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Cr(III) and Cr(VI) Removal from Aqueous Solutions by Cheaply Available Fruit Waste and Algal Biomass

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Abstract This study compared the effectiveness of different biosorbents, viz. materials commonly present in natural treatment systems (*Scenedesmus quadricauda* and reed) and commonly produced fruit wastes (orange and banana peel) to remove Cr(III) and Cr(VI) from a synthetic wastewater simulating tannery wastewater. The Cr(III) removal efficiency followed the order *S. quadricauda*>orange peel>banana peel>reed, whereas the Cr(VI) removal followed the order banana peel>*S. quadricauda*>reed>orange peel. The chromium biosorption kinetics were governed by the intraparticle diffusion mechanism. Isotherm data obtained using the different biosorbents were fitted to the Langmuir, Freundlich, and SIPS models, revealing that the experimental data followed most closely the monolayer sorption theory-based Langmuir model than the other models. The maximum Cr(III) sorption capacity, calculated using the Langmuir model, was found to be 12 and 9 mg/g for *S. quadricauda* and orange peel, respectively, and the maximum Cr(VI) sorption capacity calculated for banana peel was 3 mg/g. The influence of biosorbent size, pH, solid–liquid ratio, and competing ions were examined for Cr(III) biosorption by *S. quadricauda* and orange peel and for Cr(VI) sorption by banana peel. The solution pH was found to be the most influential parameter affecting the biosorption process: whereas pH 5 was found to be optimum for maximum removal of Cr(III), Cr(VI) was best removed at a pH as low as 3. Interference to chromium sorption by various ions revealed that Cr(III) binding onto orange peel occurs through electrostatic forces, whereas Cr(VI) binding onto banana peel through non-electrostatic forces.

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Introduction

Wastewater from industries such as leather tanning, electroplating, metal finishing, and paint and pigment manufacturing contains substantial amounts (up to 345 mg/L) of chromium [1]. Cr(III) is extensively used for leather tanning due to its excellent property to stabilize the leather by cross-linking the collagen fibers. Compared to vegetable-tanned leather, chrome-tanned leather tends to be softer and more pliable, has higher thermal stability, is very stable in water, and involves less processing time [2]. During the tanning process, the leather takes up about 60–80 % of the added chromium, the rest is usually discharged with the wastewater which may pose a serious threat to the receiving environment if it is not treated properly. Tannery effluent commonly contains both Cr(III) and Cr(VI), of which Cr(VI) is reported to be more toxic and carcinogenic [3–6]. Further, Cr(III) present in the effluent can be oxidized to Cr(VI) under aerobic and mildly anoxic conditions or by interactions with mineral oxides (e.g., with MnO_2) [7, 8]. Hence, there is a need to minimize the release of chromium to the environment, for this its removal from industrial wastewaters is instrumental.

Chromium can be removed from wastewaters by ion exchange, solvent extraction, chemical precipitation, reverse osmosis, dialysis, electrolysis, and adsorption [9, 10]. These methods suffer, however, from one or more drawbacks such as inefficient chromium removal, high reagent or energy requirements, high operation and maintenance cost as well as the generation of secondary sludge. Because of continual use of traditional methods of chrome tanning, techniques for recycling of chromium are unavailable in the developing countries [11]. Therefore, there is still a need to develop cheap and easy to apply treatment methods. Such a method might be biosorption, a passive process by which biological materials effectively sequester pollutants such as heavy metals from aqueous solution [12]. Biosorption also has distinct advantages over conventional treatment methods [12–14]. For instance, the process does not produce chemical sludge, it is highly efficient, cost-effective, and biosorption equipment is often easy to operate. Chromium removal through biosorption onto biomass involves different mechanisms and the most commonly reported mechanisms for metal sorption are ion exchange, electrostatic interaction, chelation, precipitation, and complexation [15]. In general, biomass from algae and fungi contain several functional groups that are well capable of binding or sequestering heavy metals; for example, acetamido groups in chitin (homopolymer of *N*-acetylglucosamine) and chitosan (heteropolymer of *N*-acetylglucosamine and glucosamine); amino and phosphate groups in nucleic acids; amido, amino, sulphhydryl, and carboxyl groups in proteins; hydroxyl, carboxyl, and sulfate groups in polysaccharides. The presence of some functional groups with binding abilities, however, does not always guarantee biosorption [16], due to steric or conformational hindering or other barriers.

