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ORIGINAL ARTICLE

Removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent

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Abstract The adsorptive removal of hexavalent chromium Cr(VI) from aqueous solutions was investigated by acrylonitrile grafted banana peels (GBPs). Banana peels were treated with 10% HCl, followed by alkaline hydrolysis with 10% NaOH, and washed thoroughly. The bleaching of alkali hydrolyzed peels was carried out with sodium chlorate ($NaClO_3$) in the presence of hydrogen peroxide and glacial acetic acid. The grafting co-polymerization of acrylonitrile onto the bleached pulp was initiated by Fenton's reagent (Fe^{+2}/H_2O_2). The optimum conditions for adsorption of Cr(VI) were found to be the following: pH 3, adsorbent dose 4 g/L, concentration 400 mg/L and contact time of 120 min. The surface morphology of adsorbent was characterized by scanning electron microscopy (SEM) before and after the adsorption. The adsorption of Cr(VI) onto grafted banana peels (GBPs) was recorded to be 96%. The adsorption data were fully fitted with the Freundlich and Langmuir isotherm model and followed a pseudo-second order kinetic model. Thermodynamic study showed that the adsorption is exothermic and spontaneous. Owing to high efficiency and low cost, grafted banana peels (GBPs) can be used as effective adsorbent for Cr(VI) removal from wastewater.

1. Introduction

Heavy metals are produced in large amounts during industrial activities and contaminate the environment. Metal ions are non-biodegradable and many of them are soluble in aqueous media and easily available for living organisms. Heavy metals account for a number of disorders in plants and animals and their removal from aqueous media is an important and challenging task [1,2]. Chromium exists in aqueous media in two

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oxidation states, hexavalent Cr(VI), and trivalent Cr(III) and the toxicity of chromium depends upon its oxidation state. In a solution the Cr(VI) exists in various forms depending upon the pH, such as chromate ($Cr_2O_4^{2-}$), hydrochromate ($HCrO^{4-}$), or dichromate ($Cr_2O_7^{2-}$) [3]. In human blood the chromium only exists in Cr(III) where it is responsible for maintenance of blood metabolism. The recommended daily dietary intake (DDI) of chromium for human is 50–200 μg/day [4]. Various industries and manufacturing plants such as tanneries, paints and pigments, electroplating, metal processing, wood preservatives, textile, dye industry, steel fabrication, and canning use chromium for various applications and discharge large quantity into the environment [5–7]. Chromium enters into the body through breathing, eating, drinking or skin contact of chromium and its compounds. The toxic effects of Cr(VI) include skin rashes, nose bleeding, respiratory tract infection, suppressed immune system, hepatic diseases, and lung cancer [8,9].

Numerous methods are available for the removal of heavy metals from aqueous solutions including chemical precipitation, ion exchange, ultra-filtration, reverse osmosis, and adsorption. However, these methods have some limitations due to the production of secondary wastes, large quantity of slug formation and high operational costs [10–13]. In contrast adsorption is more advantageous than the other methods due to its simple operation design with sludge free environment and low cost [14,15]. The high cost of activated carbon and other conventional adsorbents stimulates the researchers to use low-cost agricultural products and by-products as adsorbents for the removal of heavy metals from water. Agricultural wastes such as fruits peels, rice husk, saw dust, baggas, sugar beet pulp, soya bean hulls, clay and related minerals had shown better results when used as adsorbents for heavy metals in comparison with those of other physical and chemical techniques [16–19]. Cellulosic and lingo-cellulosic materials are used by several researchers as efficient adsorbents due to their higher adsorption capacity for metal ions [20,21]. The agricultural products and by-products contain cellulose, lignin, pectin and several other compounds that have potential functional groups such as hydroxyl, carbonyl, amino, carboxylic and alkoxy, which have great affinity for the metal ions [22]. The adsorption capacities of chemically treated agricultural adsorbents are much better than untreated adsorbents [23]. In raw adsorbents several viscous compounds such as lignin and pectin occupy the pores of cellulose fibers [24]. Grafting copolymerization onto cellulose incorporates side chains without destroying its whole structure. Cellulosic materials such as wood, pulp, paper, cotton, rayon and cellophane have been subjected to grafting copolymerization with vinyl or amino monomers by several researchers to produce grafted adsorbents for the removal of heavy metals from wastewater [25–27].

