Atta ul Haq*, Muhammad Saeed, Muhammad Usman, Muhammad Yameen,
Majid Muneer and Saiqa Tubbsum

A comparative sorption study of Cr^{3+} and Cr^{6+} using mango peels: kinetic, equilibrium and thermodynamic

<https://doi.org/10.1515/gps-2019-0001>

Received August 31, 2018; accepted September 11, 2018.

Abstract: The present study investigates a comparative study of the sorption of Cr^{3+} and Cr^{6+} from water using an agricultural by-product; mango peels in batch system under the effect of initial metal ion concentrations, solution pH, temperature, sorbent dose and contact time. Characterization of the mango peels was done before and after sorption of Cr^{3+} and Cr^{6+} using scanning electron microscopy, surface area pore size analyzer and FTIR spectroscopy. The pH study revealed that that maximum removal of Cr^{3+} and Cr^{6+} was obtained at pH 5.0 and 7.0 respectively. Among various kinetic models, pseudo-2nd order well explained the data owing to the higher values of R^2 and the nearness between the values of experimental and calculated sorption capacities. The isotherms study revealed that Freundlich is the suitable isotherm for explanation of the equilibrium data due to higher R^2 values. The monolayer sorption capacity of mango peels was found to be 98.039 mg g⁻¹ for Cr^{3+} and 66.666 mg g⁻¹ for Cr^{6+} . The spontaneity and exothermic nature of the sorption process of Cr^{3+} and Cr^{6+} using mango peels was reflected from thermodynamic study.

Keywords: mango peels; kinetics; equilibrium; thermodynamics

1 Introduction

Scientists have focused their attention much more on the contamination of heavy metals. The accumulation of these metals in the bodies of flora and fauna causes

serious problems [1]. The effluents of various industries such as electroplating, tanning, metallurgy, pesticide, ceramic, batteries and mining consist of heavy metals in high amount [2,3]. Among these metals, chromium is considered as toxic and usually found in the form of Cr^{3+} and Cr^{6+} . The literature showed that Cr^{3+} is an important nutrient necessary for the metabolism of sugar and fat, and its toxicity is less than Cr^{6+} [4]. However, maximum exposure of the chromium causes serious health problems such as cancer, allergic skin reaction, kidney and lung diseases [2]. Hence, the removal of chromium from the industrial effluents is necessary before discharging into the environment. Various methods have been applied so far, to treat polluted water like ion exchange, precipitation, solvent extraction, electrochemical deposition, membrane separation, adsorption, reduction etc. However, there are a number of considerable drawbacks of these methods such as high price, energy consumption, partial removal and further production of toxic sledge due to which they have not gained much attention. Therefore, it is imperative to investigate an inexpensive and eco-friendly method to remove chromium and other contaminants from water [5-8].

Recently, biosorption has become one of the alternative technologies that have been widely utilized for the decontamination of wastewater. On comparison to other conventional wastewater treatment technologies, biosorption has many potential marketing advantages such as high efficiency, low cost, no additional nutrient requirement, low biological sledge formation, eco-friendly, recycling of biosorbents, high metal binding ability and high possible metal recovery [9]. It has been reported that those materials which are obtained from various peels of the fruit have a high potential to remove heavy metal ions [10-13].

Mango is one of the delicious fruit and commonly grows in those regions of the world which occur on tropical and subtropical. The annual production of the mango is about 27 million tons which makes the mango on fifth position among major fruits [14]. The edible part of the mango is the pulp making approximately 33 to 85% of the total fruit and used in many products include juices, jams and jelly powders [15]. About 7-14% of the total fruit

* Corresponding author: Atta ul Haq, Department of Chemistry, Government College University Faisalabad 38000, Pakistan, e-mail: attaulhaq@gcuf.edu.pk

Muhammad Saeed, Muhammad Usman, Majid Muneer and Saiqa Tubbsum, Department of Chemistry, Government College University Faisalabad 38000, Pakistan

Muhammad Yameen, Department of Biochemistry, Government College University Faisalabad 38000, Pakistan

weight is the peels of mango and generated in a huge amount during the season. These peels have no proper use and the disposal of these wastes is also a serious problem.

The major components of mango peels are pectin, lipids, cellulose, hemicellulose, polyphenols and carotenoids [16]. Cellulose and pectin contain various functional groups such as carboxylic and hydroxyl. Due to these functional groups, the mango peels sequester different types of pollutants, especially metal ions [17-19]. Recently, different parts of the mango such as mango seeds, mango peels, unfertilizable fruiting buds of mango plant and phosphate treated sawdust of mango tree have been employed to sequester dyes, phenol, heavy metal ions [20-25].

The present study was performed to compare the potential removal of Cr³⁺ and Cr⁶⁺ using mango peels from aqueous solution. The study was performed regarding the influence of pH, time of contact, dosage of sorbent, initial metal ions concentration and temperature. Kinetics, equilibriums and thermodynamics of sorption were studied to recognize the nature and mechanism of Cr³⁺ and Cr⁶⁺ sorption.

