5 to 15 mg/L. However, after 15 mg/L, removal of Cr(VI) increases and reached to 45.89% at 30 mg/L (Fig. 5). From Fig. 5, it is also clear that adsorption capacity of the mosambi peel is 1.183 at higher percentage (94.6%) of the Cr(VI) removal. Almost similar variation of Cr(VI) removal by banana peel dust and orange peel dust was reported by earlier researcher (Pakshirajan et al. 2013).

Effect of adsorbents dose

Effect of adsorbent dose was carried out from 0.01 to 1.5 g under constant initial concentration (5 mg/L); pH (1); contact time (30 min) and temperature (40 °C). This indicates that percentage of Cr(VI) removal increases from 43.78 to 99.58% with increasing adsorbent dose from 0.01 to 0.5 g (Fig. 6). The percentage of Cr(VI) removal increased with increasing adsorbent dose is probably due to increase in surface area (Srividya and Mohanty 2009). However, adsorption capacity (mg/g) changes from 10.945 to 0.249 (mg/g) when percentage of removal gradually increased from 43.78 to 99.58% (Fig. 6). This can be attributed by the fact that freshly added adsorbent can make slight cover over some active sites.

Effect of pH

pH is a very important factor for adsorption of Cr(VI) from aqueous solution (Gupta et al. 2001). The present experiments were performed on 50 mL solution of 5 mg/L Cr(VI) and 0.2 g mosambi peel dust at 30 °C with varying pH from 1 to 10. The pH of the solution adjusted by using 0.1 (N) HCl or NaOH. The entire results are presented in Fig. 7. Study results revealed that removal of Cr(VI) gradually decreases with increasing pH of the solution from highly acidic to alkaline. Results indicate that 95.02% Cr(VI) was removed at pH 1. However, when pH of the solution changes to 4, 6, 8 and 10, the removal drastically changes to 41.92%, 40.96% and 29.7% and 13.26%, respectively. The higher removal of Cr(VI) at lower pH is possible due to electrostatics attraction between positive mosambi peel dust and chromium(VI) ions (Mondal et al. 2018). The metal biosorption can largely depend on the ionic functional groups available on the surface of the adsorbents and metal chemistry in the solution (Park et al. 2005). However, at higher pH, the entire surface of the adsorbents becomes negative and Cr(VI) removal

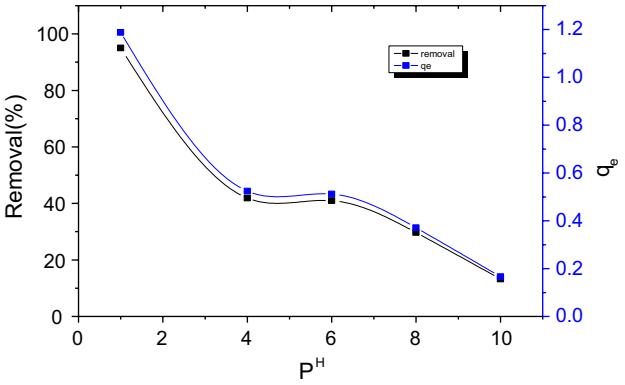

Fig. 7 Effect of pH

decreased (Khambhaty et al. 2009). A possible interaction between Cr(VI) and main chemical constituents of mosambi peel is demonstrated in Figure S1.

Effect of contact time

In adsorption chemistry, it is important that the solution be allowed appropriate time to attain equilibrium (Srividya and Mohanty 2009). Figure 8 demonstrates the effect of various time interval on removal of Cr(VI) from aqueous solution, with constant of other variables such as initial concentration (5 mg/L), pH (1), adsorbent dose (0.5 g) and temperature (40 °C). Figure 8 clearly reveals that percentage of Cr(VI) removal increase with increasing contact time. However, throughout the experimental time period, there is a lack of consistency in removal of Cr(VI) by mosambi peel. Moreover, it was also noted that the rate of Cr(VI) binding with the mosambi peel is more at initial stages, which gradually decreases and become almost constant after an optimum period of 30 min. Almost similar finding was reported by (Mohanty et al. 2006).