Although several types of plant and microbial biomass have been screened and studied for chromium removal (Table 1), the search for cheap and abundantly available biosorbent materials still continues to allow cheap large-scale applications in low-income countries. This study was aimed at screening various cheap and abundantly available biosorbents from natural treatment systems and solid waste for Cr(III) and

Table 1 Maximum chromium sorption capacity of selected algal, plant or fruit waste-based biosorbents[a]: Cr(III) and Cr(VI)

Biosorbent	Uptake capacity (mg/g)	pH
Cr(III)		
Agave bagasse	11.44	4
Cannomois virgata	7.88	4.5–5.5
Cassia fistula	114.9	5
Colocasia esculenta	6.07	4.5–5.5
Eichornia crassipes	6.61	3.5
Leersia hexandra Swartz	28.64	5
Lignin	17.97	5
Nymphaea sp	5.11	4.5–5.5
Oats straw	12.97	4
Orange waste (*Citrus cinensis*)	79.04	4
Parmelina tiliaceae	52.1	5
Rhizoclonium hieroglyphicum	11.81	4
Rhizophora mangle L	6.54	4.5–5.5
Sorghum straw	6.96	4
Spirogyra condensate	14.82	5
Spirogyra spp	30.21	5
Cr(VI)		
Agaricus bisporus	8	1
Alligator weed	83.57	1
Almond	3.40	3
Cannomois virgata	1.66	4.5–5.5
Cassia fistula	131.5	2
Chroococcus sp. *HH-11*	21.36	3–4
Colocasia esculenta	1.42	4.5–5.5
Eichornia crassipes	0.34	3.5
Hazelnut	8.28	5
Leersia hexandra Swartz	2.54	2
Maize bran	312.52	2
Marine *Aspergillus niger*	117.33	1
Nostoc calcicola HH-12	12.23	3–4
Nymphaea sp	6.11	4.5–5.5
Oedogonium hatei	35.2	2
Quercus ithaburensis2	57.80	
Rhizophora mangle L	5.72	4.5–5.5
Sargassum sp	39.61	2
Sawdust	41.5	1
Sunflower head	8.18	2
Tea factory waste	54.65	2
Walnut hull	98.13	1
Wheat bran	310.58	2

[a] Source: Sahmoune et al. [25]

Cr(VI) removal from synthetic tannery wastewater. The effect of the biosorbent dose, initial chromium concentration, pH, biosorbent size, and competing ions on chromium removal by the most suited biosorbents was examined in detail. In addition, the influence of interfering ions on chromium sorption and desorption of bound chromium from the biosorbents was investigated to understand the nature of binding between chromium and the biosorbents.

Materials and Methods

Source and Preparation of Biosorbents

The biosorbent materials used in this study comprised plant materials abundantly used in natural wastewater treatment systems (algae and reed) and fruit wastes (orange and banana peel). The plant weed reed (*Phragmites australis*) was collected from the edges of a ditch of a local farm yard in Delft (The Netherlands). Banana peel (*Musa acuminata*) and orange peel (*Citrus sinensis*) were prepared by collecting the fruits from a local market in Delft. The algae *Scenedesmus quadricauda*, obtained from the Culture Collection of Autotrophic Microorganisms (Institute of Botany, Třeboň, Czech Republic), was cultured under 60 μmole photon/m^2·s light intensity, 150 rpm agitation, and at 25 °C in the laboratory using 250-ml flasks containing 100 mL sterile BG-11 medium [14]. The medium consisted of (g/L): 0.006 citric acid, 0.006 ammonium ferric citrate, 0.001 sodium EDTA, 0.02 Na_2CO_3, 1 ogawa, 1.5 $NaNO_3$, 0.04 K_2HPO_4, 0.075 $MgSO_4$, 0.036 $CaCl_2{\cdot}2H_2O$, 0.06 $Na_2SiO_3{\cdot}9H_2O$, and pH 7.4 [13].

All the biosorbent materials, other than the algae, were processed as described by Elangoven et al. [14]. Briefly, the biosorbents were cut into small pieces and washed with de-ionized water to remove any water-soluble impurities and other surface adhered particles. The materials were then air dried for 24 h followed by oven-drying at 55 °C. The dried biosorbents were subsequently crushed and passed through sieves to obtain uniform sizes in the desired range of 500–1,400 μm. The biosorbents so prepared were stored under vacuum until use. In the case of the algae, the fully grown biomass, obtained at the end of 5 days culture, was collected by centrifugation at 3,500×*g* for 15 min. The pellet was then washed with de-ionized water and subsequently dried to constant weight in an oven at 55 °C for 24 h before use.

Biosorption Experiments

All biosorption experiments were performed in triplicate using 1 L plastic bottles with 500 ml of known chromium concentration as described by Pakshirajan et al. [17]. The aqueous solution of Cr(III) was prepared by suitably diluting a stock solution of analytical grade $CrCl_3{\cdot}6H_20$ in de-ionized water, whereas Cr(VI) solutions were prepared by suitable dilution of a $K_2Cr_2O_7$ stock solution.

Experiments were carried out at ambient room temperature under batch conditions by incubating the bottles on an orbital shaker, set at 150 rpm. The biosorption bottles were shaken for 2 h, except in case of the batch kinetic experiments which were continued for 24 h. Samples collected during the experiments were analyzed for chromium remaining in the solution following separation of the chromium-loaded biomass by filtration using Whatman Filter paper (11 μm pore size).