2 Materials and methods

2.1 Preparation of biosorbent

A bulk quantity of mango peels were collected from juice shops in Faisalabad, Pakistan. These peels were first thoroughly washed with tap water to remove any dirt particle and then washed with excess of distilled water. After washing, the materials were cut with knife to obtain small pieces of the peels and dried in sunlight. These materials were then ground in electrical grinder and made powder of the peels. Sufficient amount of the powder was then transferred in to a beaker containing distilled water and allowed the materials to settle down in the water. Distilled water was then decanted after settled down of the powder and decantation was repeated till the water become transparent. These materials were filtered and dried at a temperature of 120 °C in oven until the weight become constant. The dried materials were then stored for further study in air tight bottle.

2.2 Chemicals and reagents

In this study sulfuric acid, boric acid, phosphoric acid, hydrochloric acid, acetic acid and sodium hydroxide were

used. Solution pH was adjusted with Briton Robinson buffer solutions of different pH.

2.3 Standard solutions of Cr³⁺ and Cr⁶⁺

Stock solution of Cr³⁺ was prepared from chromium nitrate and Cr⁶⁺ was prepared from potassium dichromate in distilled water. These stock solutions were then used for preparation of working solutions using dilution formula.

2.4 Instruments

Analytical balance (Sartorius-GC 2012 Germany) was used to weigh various solid materials. Sorbent was heated in oven (Mettler Celsius 2005) and pH of the solutions was determined with the help of pH meter (WTW-Inolab 720 Series). The raw materials were ground with the help of grinder (Fritsch-Pulverisette 2 of Japan), and for shaking of the suspensions, orbital shaker was used. The amount of Cr³⁺ and Cr⁶⁺ was determined using atomic absorption spectrophotometer (Hitachi Polarized Zeeman AAS, Z-8200, Japan).

2.5 Sorption studies

The sorption studies were performed by taking 0.1 g mango peels powder in separate conical flasks and added 10 mL of Cr³⁺ and Cr⁶⁺ of a particular concentration (100 mg L⁻¹). Britton Robinson buffer was used to adjust the solution pH with optimum value and the volume of the suspensions was kept up to 25 mL. The suspensions were then shaken for two hours in an orbital shaker. After equilibration, the suspensions were filtered and the amount of Cr³⁺ and Cr⁶⁺ in filtrates was determined with atomic absorption spectrophotometer.

Percentage removal and sorption capacity were evaluated with the help of following equations:

$$\text{Sorption (\%)} = \left[\frac{C_i - C_f}{C_i} \right] \times 100 \quad (1)$$

$$q_e = \left[\frac{C_i - C_f}{m} \right] V \quad (2)$$

In the above equations C_i and C_f are the initial and final concentrations of metal ions (mg L⁻¹), m denotes mass (g)

of mango peels powder, V is the volume (mL) of metal ions solution and q_e is the sorption capacity (mg g^{-1}).

3 Results and discussion

3.1 Characterizations of mango peels

To characterize the mango peels various techniques have been employed like scanning electron microscopy, surface area pore size analyzer and Fourier transform infrared spectroscopy.

3.1.1 Scanning electron microscopic analysis

Important information regarding the surface structure has been obtained from scanning electron microscopy. Figures 1-3 showed the SEM images of the mango peels prior to and after sorption of Cr^{3+} and Cr^{6+} at a magnification of 2000x. Before sorption study, a roughness and

Figure 1: SEM of mango peels before removal of Cr^{3+} and Cr^{6+} .

Figure 2: SEM of mango peels after removal of Cr^{3+} .

Figure 3: SEM of mango peels after removal of Cr^{6+} .

irregularity was found on the surface of mango peels. However, the coarseness of the surface of the mango peels was vanished after sorption of these metal ions which suggests an indication of Cr^{3+} and Cr^{6+} sorption.

3.1.2 Surface analysis of mango peels

The removal efficiency is greatly affected by surface area and volume of pores. Therefore, surface analysis data of the mango peels powder were obtained using nitrogen adsorption isotherm. The results of the surface analysis of mango peels powder before and after removal of Cr^{3+} and Cr^{6+} are summarized in Table 1. The surface area of mango peels powder was decreased after removal of Cr^{3+} and Cr^{6+} which confirms the adsorption of these metal ions.

3.1.3 Fourier Transform Infrared analysis

The functional groups play a very important role in the sorption process. Therefore, to identify the involvement these functional groups FTIR analysis was carried out prior to and subsequent to sorption of Cr^{3+} and Cr^{6+} . The spectrum of the mango peels powder before removal of Cr^{3+} and Cr^{6+} is shown in Figure 4 which consists of major peaks at 3323, 2359, 2331, 1595, 1507 cm^{-1} corresponding to

Table 1: Surface areas, pore radius and pore volume of mango peels powder.

Parameter	Before removal of Cr^{3+} and Cr^{6+}		After removal	
			Cr^{3+}	Cr^{6+}
Surface area ($\text{m}^2 \text{g}^{-1}$)	13.455	8.751	8.345	
Pore volume (mL g^{-1})	0.055	0.0453	0.0385	
Pore radius ($\text{\AA}$)	17.065	18.755	19.235	

-OH, -CH stretching of $-\text{CH}_2$ and $-\text{CH}_3$, N-H bending and C-N stretching [26-28]. However, after removal of these metal ions the peaks intensities were somewhat decreased as shown in Figure 5 which indicates the involvement of these functional groups [29].