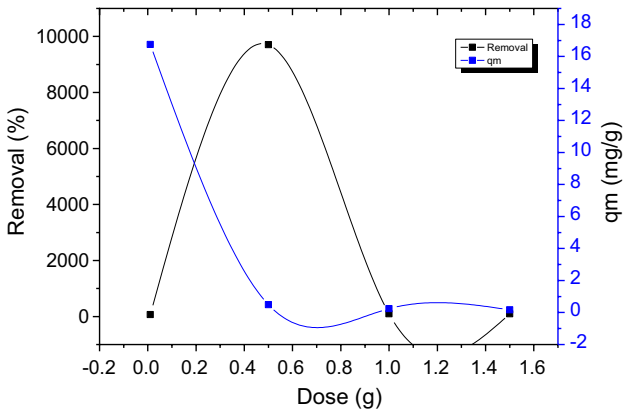

Fig. 6 Effect of adsorbent dose (g)

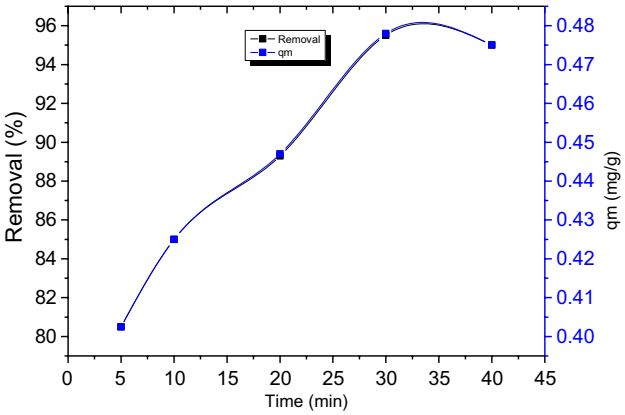

Fig. 8 Effect of contact time (min)

Effect of temperature

The study of temperature on the adsorption study is extremely important for understanding the enthalpy and entropy changes during adsorption (Alkan and Dogan 2003). Moreover, temperature is the valuable indicator to understand the exothermic or endothermic nature of adsorption process (Salleh et al. 2011). The present study results are presented in Fig. 9. Figure 9 clearly indicates that Cr(VI) removal gradually increases with increasing temperature from 30 to 45 °C. However, after 45 °C, removal again decreases. Therefore, it can be suggested that the removal of Cr(VI) by mosambi peel is an endothermic process. Almost similar observation was reported by Mondal et al. (2019a, b) for removal of Cr(VI) from aqueous solution by chicken feather. The previous literature (Senthilkumar et al. 2006) also suggested that the enhancement at adsorption capacity at higher temperature is probably due to enhancement of adsorbent pore size and activation adsorbent surface.

Isotherm study for mosambi peel

On the basis of experimental results, biosorption isotherm was used to understand the interaction pattern of Cr(VI) with mosambi peel, at equilibrium (Chattoraj et al. 2018). The Langmuir model was based on the assumption that the adsorbate only attached to the specific sites of the adsorbent surface, suggesting that the uptake of absorbate is absolutely uni-layer without interaction between adsorbate molecules. The following form of Langmuir equation is traditionally applied (Eq. 4):

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{4}$$

Equation (4) can conveniently transform to the following linearized form (Eq. 5):

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{5}$$

where q_m in the maximum uptake (mg/g), q_e the uptake capacity at equilibrium (mg/g), C_e the equilibrium solution concentration (mg/L), b the Langmuir constant (L/mg). Figure 7 depicts the Cr(VI) adsorption by mosambi peel at constant temperature. The output of Langmuir constant (q_m and b) and correlation coefficient (R^2) is presented in Table 1. As can be seen from Table 4, the adsorption isotherm of Cr(VI) exhibited Langmuir behavior, which indicates a monolayer adsorption. The adsorption of Cr(VI) by human hair is well fitted with both Freundlich and Langmuir models; therefore, the Langmuir–Freundlich equation was also applied to the data sets. Basically, combined equation of Langmuir–Freundlich is known as Sips model. The Langmuir–Freundlich model was analyzed by Sips who observed that the energy distribution function corresponds to a symmetrical quasi-Gaussian function (Sips 1948). At lower concentration, Sips model changes to Freundlich model and in the case of a homogeneous surface, it reduces to the Langmuir model. The Langmuir–Freundlich equation can be expressed in the following way (Eq. 6):