Banana is one of the world's most important crops grown by more than 130 countries. India, China, Uganda, Philippines, Ecuador, Brazil, Indonesia, Columbia, Cameroon and Ghana were the top ten bananas producing countries in the world in 2012. In India the banana production in 2012 was about 24.9 million tons while the total world production of banana during 2012 was about 139.2 million tons [28,29]. Several research groups have used raw and chemically treated banana peels and banana stalks for the removal of toxic heavy

metal ions from aqueous solutions and industrial wastewater [30–33]. In the present work the raw banana peels are first treated with acid, alkali and bleaching agents ($NaClO_3$, H_2O_2) and then the bleached pulp is functionalized with acrylonitrile. The grafted banana peels (GBPs) are used as adsorbent for the removal of Cr(VI) from water. The enhancement in adsorption capacity of banana peels after chemical treatment may be due to the removal of viscous compounds such as lignin and pectin [34–37]. The incorporation of acrylonitrile (—CH_2=CH—C≡N) side chain to the cellulosic skeleton also enhanced its interaction with adsorbate molecules.

2. Materials and methods

2.1. Preparation of adsorbent

Banana peels were collected from local fruit fields in northern part of Pakistan and dried in shade for 80 h. The dried peels were hydrolyzed with 10% NaOH in round bottom flask under reflux at 105 °C for 3 h. The pulp was washed thoroughly with distilled water to remove lignin and pectin and dried in oven at 105 °C for 24 h.

2.2. Acid hydrolysis of banana peel

Raw banana peels (500 g) were put in 1500 mL flask containing 500 mL HCl solution (10%) and heated under reflux for 3 h. The contents were washed with distilled water until neutralized. During acid hydrolysis the glycoside linkage in hemicelluloses and lignin de-polymerizes through α and β-aryl ether cleavage to soluble products.

2.3. Alkaline hydrolysis of banana peel

Banana peels (500 g) were treated with 500 mL NaOH solution (10%) under reflux for 3 h and washed with distilled water till neutrality. In alkaline hydrolysis the long cellulose chains break down into smaller monomers.

2.4. Bleaching of banana peel

Alkali hydrolyzed banana peels (100 g) were treated with 10 g sodium chlorate, 5 mL glacial acetic acid and 0.5 mL H_2O_2 in 500 mL flask. The contents were heated in a water bath for 3 h and washed with distilled water three times.

2.5. Grafting co-polymerization of acrylonitrile monomer

The grafting copolymerization was carried out by treating the bleached pulp with acrylonitrile (CH_2=CH—C≡N) using Fe^{+2}/H_2O_2 initiator. The bleached banana peels (10 g) were mixed with 3 mL hydrogen peroxide, 2.5 g ferric sulfate and 2 mL glacial acetic acid in 750 mL distilled water and heated at 40 °C for 2.5 h. The reagents were filtered, washed with distilled water three times and dried at 105 °C for 24 h. After grafting copolymerization banana peels were sealed in cotton bags and soxhlet extracted with anhydrous toluene at 100 °C. The grafted banana peels were washed with 2-propanol and acetone respectively and dried at 105 °C under vacuum.

2.6. Calculation of graft yield, graft conversion, monomer to polymer conversion, homopolymer formation and grafting efficiency

(1) Graft yield $\ (\%) = \frac{(B-A)}{A} \times 100$
(2) Graft conversion $(\%) = \frac{(B-A)}{D} \times 100$
(3) Total conversion (Monomer to polymer) $(\%) = \frac{(C-A)}{B} \times 100$
(4) Homopolymer formation $(\%) = \frac{E}{D} \times 100$
(5) Grafting efficiency $(\%) = \frac{(B-A)}{(C-A)} \times 100$

A = weight of original cellulose in grams, B = weight of product in grams after copolymerization and extraction, C = weight of product in grams after copolymerization, D = weight of monomer in grams, E = weight of homopolymer in grams.

2.7. Adsorption of Cr(VI) on modified banana peel

The adsorption of Cr(VI) was carried out using 100 mg/L test solution of ($K_2Cr_2O_7$) at constant pH 3.0, adsorbent amount (1 g/L) in 250 mL flask at 30 °C. The solution was filtered and the Cr(VI) ions concentration was determined in the filtrate by using Nicolet evolution 300, UV–visible spectrophotometer with 1,5-diphenylcarbazide in acidic medium [38]. The amount of adsorbate adsorbed per gram of adsorbent was calculated by the following equation:

$$q_e = \frac{V(C_O - C_e)}{W} \qquad (1)$$

where q_e is the amount of metal ions, V is the solution volume (L), W is the adsorbent dose (g), and C_o and C_e are the initial and equilibrium metal ions concentration in solution respectively. The percent metal removal was calculated using the following equation:

$$Adsorption \ (\%) = \frac{(C_o - C_e)}{C_0} \times 100 \qquad (2)$$

2.8. Scanning electron microscope characterization

SEM was carried out to observe the changes in surface morphology of adsorbents after adsorption. The SEM images of banana peel were taken by HITACHI (Tokyo Japan) S-4200 field emission scanning electron microscopy (FE-SEM).