3.2 Effect of pH

Solution pH is considered as one of the chief experimental variables which affect the sorption of heavy metals [30]. To observe the effect of pH, the sorption experiments were performed at pH values varying from 3 to 11 and other parameters were kept constant. Figure 6 presents a slight increase in sorption of Cr^{3+} with each increment of pH up to pH 5.0 but after that a small decrease in sorption was observed. A competition develops between H^+ and Cr^{3+} on sorption sites of mango peels at low pH owing to

Figure 4: FTIR spectrum of mango peels before removal of Cr^{3+} and Cr^{6+} .

Figure 5: FTIR spectrum of mango peels after removal of Cr^{3+} and Cr^{6+} .

Figure 6: Effect of pH (conditions for experiment: range of pH 3-11, initial Cr^{3+} and Cr^{6+} concentration $40 \mu\text{g mL}^{-1}$, dosage of sorbent 0.1 g, time of contact 1 hour, volume for sorption of Cr^{3+} and Cr^{6+} 25 mL).

which the sorption of Cr^{3+} was low but this completion was decreased with the progress in pH. Thus, maximum sorption of Cr^{3+} was obtained at pH 5.0. However, at high pH, a decline in sorption of Cr^{3+} was noted which may be owing to the conversion of Cr^{3+} into $\text{Cr}(\text{OH})_4^-$ and $\text{Cr}(\text{OH})_3$ in alkaline medium. Consequently, an electrostatic repulsion develops between the negative charges on both chromium species and the surface of mango peels at higher pH. Conversely, in case of Cr^{6+} , the sorption onto mango peels was more effective at low pH and become all most remain constant between 5.0 and 7.0, followed by a major decrease in sorption of Cr^{6+} . The sorption of Cr^{6+} is high at low pH may be owing to the presence of Cr^{6+} in various anionic forms in acidic medium such as $[\text{HCrO}_4^-]$, $[\text{Cr}_3\text{O}_{10}]^{2-}$, $[\text{Cr}_2\text{O}_7]^{2-}$ and $[\text{Cr}_4\text{O}_{13}]^{2-}$. Therefore, a strong attractive force created between the anionic species of Cr^{6+} and sorption sites of mango peels due to which the sorption process is high at low pH. However, a considerable decrease in sorption of Cr^{6+} was noted at higher pH. It may be perhaps due to the completion of anionic species of Cr^{6+} and OH^- for sorption sites of mango peels [31]. Consequently, pH 5.0 was then used for further study as optimum pH for Cr^{3+} while pH 7.0 for Cr^{6+} removal.

3.3 Effect of sorbent dose

To scrutinize the effect of mango peels dosage on sorption of Cr^{3+} and Cr^{6+} , the experiments were conducted by varying the amount of mango peels powder from 0.1 to 0.7 g with a constant concentration (40 mg L^{-1}) of both metal ions. Figure 7 demonstrates that the percent sorption was increased with each increment of sorbent dose. Such type of trends is commonly reflects that surface area increases with increase in sorbent dose and

more sites are available for binding of metal ions. After certain point, however, the sorption process become steady and no further significant increase in sorption was observed due to keeping constant the concentration of metal ions.

3.4 Effect of contact time

One of the most significant variables in sorption study is contact time because it gives information about practical usage of sorbent as well as the rate of sorption process [32]. Therefore, the influence of contact time on sorption was scrutinized by varying it from 10 to 70 min and the result is depicted in Figure 8. An increase in sorption of Cr^{3+} and Cr^{6+} onto mango peels powder was observed with the progress of time of contact and equilibrium was established within 50 min. After 50 min time of contact no prominent change in sorption was

observed. A steady increase in percent sorption was noted with agitation of the suspension of metal ions and sorbent. In fact the sorptive sites exposed more to the metal ions with agitation, resultantly; the metal ions sorption was increased. Therefore, the sorption of Cr^{3+} was increased from 85% to 98% while Cr^{6+} was increased from 97% to 98% with agitation of the metal ions and sorbent.

3.5 Sorption kinetics

Important information about designing and modeling of sorption process can be obtained from the prediction of kinetic parameters and these parameters can also be used to select the optimized conditions for batch process [33-36]. The nature and pathway of the sorption of Cr^{3+} and Cr^{6+} onto mango peels powder was elucidated by applying pseudo-1st order, pseudo-2nd order, Elovich, intra-particle and liquid film diffusion models.

Figure 7: Effect of sorbent dose (conditions for experiment: dose range 0.1-0.7, initial Cr^{3+} and Cr^{6+} concentration $40 \mu\text{g mL}^{-1}$, time of contact 1 hour, volume for sorption of Cr^{3+} and Cr^{6+} 25 mL, pH 5.0 for Cr^{3+} and 7.0 for Cr^{6+}).

Figure 8: Effect of contact time (conditions for experiment: range of contact time 10-70, initial Cr^{3+} and Cr^{6+} concentration $40 \mu\text{g mL}^{-1}$, dosage of sorbent 0.1 g, volume for sorption of Cr^{3+} and Cr^{6+} 25 mL, pH 5.0 for Cr^{3+} and 7.0 for Cr^{6+} , shaking speed 100 rpm).