$$q_e = \frac{q_s b_s C_e^{\frac{1}{n}}}{1 + b_s C_e^{\frac{1}{n}}} \tag{6}$$

This equation can be easily linearized as (Eq. 7):

$$\ln\left[\frac{q_s}{q_e} - 1\right] = -\ln b_s - \frac{1}{n_s}\ln C_e \tag{7}$$

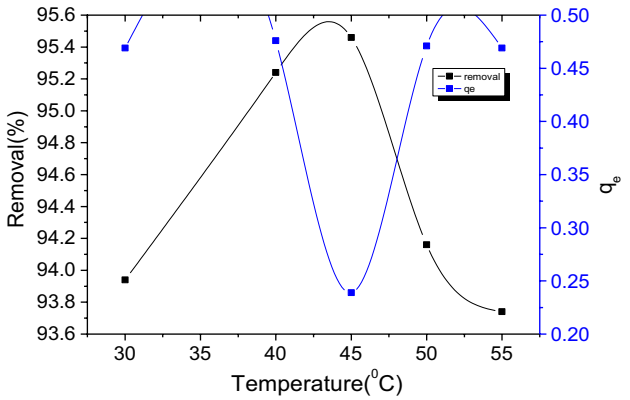

Fig. 9 Effect of temperature

Table 1 Isotherm date for Cr(VI) adsorption using mosambi peel

Adsorption isotherm	Equations	Parameters	Values	R^2
Langmuir isotherm	$\frac{1}{q_e} = \frac{1}{q_{max} K_L C_e} + \frac{1}{q_{max}}$	q_{max} K_L	3.623 0.504	0.924
Freundlich isotherm	$\log q_e = \log K_F + \frac{1}{n}\log C_e$	K_F (mg/g)(L/mg)$^{1/n}$ n	1.918 1.085	0.412
D–R isotherm	$\ln q_e = \ln q_{max} - \frac{1}{2E^2} * \left[RT \ln\left(1 + \frac{1}{C_e}\right)^2\right]$	q_{max} E (kJ/mol)	2.053 3.654	0.802

Table 2 Summary of parameters for various kinetic models by mosambi peel

Kinetics model	Equations	Parameters	Values	R^2
Pseudo-first order	$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}$	q_e (mg/g) K_1 (min^{-1})	3.592 71.025	0.885
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}$	q_e (mg/g) K_2 (g mg^{-1} min^{-1})	2.331 0.128	0.999
Intraparticle diffusion	$q_t = K_1 t^{\frac{1}{2}} + C$	K_1 ($min^{-1/2}$) C	50.10 17.98	0.925

Kinetics study for mosambi peel

To predict the kinetics of Cr(VI) adsorption by mosambi peel, pseudo-first-order (Lagergren), pseudo-second-order (Ho and Mekay 1999) and intraparticle diffusion kinetics models were used to fit the experimental data (Table 2). The values of q_e and k_2 can be determined from the slope and intercept of the plot (plot not shown) (Roy and Mondal 2017). From Table 2, it is clear that the experimental data well fitted with pseudo-second-order kinetics model with very high correlation coefficient ($R^2 = 0.997$).

On the other hand, pseudo-first-order and intraparticle diffusion model are moderately fitted with the experimental data (Table 2). These results suggest the adsorption on to the adsorbent at specific temperature was best presented by the pseudo-second-order equation, which is based on the assumption that the rate-limiting step may be the chemisorption (Aksu 2001).