2.9. Adsorption isotherm studies

The adsorption equilibrium data of Cr(VI) on GBPs were computed by Langmuir and Freundlich isotherm models. The Freundlich isotherm model explains the interaction between adsorbate molecules and adsorbents with multilayer adsorption on heterogeneous surfaces [34]. The Langmuir model suggests a monolayer adsorption on a homogenous surface, and there was no interaction between adsorbed species. The regression coefficient values were judged to find the applicability of these models. Origin pro-8 and Ms Excel were used for linear regression calculations.

2.10. Kinetics study

Potassium dichromate ($K_2Cr_2O_7$) 400 mg/L was taken in a round bottom flask with 1 g adsorbent (GBPs) with continuous shaking for different time intervals, filtered and the Cr (VI) concentration in the filtrate was analyzed. It was found that adsorption of Cr(VI) was increased with increase in shaking time until the equilibrium was established. The optimum adsorption equilibrium time was found to be 1 h. This optimized equilibrium time was used for further adsorption studies.

3. Results and discussion

3.1. Effect of initiator (Fe^{+2}) concentration on grafting copolymerization

The effect of initiator (Fe^{+2}) concentration on grafting copolymerization is shown in Table 1. The grafting yield was increased with increasing initiator ($FeSO_4$) concentration from 0.5 g to 3.5 g/10 g of the bleached pulp. The increase in grafting yield occurred due the production of more active grafting sites on the cellulosic backbone. The increase in initiator concentration above 4 g decreased the grafting yield. The decrease in grafting yield at higher concentration may be due to the filling of active sites of cellulose by the initiator instead of monomers and the monomers form bulk polymers i.e. homopolymers [35,36].

3.2. Effect of temperature on grafting copolymerization

The effect of temperature on grafting co-polymerization is shown in Table 2, and it is clear that increasing the temperature up to 90 °C increases the diffusion of monomers through cellulose chains, swelling of cellulose, as well as the rate of initiation and propagation of the grafting reaction. Above 90 °C the grafting copolymerization decreases due to the oxidation of free radicals, and mutual termination of growing macro radicals favors more homopolymer formation [37,38].

3.3. Effect of acrylonitrile concentration on grafting co-polymerization

The change in grafting yield with monomer concentration is shown in Table 3. The results show that increasing the acrylonitrile concentration up to 3 g increases the grafting yield due to the increasing the number of monomer molecules. Further increasing monomer concentration above 3 g, increases the viscosity of the reaction mixture and retards the penetration of monomer molecules to the active sites of the cellulosic backbone due to formation of bulk polymer and grafting yield decreases [39,40].

3.4. Effect of time on grafting

The graft yield increases up to 3 h, where the equilibrium was established as shown in Table 4. Initially the monomers interact with the cellulosic skeleton to form co-polymers and the active site of cellulosic skeleton fully saturates in 3 h. Further increase in reaction time has no effect on grafting yield as

Table 1 Effect of initiator concentration on grafting of acrylonitrile on cellulose obtained from banana peels.

Amount of initiator (Fe^{+2}) (g)/2 g pulp	Graft yield (%)	Graft conversion (%)	Total conversion (%)	Homopolymer formation (%)	Grafting efficiency (%)
0.3	40	13.33	16.32	5.78	49
0.6	80	26.66	38.25	11.35	69.5
0.9	135	45	45.81	25	78.33
1.2	170	56	81.20	38	85.44
1.5	150	46.66	75.16	32	77.21

Table 2 Effect of temperature on grafting of acrylonitrile on cellulose from banana peels.

Grafting temp (°C) /2 g of pulp	Graft yield (%)	Graft conversion (%)	Total conversion (%)	Homo polymer formation (%)	Grafting efficiency (%)
30	10	15	5	15	40
40	60	23	33.33	23	55.23
50	70	31	45.32	32	66.31
60	125	45	90	45	74.23
70	120	43	85	38	68

Table 3 Effect of monomer ratio on grafting of acrylonitrile on cellulose obtained from banana peels.

Pulp (g): monomer (acrylonitrile) (g)	Graft yield (%)	Graft conversion (%)	Total conversion (%)	Homo polymer formation (%)	Grafting efficiency (%)
2:1	05	10	30	20	33.33
2:2	25	25	35	22	71.42
2:3	40	26.66	37	25	80
2:4	75	37.5	55	30	86
2:5	60	32	50	28	70

Table 4 Effect of time on grafting of acrylonitrile on cellulose obtained from banana peels.

Time (h)	Grafting yield (%)	Grafting conversion (%)	Total conversion (%)	Homo polymer formation (%)	Grafting efficiency (%)
0.5	45	15	35	18	42.85
1	70	26.66	45	20	54.48
2	85	35.23	51.66	28	58.33
3	140	46.66	80	37	65.78
4	132	42	74	33	60

the available active sites have saturated and the equilibrium has been established after 3 h [41,42].