3.5.1 Pseudo-1st order

According to pseudo-1st order, the difference in sorption capacity at equilibrium and at a given time is directly related to the rate of change of sorption capacity with regard to time [37]. The following equation shown pseudo-1st order:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (3)$$

In this equation K_1 denotes the rate constant (min^{-1}), q_t and q_e (mg g^{-1}) represent the sorption capacities at time t and at equilibrium respectively.

3.5.2 Pseudo-2nd order

This model explains that the nature of sorption process is a chemisorption which often occurs due to the exchange of electrons or some time due to sharing of valance force between sorbate and sorbent [38]. The following equation expresses pseudo-2nd order:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (4)$$

In this equation K_2 denotes the rate constant ($\text{g mg}^{-1} \text{min}^{-1}$), q_t and q_e represent the sorption capacities (mg g^{-1}) at time t and at equilibrium respectively.

3.5.3 Intraparticle diffusion model

Diffusion of sorbate species in to the pore of adsorbent is explained by intraparticle diffusion model and considers this step as the rate determining step. This model describes a direct association between the sorption of sorbate species and $t^{0.5}$. To apply this model the following equation is used:

$$q_t = K_{int} t^{1/2} + C \quad (5)$$

In the above equation K_{int} ($\text{mg g}^{-1} \text{min}^{-1/2}$) represents the rate constant and C is the intercept and associated to the thickness of the boundary layer. If a straight line is obtained from the plot of q_t versus $t^{1/2}$ having zero intercept, then the rate determining step is the intraparticle diffusion [39]. However, it may be suggested that intraparticle diffusion is not involved in our study because the line does not passing through the origin.

3.5.4 Elovich model

Zeldowitsch developed the Elovich kinetic model which explains the heterogeneity of the sorbent surface energetically and no interactions taking place among sorbed species [40]. This model can be expressed as given:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (6)$$

In this equation α ($\text{mg g}^{-1} \text{min}^{-1}$) denotes the initial sorption rate and β ($\text{g mg}^{-1} \text{min}^{-1}$) is the desorption coefficient.

3.5.5 Liquid film diffusion model

This model is commonly applied in those situations in which the boundary plays a significant function in transportation of solute from liquid to the solid phases [41]. The following equation expressed this model:

$$\ln(1-F) = -K_{fd} t \quad (7)$$

In this equation K_{fd} is the rate constant for sorption and F expresses the fractional achievement of equilibrium and is equal to q_t/q_e .

The plot of $-\ln(1-F)$ against time having zero intercept indicates fitness of kinetic data into liquid film diffusion model [42]. However in case of our study, the intercept

is not zero which may be suggested from this result that some other mechanisms controlled the sorption of these metal ions.

Constant parameters of each model were evaluated from slopes and intercepts of their respective linear equations and summarized in Table 2. By comparing all these kinetic models, pseudo-2nd order is one of the most suitable models to explain the sorption process of Cr³⁺ and Cr⁶⁺ onto mango peels due to highest value of R^2 . Moreover, the closeness between the values of experimental sorption capacity and calculated sorption capacity of the pseudo-2nd order kinetic model further confirms that pseudo-2nd order is a suitable model to express the sorption process.

3.6 Effect of initial metal ion concentration

Among those variables which significantly affect the sorption process is initial concentration of sorbate because it provides a driving force which over comes on the mass transfer resistance of molecules [43]. Therefore, the effect of initial Cr³⁺ and Cr⁶⁺ concentration on removal (%) was studied by changing the concentration of these metal ions from 20 to 180 $\mu\text{g mL}^{-1}$ and the result is depicted in Figure 9. This figure showed that % sorption of Cr³⁺ and Cr⁶⁺ was decreased with each increment in initial metal ion concentration. Possibly, this type of results may take place owing to the occupation of sites on the sorbent as the initial concentration of these metal ions was increased [44].

Table 2: Comparison of the kinetic parameters for the sorption of Cr³⁺ and Cr⁶⁺ onto mango peels.

Model	Parameter	Cr ³⁺	Cr ⁶⁺
Pseudo-1 st -order	q_e , mg g^{-1} , (exp)	9.032	9.925
	q_e , mg g^{-1} , (cal)	1.969	5.780
	K_1 , min^{-1}	0.009	0.023
	R^2	0.9350	0.9264
Pseudo-2 nd - order	K_2 , $\text{g mg}^{-1} \text{min}^{-1}$	0.027	0.017
	q_e , mg g^{-1}	9.165	10.504
	R^2	0.9973	0.9982
Intraparticle diffusion	K_{int} , $\text{mg g}^{-1} \text{sec}^{1/2}$	0.223	0.371
	C	6.765	6.589
	R^2	0.9610	0.9772
Elovich	α , $\text{mg g}^{-1} \text{min}^{-1}$	5630.761	113.738
	β , g mg^{-1}	1.545	0.9195
	R^2	0.9323	0.9674
Liquid film diffusion	K_{fd} , min^{-1}	0.021	0.053
	Intercept	1.523	0.540
	R^2	0.9350	0.9264

Figure 9: Effect of initial metal ion concentration (conditions for experiment: initial metal ion concentration range 20-180 $\mu\text{g mL}^{-1}$, dosage of sorbent 0.1 g, volume for sorption of Cr³⁺ and Cr⁶⁺ 25 mL, pH 5.0 for Cr³⁺ and 7.0 for Cr⁶⁺, time of contact 1 hour).