Thermodynamic study for mosambi peel

The thermodynamic parameters for the obtained equilibrium data on temperature variation by the use of Eqs. (8–9) were evaluated. The equilibrium constant K_c was calculated based on C_{Ae} and C_e values (Eq. 8):

$$K_c = \frac{C_{Ae}}{C_e} \tag{8}$$

where C_{Ae} indicates adsorption in mg/L at equilibrium and C_e is the equilibrium concentration of the metal in mg/L. The respective values of other thermodynamic parameters such as ΔH° and ΔS° were obtained from the slope, and interpret of the plot of log K_c against $1/T$ (Eq) revealed the values of free energy (ΔG°) at different temperatures were obtained using Eq. 9.

$$\log K_c = \frac{\Delta S^\circ}{2.303RT} - \frac{\Delta H^\circ}{2.303RT} \tag{9}$$

where T is the temperature in Kelvin and R is the gas constant (kJ mol^{-1} K^{-1}).

The entire results for the thermodynamic parameters are presented in Table 3. From Table 3, it is clear that both ΔH° and ΔS° is positive; the positive value of ΔH° for Cr(VI) removal by mosambi peel confirms that the adsorption process is endothermic in nature, and positive ΔS° indicates that the adsorption process is spontaneous (Ghosh and Mondal 2019). However, the spontaneity of chromium adsorption is also supported by the free energy value at different temperature (Table 3), according to the equation.

Modeling outcome

In the present study, Box–Behnken design was applied based on three levels four factors. The linear and second-order polynomial equation was fitted to the experimental data to obtain the regression equations. The various indicators such as lack-of-fit test, the sequential F test and other statistical tests were used for screen out the results such as sequential model sum of square, lack of fit and model summary statistics revealed that cubic model is aliased. The model is aliased, which means that the model is not sufficient for further investigation. However, model summery statistical of the mosambi peel adsorbents exhibited the goodness of fit is quite high ($R^2 = 0.980$) compared to the quadratic model ($R^2 = 0.932$) Table 4.

The model adequacy of the Cr(VI) adsorption by mosambi peel was assisted by different statistical test such as sequential model summary of square, lack of fit and model summary statistics and all the clearly demonstrate ($p < 0.01$) the said adsorption process is statistically viable. The second-order polynomial equations for Cr(VI) removal efficiency in terms of coded factors are given by Eq. 10;

Table 3 Thermodynamics parameters for adsorption of Cr(VI) by mosambi peel

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
303	−420.216		
313	−725.165	$+1.914 \times 10^{-3}$	57.441
318	−726.246		
323	−2044.332		
328	−1151.517		

Table 4 ANOVA for Cr(VI) adsorption by mosambi peel

Source	Sum of squares	*df*	Mean square	F value	*p* value Prob > F	
Model	18447.48	14	1317.68	13.76	< 0.0001	S
A-Initial conc.	3707.87	1	3707.87	38.71	< 0.0001	
B-pH	3318.68	1	3318.68	34.65	< 0.0001	
C-Dose	58.62	1	58.62	0.61	0.4470	
D-Contact time	48.40	1	48.40	0.51	0.4888	
AB	8.82	1	8.82	0.092	0.7660	
AC	13.78	1	13.78	0.14	0.7102	
AD	0.42	1	0.42	4.411E−003	0.9480	
BC	462.25	1	462.25	4.83	0.0454	
BD	315.06	1	315.06	3.29	0.0912	
CD	2505.00	1	2505.00	26.15	0.0002	
A^2	566.43	1	566.43	5.91	0.0290	
B^2	5770.85	1	5770.85	60.25	< 0.0001	
C^2	830.13	1	830.13	8.67	0.0107	
D^2	737.08	1	737.08	7.70	0.0149	
Residual	1340.88	14	95.78			
Lack of Fit	1191.88	10	119.19	3.20	0.1368	NS
Pure Error	149.00	4	37.25			
Cor Total	19788.35	28				