3.5. Scanning electron microscopic (SEM) studies

The scanning electron micrographs of raw, bleached and grafted banana peels are shown in Fig. 1. The SEM micrographs of raw banana peels (Fig. 1A), showed that the fibers are stuck together due to the presence of lignin, pectin and other viscous compounds. The bleached banana peels (Fig. 1B), show that the viscous compounds are removed during chemical treatment. The morphology of grafted banana peels (Fig. 1C) looks different from that of the raw and bleached banana peels. The close view grafted banana peels before adsorption are shown in Fig. 1D, which show some open pores and fibers and the surface is not too smooth. The surface morphology of the adsorbent became much smoother

after the adsorption of Cr(VI) (Fig. 1E and F), and the pores and caves are filled by Cr(VI) ions.

3.6. Effect of Cr(VI) concentration on adsorption

The Cr(VI) solutions of different concentrations (100, 200, 300, 400 and 600 mg/L) were taken at constant temperature 25 °C, pH 4, agitation speed 300 rpm, contact time 1.5 h, and the adsorbent dose (4 g/L). The adsorption increases initially by increasing the concentration, and reaches to maximum at 400 mg/L (Fig. 2). The equilibrium was established at 400 mg/L, and there was no further increase in the adsorption of both ions by further increasing metal ions concentration up to 600 mg/L. The ratio of number of moles of metal ions to the surface area of adsorbent is large at optimum concentration (400 mg/L), so adsorption takes place without any interruption. The adsorbent surface
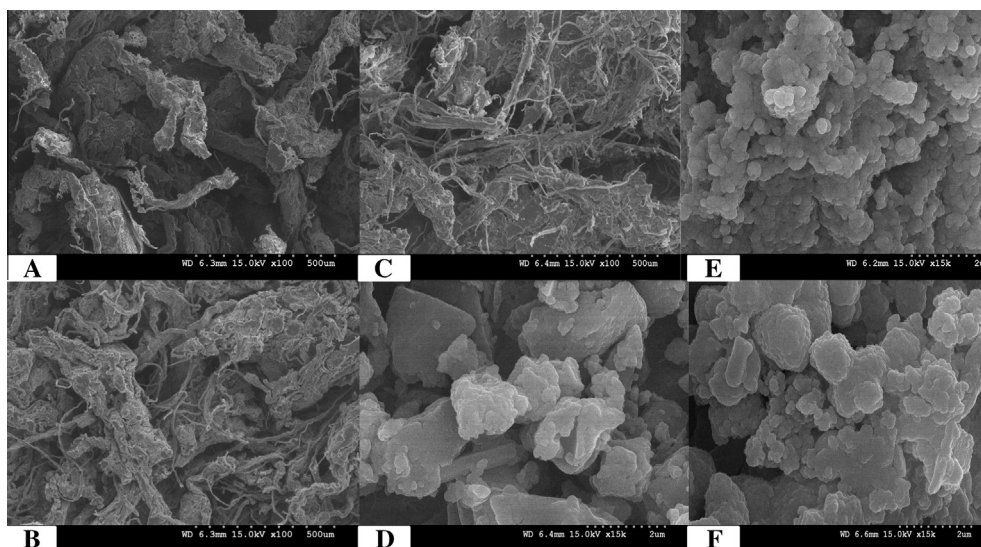
Figure 1 (A) SEM image of raw banana peel. (B) Bleached banana peel. (C) Acrylonitrile grafted banana peel. (D) GBPs before adsorption (close view). (E and F) GBPs after Cr(VI) adsorption (close views).

area saturates at higher concentration and the ions diffusion from the solution bulk to the adsorbent surface decreases [43,44].

3.7. Effect of adsorbent dose on Cr(VI) removal

The effect of sorbent dose on Cr(VI) removal is shown in Fig. 3. Cr(VI) solution 400 mg/L having pH 4, was equilibrated with 1–5 g/L adsorbent (GBPs) separately in five flasks for 60 min. Results show that the removal of Cr(VI) increases with increase in adsorbent (GBPs) amounting up to 4 g/L. The increase in adsorbent amount increases the number of available active sites for the uptake of metal ions. The Cr(VI) adsorption doesn't increase by further increasing the mass of adsorbent because the available metal ions are already adsorbed by the adsorbent [45].