3.7 Adsorption isotherm studies

A number of isotherms are available in literature which can be used to analyze the sorption process. The sorption equilibrium isotherm models are characterized by certain parameters whose values describe the affinity of sorbent for various solutes and the surface properties of sorbents. In the present study, various isotherms such as Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (D-R) were used to interpret the sorption data of Cr³⁺ and Cr⁶⁺.

3.7.1 Freundlich isotherm

This isotherm considered multilayer sorption on a surface of heterogeneous in nature and is given in the following equation:

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

In this equation K_F represents Freundlich isotherm constant which indicates sorbent capacity (mg g^{-1}) while n (g L^{-1}) is the Freundlich exponent; use to measure the sorption intensity. Similarly, q_e represents the amount of Cr³⁺ and Cr⁶⁺ sorbed (mg g^{-1}) while C_e denotes the concentration Cr³⁺ and Cr⁶⁺ at equilibrium ($\mu\text{g mL}^{-1}$).

The magnitude of n represents the nature of sorption either it occurs chemically or physically. The value of n for chemical sorption is less than one and for physical sorption its value is greater than one [45].

3.7.2 Langmuir isotherm

This isotherm assumes that solutes are sorbed in the form of a monolayer on a surface having fixed number of sorptive sites with homogeneous energy and its linear form is following:

$$\frac{C_e}{q_e} = \frac{1}{K_1 Q_m} + \frac{C_e}{Q_m} \quad (9)$$

Where K_1 is related with sorption free energy (L mg^{-1}) while Q_m is theoretical sorption capacity (mg g^{-1}).

3.7.3 Temkin isotherm

This isotherm describes the interaction of sorbate with sorbent and expressed that the sorption energy decreases with surface coverage and given in the following equation:

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (10)$$

Where B_T is related with sorption heat and A_T is related with maximum binding energy.

3.7.4 Dubinin-Radushkevich (D-R) isotherm

This isotherm describes sorption mechanism i.e. whether the sorption occur chemically or physically on a heterogeneous surface [46]. This isotherm can be represented in the following equation:

$$\ln q_e + \ln Q_m - K\varepsilon^2 \quad (11)$$

Where Q_m (mg g^{-1}) denotes theoretical saturation capacity, K is associated to the sorption energy ($\text{mol}^2 (\text{kJ}^2)^{-1}$) and ε represents Polanyi potential and its value can be evaluated as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (12)$$

Whether the sorption process is physical or chemical can be revealed from the magnitude of mean free energy of sorption (E). The magnitude of E may be calculated as:

$$E = \frac{1}{\sqrt{2K}} \quad (13)$$

The process which occurs physically has E value below 8 (KJmol^{-1}) and the process which occur through chemical has E value between 8 and 16 (KJmol^{-1}) [47].

The linear form of these equations were used for calculation of the constant parameters of each isotherm and listed in Table 3 which revealed that R^2 values of Freundlich isotherm are highest among the studied isotherms suggesting that equilibrium data followed Freundlich isotherm. It can be seen from this table that n is greater than one which point out that the sorption of Cr³⁺ and Cr⁶⁺ onto mango peels is physical in nature. The linear form of Langmuir isotherm was used to evaluate the monolayer sorption capacity of the mango peels for Cr³⁺ and Cr⁶⁺ and was found to be 98.039 and 66.666 mg g⁻¹ respectively. The table also showed that E has greater value than 8 KJmol⁻¹ for both Cr³⁺ and Cr⁶⁺ suggesting that the sorption of Cr³⁺ and Cr⁶⁺ is physical in nature.

3.8 Effect of temperature

The exothermic and endothermic nature of the sorption was determined by checking the influence of temperature on sorption of Cr³⁺ and Cr⁶⁺ using mango peels. The temperature was varied from 303 to 353 K while the rest of parameters were kept unchanged. Figure 10 showed that % sorption of Cr³⁺ and Cr⁶⁺ onto mango peels powder decreased with the increment of temperature demonstrating the exothermic nature of the sorption process. Infact, a decrease in the thickness of the boundary layer took place owing to the escaping of metal ions from the surface of sorbent into the bulk of solution. Consequently, decrease in sorption of Cr³⁺ and Cr⁶⁺ was observed with increase in temperature [48].

Table 3: Comparison of the isotherm constant parameters for the sorption of Cr³⁺ and Cr⁶⁺.

Isotherm	Parameter	Cr ³⁺	Cr ⁶⁺
Freundlich	K_f , mg g ⁻¹	3.057	4.303
	n	1.239	1.417
	R^2	0.9991	0.9669
Langmuir	K_1 , L mg ⁻¹	0.0264	0.053
	Q_0 , mg g ⁻¹	98.039	66.666
	R^2	0.9114	0.9406
Temkin	A_T , L g ⁻¹	0.5869	0.8512
	B_T , mg L ⁻¹	13.007	11.588
	R^2	0.9158	0.9292
Dubinin-Radushkevich	Q_m , mg g ⁻¹	25.267	25.508
	K	1×10^{-6}	9×10^{-7}
	E , kJ mol ⁻¹	0.707	0.745
	R^2	0.7611	0.7779

Figure 10: Effect of temperature (conditions for experiment: range of temperature 303-353 K, initial concentration of Cr³⁺ and Cr⁶⁺ 40 µg mL⁻¹, dosage of sorbent 0.1 g, volume for sorption of Cr³⁺ and Cr⁶⁺ 25 mL, pH 5.0 for Cr³⁺ and 7.0 for Cr⁶⁺, time of contact 1 hour).