S significant, *NS* non-significant

$$Y = 81.50 - 17.58A - 16.63B - 2.21C - 2.01D - 1.49AB + 1.86AC - 0.32AD + 10.75BC + 8.87BD - 25.02CD + 9.34A^2 - 29.83B^2 - 11.31C^2 - 10.66D^2 \quad (10)$$

Multiple regression analysis clearly suggests that the removal of Cr(VI) by mosambi peel is statistically viable. On the other hand, the adequacy of the model was assessed by ANOVA (Table 4). From Table 4, it was found that removal of Cr(VI) by mosambi peel is significant ($p < 0.0001$) with *F* value 13.76. The operating parameters such as initial concentration and pH of the Cr(VI) solution are statistically significant ($p < 0.0001$). However, the lack-of-fit F value (3.20) was recorded not significant relative to pure error. The adequate precision ratio is 12.217 which measures the signal to noise and as the value of adequacy precisions is > 4, therefore this model can be used to navigate the design space.

Judgment of model adequacy

The judgment of model can be done by the assumption to develop the model in such a way where the error in prediction is normally distributed. The difference between experimental value and predicted value is called residual value. The removal of Cr(VI) by mosambi peel can be presented by predicted removal versus residual removal of Cr(VI).

3D response surface plots

3D response surface plot is presented in Fig. 10a–f. Figure 10a–f represents the removal of Cr(VI) with variation of (a) pH and initial concentration (b) dose and initial concentration (c) contact time and initial concentration (d) dose and pH (e) contact time and pH and (f) contact time and dose. All these 3D plots show how the removal of Cr(V) simultaneously affected by two factors. Further, from 3D plot, it is clear that low pH and lower initial concentration are favorable for removal of Cr(VI) from aqueous solution (Das et al. 2013).

On the other hand, a normal probability plot and dot diagram of these residuals and actual versus predicted are presented in Fig. 11a, b. Figure 11a depicts that maximum data points are close to straight line leading to support to the conclusion that operating variables, interaction and square terms were significant. Similarly, Fig. 11b shows the relationship between the actual and predicted values for removal of Cr(VI) by mosambi peel. Again, it can be seen in Fig. 11b that the developed model is adequate due to residuals for the prediction of each response is minimum. The desirability plot of the chromium(VI) removal by mosambi peel clearly indicates that for achieving desirability 1.0, the operating variable should be fixed at initial concentration 6.75,