3.8. Effect of contact time on Cr(VI) removal

The effect of contact time on Cr(VI) removal by grafted banana peel (GBPs) is shown in Fig. 4. The adsorption was carried out for several time intervals by taking 100 mg/L of each solution ($K_2Cr_2O_7$) at optimum pH 3, adsorbent dose (3 g/L) and agitated at 300 rpm at 25 °C. The Cr(VI) removal increased up to 1 h, and further increase in adsorption time up to 2 h brings no significant change in the equilibrium concentration. The increase in Cr(VI) removal with increase in time is due to the higher interaction between the sorbent surface and metal ions [46].

3.9. Effect of pH on Cr(VI) removal

The effect of pH on Cr(VI) removal by (GBPs) was investigated and the results are presented in Fig. 5. The optimum pH for the maximum uptake of Cr(VI) was found to be pH 3. Cr(VI) exists in solution as $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-} at lower pH and the adsorbent (GBPs) surface is also protonated and there is a strong electrostatic attraction between the positively charged surfaces of adsorbent with oxyanions of Cr(VI). The interaction between these ions $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-} with adsorbent surface decreases at higher pH, as at higher pH the surface of adsorbent becomes negatively
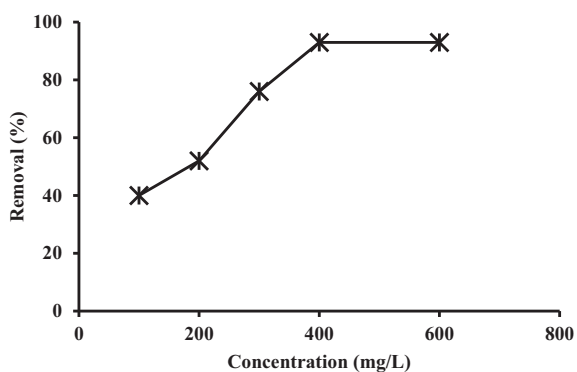

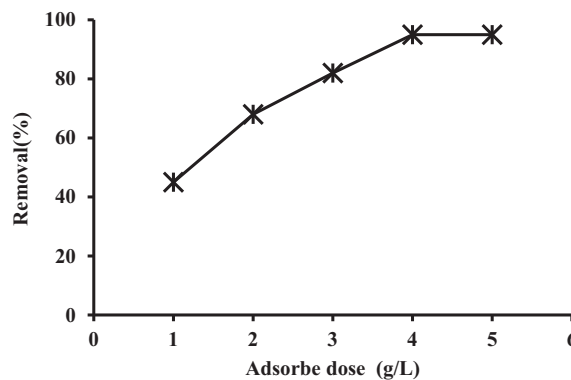**Figure 2** Effect of concentration on Cr(VI) removal from aqueous solution by GBPs.

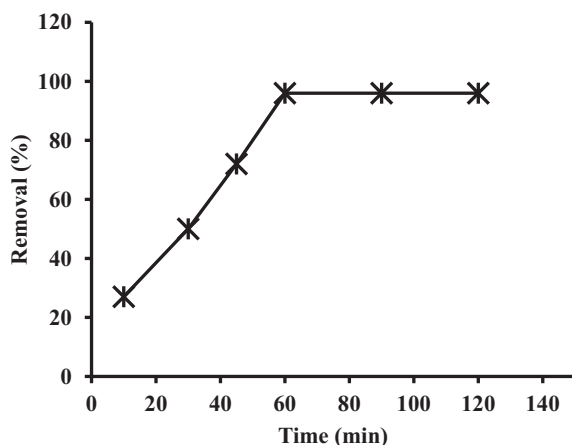**Figure 3** Effect of adsorbent dose on Cr(VI) removal from aqueous solution by GBPs.

Figure 4 Effect of contact time on Cr(VI) removal from aqueous solution by GBPs.
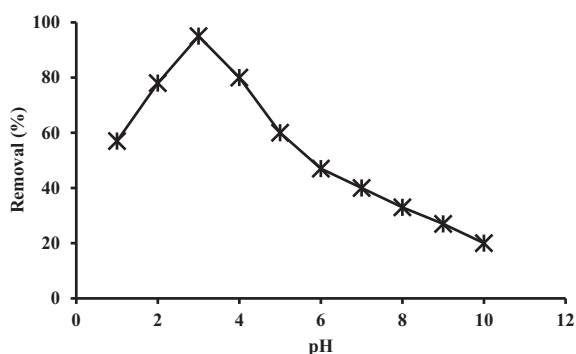

Figure 5 Effect of pH on Cr(VI) removal from aqueous solution by GBPs.

charged and also there is abundance of hydroxyl ions in aqueous solution [47].

3.10. Adsorption isotherm study

Freundlich and Langmuir adsorption models were used to study the interaction of Cr(VI) with adsorbent (GBPs).