3.9 Thermodynamic studies

The spontaneity and favorability of the sorption process of Cr³⁺ and Cr⁶⁺ using mango peels powder was determined with the help of enthalpy, free energy and entropy [49]. These parameters were evaluated using the following equations:

$$K_d = \frac{q_e}{C_e} \quad (14)$$

$$\Delta G^\circ = -RT \ln K_d \quad (15)$$

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (16)$$

Where K_d represents distribution coefficient (L g⁻¹) while ΔS° , ΔG° and ΔH° represent entropy, free energy and enthalpy of the system respectively. Similarly, the absolute temperature is denoted by T (K) and R is the general gas constant.

The values of these parameters are listed in Table 4 which revealed that all the values of ΔG° are negative

Table 4: Thermodynamic parameters for the sorption of Cr³⁺ and Cr⁶⁺ onto mango peels.

Temperature (K)	ΔG° (kJ mol ⁻¹)		ΔH° (kJ mol ⁻¹)		ΔS° (kJ mol ⁻¹)	
	Cr ³⁺	Cr ⁶⁺	Cr ³⁺	Cr ⁶⁺	Cr ³⁺	Cr ⁶⁺
303	7.783	6.618				
313	4.282	3.987				
323	4.100	2.781				
333	4.022	2.199	-9.083	-28.259	-0.0018	-0.0094
343	3.805	1.253				
353	3.660	0.880				

suggest that the sorption of Cr^{3+} and Cr^{6+} using mango peels powder is spontaneous and feasible. The value of ΔH° is negative which demonstrates the exothermic nature of the sorption process of Cr^{3+} and Cr^{6+} while the negative value of ΔS° suggests a reduction in the randomness at the solid/solution interface during the sorption process [50-54].

4 Conclusions

The present work demonstrates the usability of mango peels powder for the sorption of Cr^{3+} and Cr^{6+} from aqueous media in batch system. Solution pH was found to be the effective parameter and maximum sorption of Cr^{3+} and Cr^{6+} was achieved at pH 5.0 and 7.0 respectively. Sorption kinetics fitted well in to pseudo-2nd order among different kinetic models owing to high R^2 values. Due to high values of the correlation coefficient, sorption data followed Freundlich isotherm as compared to other isotherm models. Maximum monolayer sorption capacities for Cr^{3+} and Cr^{6+} were found to be 98.039 and 66.666 mg g⁻¹ respectively. The sorption process of Cr^{3+} and Cr^{6+} was exothermic and spontaneous as indicated by values of thermodynamic parameters. It can be concluded from these results that mango peels powder can be used as an efficient and eco-friendly sorbent for the sorption of Cr^{3+} and Cr^{6+} from aqueous media.

Acknowledgements: The authors highly acknowledge the support of Higher Education Commission Pakistan.