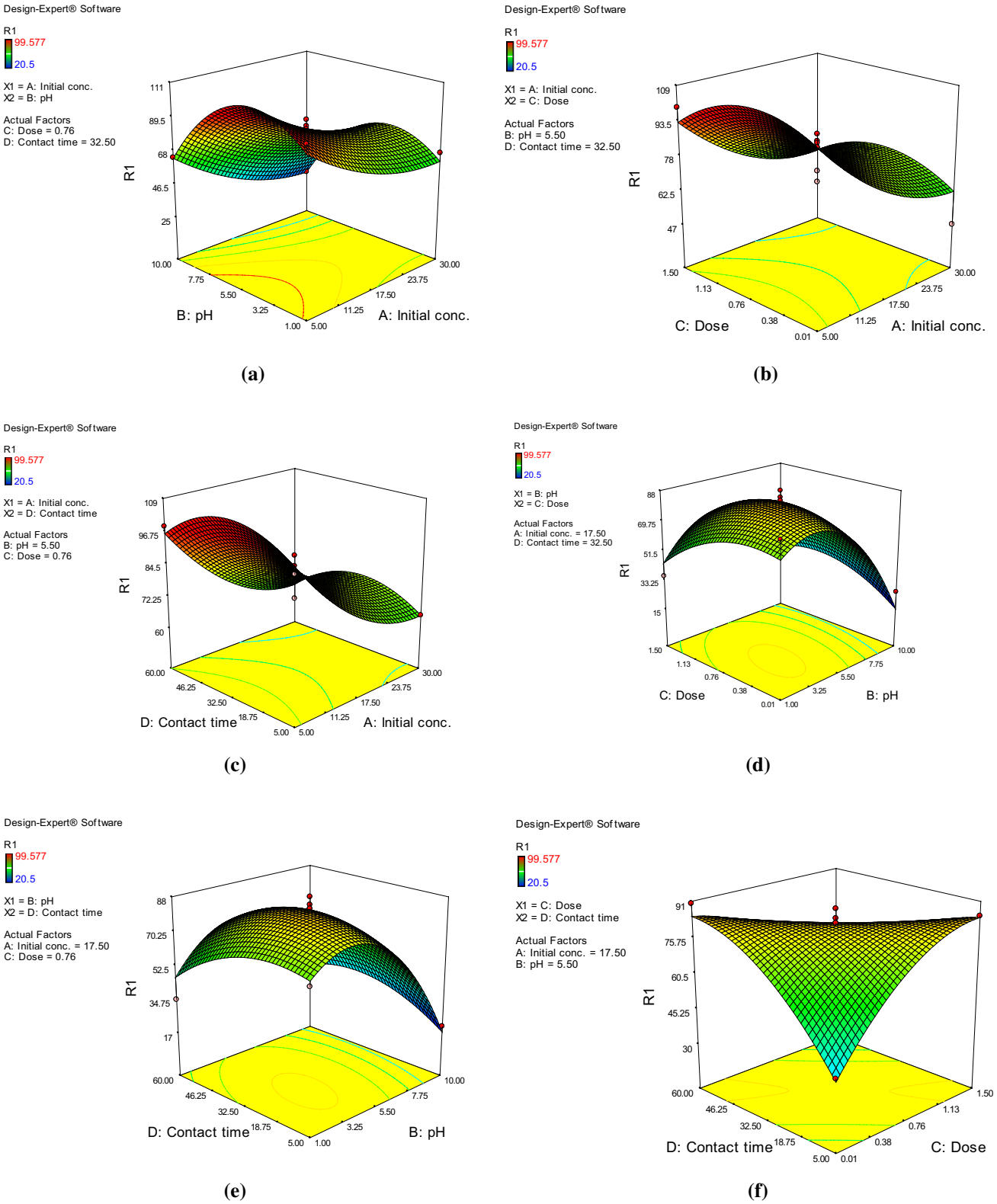

Fig. 10 Response surface plot showing the effect of independent variables for removal of Cr(VI) onto mosambi peel