3.10.1. Freundlich adsorption isotherm

The linear form of Freundlich adsorption isotherm is given as [48],

$$ln\, q = ln\, K + \frac{1}{n} ln\, C_e \tag{3}$$

Freundlich isotherm presumes that the adsorption of metal ions takes place on heterogeneous surface with multilayer adsorption and the adsorption increases with increase in concentration. Linear plots were obtained by plotting $ln\, q$ vs $ln\, C_e$ with slope $1/n$ as shown in Fig. 6. The n and K (L mg^{-1}) (adsorption capacity) were calculated from Fig. 6. The "n" values show that the adsorbent is effective; the surface is heterogeneous and possesses great affinity for metal ions [49].
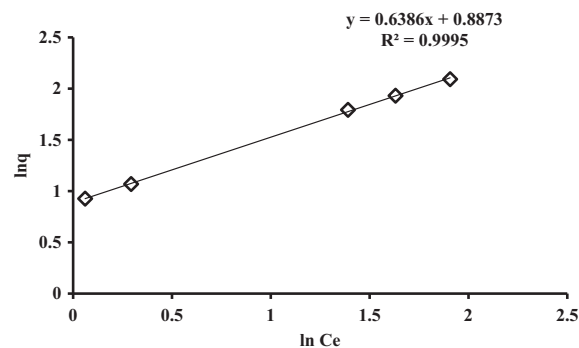

Figure 6 Freundlich adsorption isotherm of Cr(VI) onto GBPs.

Table 5 Comparison of adsorption isotherm constants of Cr (VI) on GBPs.

Isotherm	Parameters	Cr(VI)
Freundlich	$1/n$	1.2376
	K_F (mg/g)	3.8308
	R^2	0.997
Langmuir	q_{max} (mg/g)	6.1728
	K (L/mg)	0.9884
	K (L/mg)	0.9884

3.10.2. Langmuir adsorption isotherm

Langmuir adsorption isotherm model assumed that the adsorption occurs with monolayer adsorption on specific homogeneous surfaces containing finite number of adsorption sites.

The linear form of Langmuir adsorption isotherm is given as [50]

$$\frac{C_e}{q} = \frac{1}{q_{max}k} + \frac{C_e}{q_{max}} \tag{4}$$

where C_e (mg L^{-1}), is the equilibrium concentration of adsorbate, q_e (mg g^{-1}) is the amount of adsorbate per unit mass of adsorbent, q_{max} (mg g^{-1}) is the maximum adsorption capacity, and KL (L mg^{-1}) is Langmuir constant related to energy of adsorption [51].

The plot of C_e/q against C_e gives straight lines with intercepts $1/q_{max}k$ and slope $1/q_{max}$. The isotherm constants were calculated from the linear regression of the experimental data. The characteristics of the Langmuir isotherm can be represented in terms of a dimensionless equilibrium parameter (R_L) which is given as

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

The isotherm constants and regression values (Table 5) show that the adsorption data are in close agreement with Langmuir isotherm model. The R_L values are less than one which shows that the adsorption data are fully fitted with Langmuir isotherm model and the adsorption of Cr(VI) onto GBPs is favorable. The literature study shows that the Langmuir model is more suitable for describing the adsorption isotherm of Cr (VI) onto various adsorbents [52,53] (see Fig. 7).

3.11. Adsorption kinetics

The kinetics study is required to find out the mechanism and rate determining step of a chemical reaction. Experiments were performed to find the required time for Cr(VI) adsorption onto grafted banana peels (GBPs). It was found that the Cr(VI) uptake by GBPs was rapid initially up to 60 min and then became slow until the equilibrium was established. This mode of adsorption showed that the Cr (VI) ions chemically interact with the adsorbent (GBPs) functional groups. In the present work pseudo first-order, pseudo second-order and intra particle diffusion have studied to find out the rate determining step of Cr(VI) adsorption onto GBPs.

3.11.1. Pseudo-first order model

The linear form of Lagergren pseudo 1st order rate expression is given by Eq. (6),

$$In(q_e - q_t) = In\,q_e - k_1 t \tag{6}$$

where q_e and q_t are the amount of Cr(VI) adsorbed (mg/g) on adsorbent at equilibrium and at time t, respectively and K_1 is the rate constant of pseudo first order adsorption (min^{-1}). The plot of $ln(q_e - q_t)$ vs. t, gives a straight line as shown in Fig. 8. The rate constant k_1 (min^{-1}) can be calculated from the slope of the linear plots [54,55].