References

- [1] Bansal M., Singh D., Garg V.K., A Comparative Study for the Removal of Hexavalent Chromium from Aqueous Solution by Agriculture Wastes, Carbons. J. Hazard. Mater., 2009, 171, 83-92.
- [2] Garcia M.L., Lodeiro P., Barriada J.L., Herrero, R., Vicente M.E.S., Vicente M E S. Reduction of Cr (VI) levels in solution using bracken fern biomass: batch and column studies. Chem. Eng. J., 2010, 165, 517-523.
- [3] Bhatti I., Qureshi K., Kazi R.A., Ansari A.K., Preparation and Characterisation of Chemically Activated Almond Shells by Optimization of Adsorption Parameters for Removal of Chromium VI from Aqueous Solutions. Int. J. Chem. Biomol. Eng., 2008, 1, 150-155.
- [4] Rane N.M., Sapkal D.R.S, Sapkal D.V.S., Patil M.B., Shewale S.P., Use of naturally available low cost adsorbents for removal of Cr (VI) from waste water. Int. J. Chem. Sci. App., 2010, 1, 65-69.
- [5] Karaoglu M.H., Mehmet U., Ibrahim K., Adsorption characterization of Co (II) ions onto chemically treated Quercus coccifera shell: equilibrium, kinetics and thermodynamic studies. Bioresources, 2011, 6, 1954-1971.
- [6] Ahalya N., Ramachandra T.V., Kanamadi R.D., Biosorption of heavy metals. Res. J. Chem. Environ., 2003, 7, 71-79.
- [7] Ebrahimi M., Panahi R., Dabbagh R., Evaluation of native and chemically modified sargassum glaucescens for continuous biosorption of Co (II). Appl. Biochem. Biotechnol., 2009, 158, 736-746.
- [8] Rich G., Cherry K., Hazardous Waste Treatment Technologies. Pudvan Publishers, New York, NY, USA. 1987, 127-131.
- [9] Ekmekyapar F., Aslan A., Bayhan Y.K., Kakici A., Biosorption of copper (II) by nonliving lichen biomass of *Cladonia rangiformis hoffm.* J. Hazard. Mater., 2006, 137, 293-298.
- [10] Al-Masri M.S., Amin Y., Al-Akel B., Al-Naama T., Biosorption of cadmium, lead, and uranium by powder of poplar leaves and branches. Appl. Biochem. Biotechnol., 2010, 160, 976-987.
- [11] Elifantz H., Tel-Or E., Heavy metal biosorption by plant biomass of the Macrophyte *Ludwigia stolonifera*. Water Air and Soil Pollut., 2002, 141, 207-218.
- [12] Nagpal U.M.K., Bankar A.V., Pawar N.J., Kapadnis B.P., Zinjarde S.S., Equilibrium and kinetic studies on biosorption of heavy metals by leaf powder of paper mulberry (*Broussonetia papyrifera*). Water Air and Soil Pollut., 2011, 215, 177-188.
- [13] Nigam S., Gopal K., Padma S.V., Biosorption of arsenic in drinking water by submerged plant: *Hydrilla verticillata*. Environ. Sci. Pollut. Res., 2013, 20, 4000-4008.
- [14] FAOSTAT, FAO Statistical Database – Agriculture, <http://apps.fao.org>. 2005.
- [15] Wu J.S.B., Chen H., Fang T., Mango Juice. In: Nagy S., Chen C.S., Shaw P.E. (Eds.), Fruit juice processing technology Auburndale. Agscience Inc., Florida, USA, 1993, 620-655.
- [16] Ajila C.M., Bhat S.G., Rao U.J.S.P., Valuable components of raw and ripe peels from two Indian mango varieties. Food Chem., 2007, 102, 1006-1011.
- [17] Pehlivan E., Yanik B.H., Ahmetli G., Pehlivan M., Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp. Bioresour. Technol., 2008, 99, 3520-3527.
- [18] Shukla S.R., Pai R.S., Removal of Pb (II) from solution using cellulose containing materials. J. Chem. Technol. Biotechnol., 2005, 80, 176-183.
- [19] Xuan Z.X., Tang Y.R., Li X.M., Liu Y.H., Luo F., Study on the equilibrium, kinetics and isotherm of biosorption of lead ions onto pretreated chemically modified orange peel. Biochem. Eng. J., 2006, 31, 160-164.
- [20] Singh K., Padmesh T.V.N., Biosorption of Dyes onto Mango Seed and Pineapple Peel. EURECA <http://www.taylors.edu.my/EURECA/2014/downloads/56.pdf>
- [21] Gupta A., Rafe M.A., Removal of Phenol from Waste Water using Mango Peel. Int. J. Eng. Tech. Res., 2013, 1, 58-62.