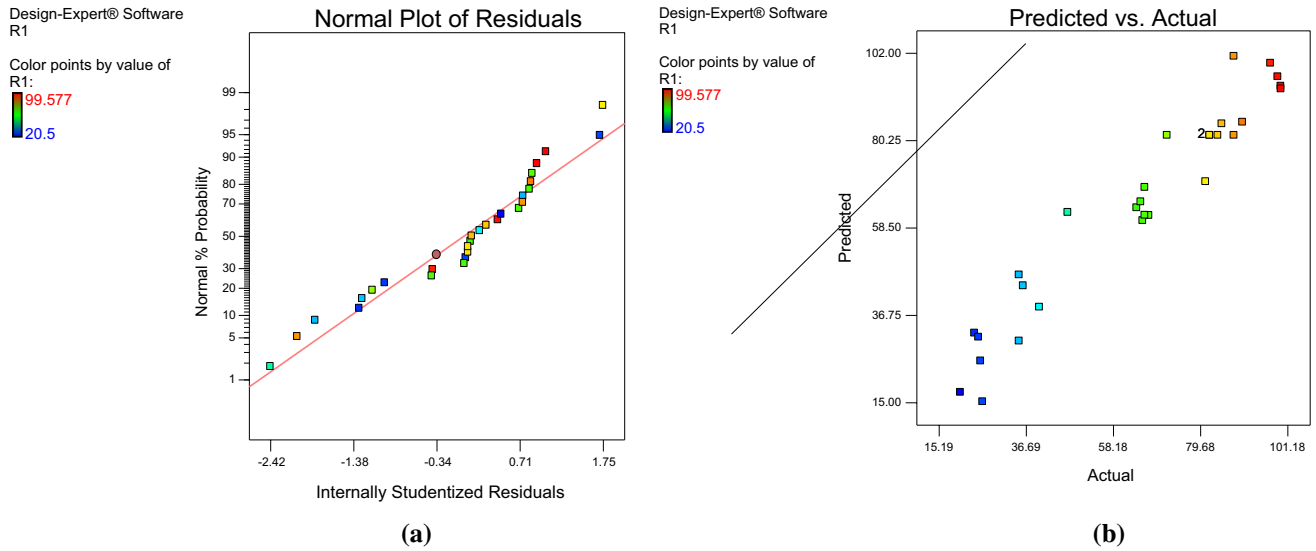

Fig. 11 **a** Plot of normal (%) probability versus residuals, **b** plot of predicted versus actual

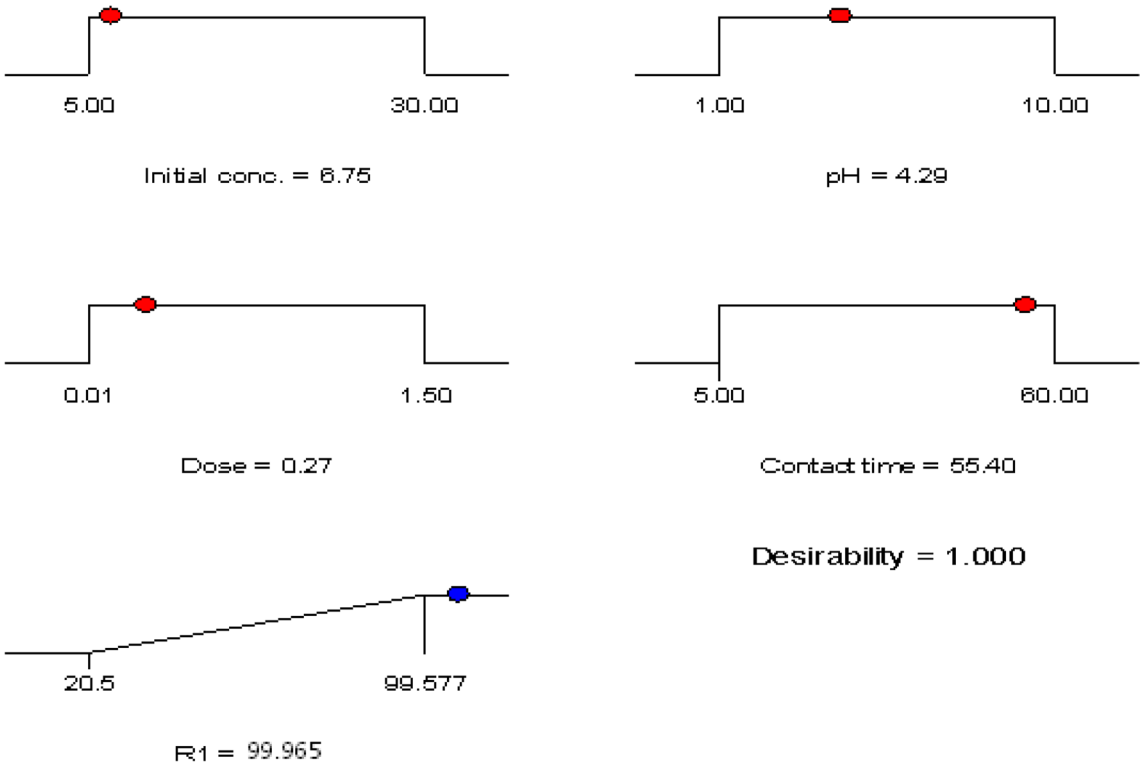

Fig. 12 Desirability for screening out the optimized parameters toward maximum Cr(VI) removal

pH 4.29, dose 0.27 g/100 mL and contact time 56.40 min (Fig. 12). Very recently, Mondal et al. (2019b) reported almost similar desirability value (1.0) with operating variables pH, initial concentration, contact time and adsorbent dose for removal of chromium (VI) by chicken feather.