3.11.2. Pseudo-second order model

The linear form of pseudo-second order model may be described as below,

$$\frac{t}{q^t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second order kinetic equation, and q_e and q_t are the amount of Cr(VI) adsorbed (mg/g) onto GBPs at equilibrium and at time t, respectively. The rate constant k_2 (g mg^{-1} min^{-1}) and equilibrium adsorption capacity q_e were calculated from the slop and intercept of the linear plot of t (time) vs t/q_t [56]. The results show that the second order model is applicable to describe the adsorption kinetics of Cr(VI) onto GBPs (see Fig. 9).
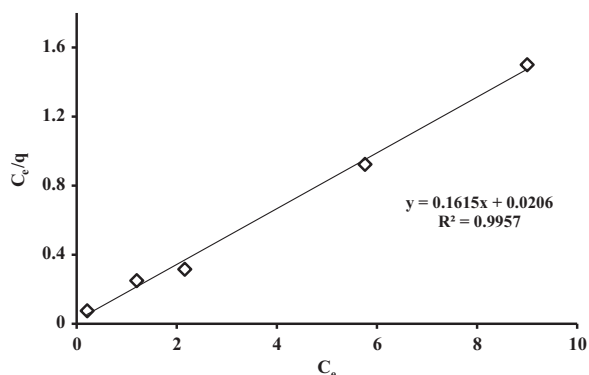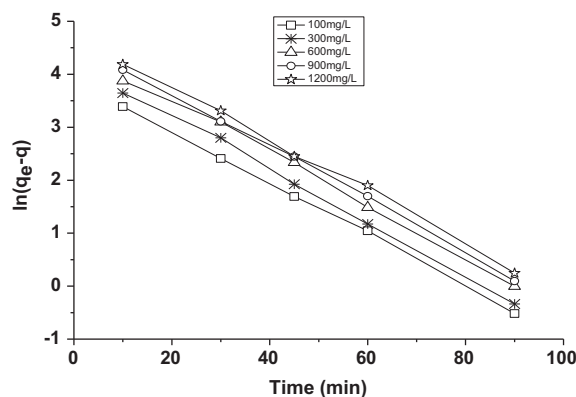

Figure 8 Pseudo-first order plot for Cr(VI) adsorption onto GBPs.

3.11.3. Intra-particle diffusion

The intra-particle diffusion model was used to investigate the diffusion mechanism of Cr(VI) onto GBPs. The metal ions transferred from solution into the solid phase during intra-particle diffusion process [57]. The intra-particle diffusion equation can be represented as

$$q_t = K_p t^{0.5} + C \tag{8}$$

where q_t (mg g^{-1}) is the amount of Cr(VI) adsorbed onto the adsorbent (GBPs) at time t, K_p (mg g^{-1} min$^{0.5}$) is the intra-particle diffusion rate constant and C is the intercept. The boundary layer effect is directly proportional to the intercept and it can be determined from the value of the intercept (Table 6). The plots are linear, which show the applicability of all three models. From Table 6 it is clear that r^2 for the pseudo-second-order kinetic model is 0.99 and the calculated q_e values are nearly close to the experimental q_e values. The intra-particle diffusion rate increased constantly with increase in Cr(VI) concentration as shown in Fig. 10.

3.12. Thermodynamic studies

The thermodynamic parameters such as entropy change (ΔS), enthalpy change (ΔH) and Gibb's free energy (ΔG) were determined to evaluate the feasibility and nature of adsorption by using the following equation:

Figure 7 Langmuir adsorption isotherm model for Cr(VI) onto GBPs.
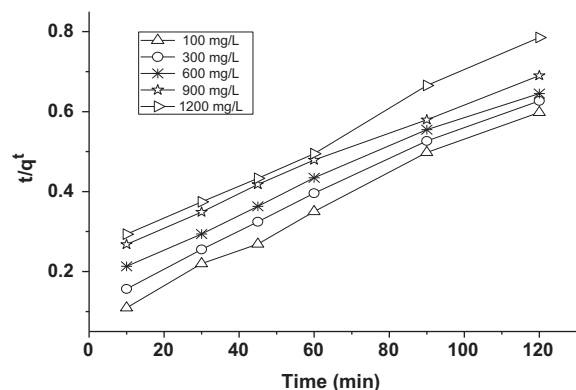

Figure 9 Pseudo-second order plot for Cr(VI) adsorption onto GBPs.

Table 6 Pseudo-first-order, pseudo-second order and intra-particle diffusion values for Cr(VI) adsorption on GBPs.