- [22] Iqbal M., Saeed A., Kalim I., Characterization of Adsorptive Capacity and Investigation of Mechanism of Cu²⁺, Ni²⁺ and Zn²⁺ Adsorption on Mango Peel Waste from Constituted Metal Solution and Genuine Electroplating Effluent. *Sep. Sci. Technol.*, 2009, 44, 3770-3791.
- [23] Ashraf M.A., Maah M.J., Yusoff I., Study of mango biomass (*Mangifera indica* L) as a cationic biosorbent. *Int. J. Environ. Sci. Technol.*, 2010, 7, 581-590.
- [24] Iqbal M., Saeed A., Zafar S.I., FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd²⁺ and Pb²⁺ removal by mango peel waste. *J. Hazard. Mater.*, 2009, 164, 161-171.
- [25] Ajmal M., Rao R.A.K., Siddiqui B.A., Studies on Removal and recovery of Cr (VI) from electroplating wastes. *Water Res.*, 1996, 30, 1478-1482.
- [26] Li X., Ding C., Liao J., Lan T., Li F., Zhang D., et al., Biosorption of uranium on *Bacillus* sp. dwc-2: preliminary investigation on mechanism. *J. Environ. Radioact.*, 2014, 135, 6-12.
- [27] Xu H., Tan L., Cui H., Xu M., Xiao Y., Wu H., et al., Characterization of Pd(II) biosorption in aqueous solution by *Shewanella oneidensis* MR-1. *J. Mol. Liq.*, 2018, 255, 333-340.
- [28] Xu H., Tan L., Dong H., He J., Liu X., Qiu G., et al., Competitive biosorption behavior of Pt(IV) and Pd(II) by *Providencia vermicola*. *RSC Advances*, 2017, 7, 32229-32235.
- [29] Temesgen F., Gabbiye N., Sahu O., Biosorption of reactive red dye (RRD) on activated surface of banana and orange peels: Economical alternative for textile effluent. *Surf. Interfaces*, 2018, 12, 151-159.
- [30] Goyal N., Jain C.S., Banerjee C.U., Comparative studies on the microbial adsorption of heavy metals. *Adv. Environ. Res.*, 2003, 7, 311-319.
- [31] Li J., Lin Q., Zhang X., Yan Y., Kinetic parameters and mechanisms of the batch biosorption of Cr(VI) and Cr(III) onto *Leersia hexandra* Swartz biomass. *J. Colloid Interface Sci.*, 2009, 333, 1, 71-77.
- [32] Akar T., Tunali S., Biosorption performance of *Botrytis cinerea* fungal byproducts for removal of Cd(II) and Cu(II) ions from aqueous solutions. *Miner. Eng.*, 2005, 18, 1099-1109.
- [33] Aksu Z., Gonen F., Demircan Z., Biosorption of chromium (VI) ions by Mowital®B₃OH resin immobilized activated sludge in a packed bed: comparison with granular activated carbon. *Process Biochem.*, 2002, 38, 175-186.
- [34] Ma W., Song X., Pan Y., Cheng Z., Xin G., Wang B., Adsorption behavior of crystal violet onto opal and reuse feasibility of opal-dye sludge for binding heavy metals from aqueous solutions. *Chem. Eng. J.*, 2012, 193-194, 381-390.
- [35] Silva L.G., Ruggiero R., Gontijo P.M., Pinto R.B., Royer B., Lima E.C., Adsorption of Brilliant Red 2BE dye from water solutions by a chemically modified sugarcane bagasse lignin. *Chem. Eng. J.*, 2011, 168, 620-628.
- [36] Berrios M., Martin M.A., Martin A., Treatment of pollutants in wastewater: Adsorption of methylene blue onto olive-based activated carbon. *J. Ind. Eng. Chem.*, 2012, 18, 780-784.
- [37] Yao S., Lai H., Shi Z. Biosorption of methyl blue onto tartaric acid modified wheat bran from aqueous solution. *Iranian J. Environ. Health Sci. Eng.*, 2012, 9, 1-6.
- [38] Yaun H.P., Zhang J.H., Lu Z.M., Min H., Wu C., Studies on biosorption equilibrium and kinetics of Cd²⁺ by *Streptomyces* sp. K33 and HL-12. *J. Hazard. Mater.*, 2009, 164, 423-431.
- [39] Yadav S., Srivastava V., Banerjee, S., Chih-Huang W., Sharma Y.C., Adsorption characteristics of modified sand for the removal of hexavalent chromium ions from aqueous solutions: Kinetic, thermodynamic and equilibrium studies. *Catena*, 2013, 100, 120-127.
- [40] Ho Y.S., McKay G., The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. *Can. J. Chem. Eng.*, 1998, 76, 822-827.
- [41] Oladoja N.A., Aboluwoye C.O., Oladimeji Y.B., Kinetics and isotherm studies on Methylene Blue adsorption onto ground palm kernel coat. *Turkish J. Eng. Environ. Sci.*, 2008, 32, 303-312.
- [42] Khan T.A., Chaudhry S.A., Ali I., Equilibrium uptake, isotherm and kinetic studies of Cd (II) adsorption onto iron oxide activated red mud from aqueous solution. *J. Mol. Liq.*, 2015, 202, 165-175.
- [43] Pillai S.S., Mullassery D.M., Fernandez B.N., Girija N., Geetha P., Koshy M., Biosorption of Cr(VI) from aqueous solution by chemically modified potato starch: Equilibrium and kinetic studies. *Ecotoxicol. Environ. Saf.*, 2013, 92, 199-205.
- [44] Ngah W.S.W., Fatinathan S., Chitosan flakes and chitosan-GLA beads for adsorption of *p*-nitrophenol in aqueous solution. *Colloids Surf. A Physicochem. Eng. Asp.*, 2006, 277, 214-222.
- [45] Donmez G., Aksu Z., Removal of chromium (VI) from saline wastewaters by *Dunaliella* species. *Process Biochem.*, 2002, 38, 751-762.
- [46] Khalaf M.A., Biosorption of reactive dye from textile wastewater by nonviable biomass of *Aspergillus niger* and *Spirogyra* sp. *Bioresour. Technol.*, 2008, 99, 6631-6634.
- [47] Foo K.Y., Hameed B.H., Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.*, 2010, 156, 2-10.
- [48] Hasany S.M., Saeed M.M., Ahmed M., Sorption of traces of silver ions onto polyurethane foam from acidic solution. *Talanta*, 2001, 54, 89-98.
- [49] Polipalli K., Pulipati K., Equilibrium, Kinetic and Thermodynamic studies of biosorption of Methylene Blue dye using plant biomass as biosorbent: Optimization using Response Surface Methodology (RSM). *Int. J. Sci. Eng. Res.*, 2013, 4, 1244-1252.
- [50] Tanyildizi M.S., Modeling of adsorption isotherms and kinetics of reactive dye from aqueous solution by pea hull. *Chem. Eng. J.*, 2011, 168, 1234-1240.

- [51] Ghaedi M., Hajati S., Karimi F., Barazesh B., Ghezelbash G., Equilibrium, kinetic and isotherm of some metal ion biosorption. J. Ind. Eng. Chem., 2013, 19, 987-992.
- [52] Dehghani M.H., Sanaei D., Ali I., Bhatnagar A., Removal of chromium (VI) from aqueous solution using treated waste newspaper as a low-cost adsorbent: Kinetic modeling and isotherm studies. J. Mol. Liq., 2016, 215, 671-679.
- [53] Torab-Mostaedi M., Asadollahzadeh M., Hemmati A., Khosravi A., Equilibrium, kinetic, and thermodynamic studies for biosorption of cadmium and nickel on grapefruit peel. J. Taiwan Inst. Chem. Eng., 2013, 44, 295-302.
- [54] Sari A., Mendil D., Tuzen M., Soylak M., Biosorption of Cd(II) and Cr(III) from aqueous solution by moss (*Hylocomium splendens*) biomass: equilibrium, kinetic and thermodynamic studies. Chem. Eng. J., 2008, 144, 1-9.