Comparison of mosambi peel for Cr(VI) adsorption

The previous literature highlighted that Cr(VI) can be removed by various biosorbents such as materials including orange peel (Park et al. 2007), pine bark (Park et al. 2007), pine needles (park et al. 2007), rice bran (Sing et al.

Table 5 Comparison of mosambi peel dust with other reported adsorbents

Absorbents	Sorption capacity {(mg/g)(a)} or removal efficiency{(%)(b)}	References
Chemically modified chicken feather	14.47 (a)	Sun et al. (2009)
Waste news paper	59.88	Dehghani et al. (2016)
Orange peel	49.9 (b)	Park et al. (2007)
Ocimum americanum L. seed pods	83.33 (a)	Kumar et al. (2009)
Pine bark	85 (b)	Park et al. (2007)
Pine needles	21.5 (a)	Park et al. (2007)
Pine cone	71.8 (b)	Park et al. (2007)
Pomegranate husk carbon	35.2 (a)	Nemr (2009)
Rice bran	58.89 (a)	Wang et al. (2008a, b, c)
Rice straw	26.3 (b)	Park et al. (2007)
Sugarcane bagasse	92.23 (b)	Garg et al. (2009)
Sugarcane bagasse	0.63 (a)	Garg et al. (2007)
Sawdust	1.482 (a)	Sumathi et al. (2005)
Sawdust	19.9 (b)	Park et al. (2007)
Sunflower stem	4.9 (a)	Jain et al. (2009)
Soya cake	0.28 (a)	Daneshvar et al. (2002)
Water lily	7.559 (a)	Elangovan et al. (2008)
Water hyacinth	6.378 (a)	Elangovan et al. (2008)
Walnut shell	18.51 (a)	Agarwal et al. (2006)
Wheat bran	40.80 (a)	Wang et al. (2008a, b, c)
Mosambi peel	26.053	Present study

2005), rice husk (Oliveira et al. 2005), sawdust (Sumathi et al. 2005; Park et al. 2005), sunflower stem (Jain et al. 2009), sugarcane bagasse (Garg et al. 2007), sugar beet pulp (Garg et al. 2007) and soya cake (Daneshvar et al. 2002) (Table 5). Hexavalent chromium adsorption capacity is usually determined by Langmuir and Freundlich adsorption isotherms but often calculated on different basis in different studies, such as mg/kg, mg/g or m mol/g for q_e. A comparison of Cr(VI) adsorption capacity on with other of different reported adsorbents with mosambi peel has been presented in Table 5. It shows that the Cr(VI) adsorption capacity on mosambi peel is much higher than rice husk, sugar bagasse, soya cake and fly ash. However, other adsorbents such as orange peel, pine bark, rice bran, rice straw, fly ash and modified hectorite clays showed much higher Cr(VI) adsorption capacity than mosambi peel. Overall, all the three tested adsorbents exhibited the potential to be an efficient and low-cost adsorbent for Cr(VI) immobilization.

Conclusion

The equilibrium of Cr(VI) adsorption nicely fitted with Langmuir isotherm indicating a monolayer adsorption capacity of 1.1694 mg/g. Moreover, the kinetics of Cr(VI) adsorption in mosambi peel data showed a good agreement with pseudo-second-order which suggests that the rate-limiting step is controlled by chemical adsorption. On the other hand, thermodynamic study revealed that the adsorption of Cr(VI) by mosambi peel is endothermic reaction and entropy-driven process. The modeling results by the Box–Behnken model were used to screen out the influence of four operating variables on hexavalent chromium removal. Results demonstrated the nice fitting of second-order polynomial regression model with high R^2 value of 0.932 with F value of 13.76. Therefore, the present study results concluded that use of mosambi peel power is a cost-effective method for the abatement of Cr(VI) from aqueous solution.

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Compliance with ethical standards

Conflict of interest Authors declare that they have no conflict of interest in publishing the current paper.

Ethical approval The research is based on effective and efficient use of waste material and the nature of waste is biological origin. Therefore, this particular research does not require any ethical approval.

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