C_0 (mg/L)	Pseudo first order experimental		Pseudo first order calculated		Pseudo second order calculated			Intra-particle calculated	
	q_e (mg/g)	K_1	q_e	R^2	q_e (mg/g)	K_2	R^2	R^2	K_i (mg g^{-1} min^{-1})
200	135.30	0.0594	64.21	−0.9957	135.75	0.0417	0.999	0.9954	2.187
300	240.62	0.0508	87.03	−0.9937	242.02	0.0365	0.999	0.9905	1.56
600	312.80	0.0738	129.89	−0.9971	315.40	0.0329	0.999	0.9992	3.04
900	341.31	0.0649	138.92	−0.9995	343.71	0.0315	0.999	0.9815	3.75
1200	357.27	0.0520	139.05	−0.9981	359.97	0.0315	0.999	0.9978	3.90
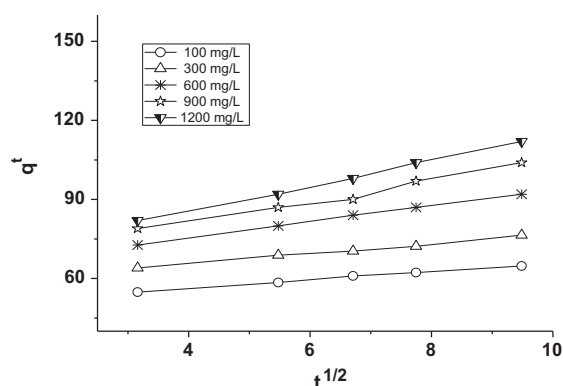
Figure 10 Intra-particle diffusion plot of Cr(VI) adsorption onto GBP.
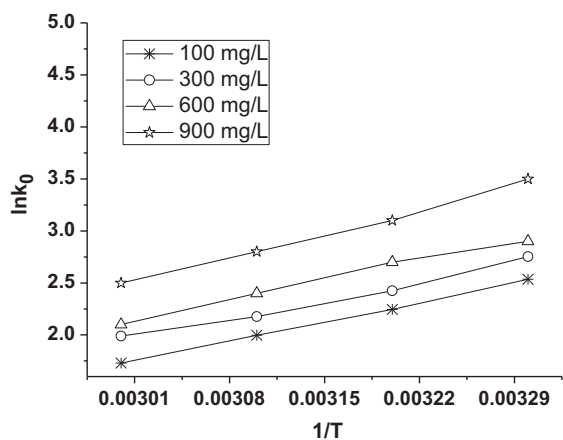
Figure 11 Von't Hoff plot of temperature effect on Cr(VI) initial concentration.

$$k_c = \frac{C_a}{C_s} \tag{9}$$

where C_a and C_s are the equilibrium concentration of solutes on adsorbent and in solution respectively and K_c is the

equilibrium constant. The Gibb's free energy change (ΔG) is related to equilibrium constant by the following equation:

$$\Delta G = -RT \ln K_c \tag{10}$$

The Gibb's free energy change is also related to entropy change (ΔS) and enthalpy change (ΔH) at constant temperature by the following equation:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{11}$$

The values of ΔH and ΔS were calculated from the plot of K_c vs. $(1/T)$ as shown in Fig. 11. The values of K_c, ΔH, ΔG and ΔS for the adsorption of Cr(VI) onto GBPs at various temperatures are given in Table 7. The negative values of ΔG and ΔH show that the adsorption is feasible, spontaneous and exothermic in nature [58]. The negative values of ΔG implied that the adsorption process is spontaneous and does not require an external energy source. The ΔG values decrease with increase in temperature indicating the decline in the feasibility of adsorption at higher temperature. The ΔS values are positive, which suggested that the randomness increased at solid/liquid interface during the adsorption of Cr(VI) onto GBPs.

4. Conclusion

(1) Chemically treated banana peels act as a good adsorbent for the removal of Cr(VI) from water.
(2) The optimized pH for Cr(VI) was found to be 3.0, adsorbent dose 4 g/L, concentration 400 mg/L and contact time of 120 min.
(3) Chemical treatment of banana peels results in the removing of peptic and viscous compounds and exposure of the functional groups of cellulose.
(4) The incorporation of a side chain ($-CH_2=CH-C\equiv N$) during grafting copolymerization onto banana peels can further increase its interaction with metal ions.
(5) The efficiency grafting copolymerization depends upon monomer concentration, temperature, initiator (Fe^{+2}) concentration and time.
(6) The adsorption data are fully fitted with Langmuir isotherm's model and follow pseudo-second order kinetic model.

Table 7 Equilibrium constants and thermodynamic parameter values for Cr(VI) adsorption on GBPs.

Adsorbate	$K_0 \times 10^{-4}$ (m^3 mol^{-1})				$-\Delta G^0$ (kJ mol^{-1})				ΔS^0 (kJ mol^{-1} K^{-1})	ΔH^0 (kJ mol^{-1})
	298 K	308 K	318 K	328 K	298 K	308 K	318 K	328 K		
Cr(VI)	71.02	64.25	57.00	52.31	34.54	36.86	38.53	40.68	0.095	63.32

(7) The adsorption capacity of grafted banana peels is much better than other agricultural adsorbents.
(8) The grafting banana peels can be used as an alternative to expansive activated carbon.

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