Results were expressed as either % chromium removal or sorption capacity (q, milligrams of chromium removed per gram of biosorbent) as given in Eqs. 1 and 2 below:

$$\%\ \text{chromium removal} = \frac{(\mathrm{C_i} - \mathrm{C_e})}{\mathrm{C_i}} \times 100 \tag{1}$$

$$q = \frac{V(C_i - C_e)}{m} \tag{2}$$

where C_i and C_e are, respectively, the initial and final chromium concentrations in solution (milligrams per liter), q is the chromium uptake/sorption capacity (milligrams per gram of biomass), V is the volume of chromium containing solution (liters), and m is the biosorbent dry weight (grams).

Screening Biosorbent Performance in Batch Equilibrium Test

The best biosorbent(s) among *S. quadricauda*, reed, orange peel, and banana peel for removing Cr(III) and Cr(VI) from aqueous solution were first screened in batch equilibrium tests. The contact time required to reach equilibrium between dissolved and solid-bound chromium was determined with 20 mg/L Cr(III) and Cr(VI) solutions each at unadjusted solution pH and 0.4 g of each of the biosorbents. Samples were collected at regular contact time intervals (20, 40, 60, 120, 180, and 360 min) for chromium analysis.

The kinetics of chromium sorption by the various biosorbents tested was studied by fitting the experimental data to the pseudo second-order and the intraparticle diffusion models. The pseudo second-order kinetic rate equation is expressed as [18]:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{3}$$

where q_e and q_t are the amount of solute sorbed per gram of a sorbent at equilibrium and at time t, respectively, and k_2 is the second-order sorption rate constant. The above equation can be linearized as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

From a linear plot of t/q_t vs t, the values of q_e and k_2 were calculated from its slope and intercept, respectively. The initial sorption rate according to this equation was further defined as [19]:

$$h = k_2 q_e^2 \tag{5}$$

The intraparticle diffusion model is given by [20, 21]:

$$q_t = k_{\mathrm{id}} t^{0.5} \tag{6}$$

where k_{id} is the intraparticle diffusion rate constant (mg/g $\mathrm{min}^{0.5}$).

For estimating the maximum chromium sorption capacity and values of the other sorption kinetic parameters, the results obtained from the isotherm study (refer Section "Influence of Process Parameters on Chromium Sorption") were fitted to isotherm sorption models that are widely reported in the literature. These model equations are presented in Table 2. For non-linear estimation of the model parameters, the Solver add-in function of Microsoft Excel was used. To evaluate the fit of the models, the coefficient of determination (R^2) was calculated.

Table 2 Models applied to fit the chromium sorption isotherms

Model	Equation[a]	Reference
Langmuir	$q_e = \frac{q_{\max} b C_e}{(1+bC_e)}$	[31]
Freundlich	$q_e = K_F C_e^{1/n}$	[31]
SIPS	$q_e \frac{q'_{\max} b C_e^{1/n'}}{\left(1+bC_e^{1/n'}\right)}$	[31]

[a] q_e solid-phase equilibrium chromium concentration (mg/g), C_e liquid-phase chromium concentration (mg/L), $q_{\max}$ maximum uptake capacity in Langmuir model (mg/g), b constant in Langmuir model (L/mg), K_F Freundlich equilibrium constant (L/mg), n dimensionless parameter in Freundlich model, $q'_{\max}$ maximum sorption capacity in SIPS model (mg/g), b a constant in SIPS model (L/μg), n' dimensionless parameter in SIPS model

Influence of Process Parameters on Chromium Sorption

Based on the results of batch equilibrium tests, orange peel and *S. quadricauda* were selected to study the effect of various parameters, viz. biosorbent dose, initial chromium concentration, solution pH, particle size, and competing ions on Cr(III) removal. Similarly, banana peel was chosen to investigate the effect of these parameters on Cr(VI) biosorption.

The effect of the biosorbent dose on chromium biosorption was studied in the range 1–14 g/L with 25 mg/L initial chromium concentration and at solution pH 5. To study the effect of the initial Cr(III) and Cr(VI) concentration on its biosorption, the concentration range chosen was 10–125 mg/L at solution pH 5. The effect of solution pH on chromium removal was studied by varying the initial pH of the solution from 1 to 9. Although compared to Cr(VI), Cr(III) may get precipitated at a solution pH above 6, the range chosen for studying the effect of this parameter was the same in order to maintain uniformity in the experiments. For studying the effect of the particle size, a known amount of the dry biosorbent was crushed and sieved to different particle sizes in the range 0.28–1.4 mm and then subsequently used in the experiments. For these experiments to determine the effects of pH and particle size on chromium biosorption, the initial chromium concentration used was 25 mg/L. Based on the results of previous experiments to examine the effect of biosorbent dose on chromium biosorption, the amounts of orange peel, *S. quadricauda* and banana peel taken in the three latter experiments were 5, 2.5, and 10 g/L, respectively.

The influence of competing ions on Cr(III) and Cr(VI) biosorption by orange peel and banana peel, respectively, was investigated using different salts that are commonly encountered in tannery wastewater. The ions tested in the case of Cr(III) sorption experiments were Na^+, K^+, and Mg^{2+} at initial concentrations of 50, 75, and 100 mg/L for each ion. The respective salts NaCl, KNO_3, and $MgSO_4 \cdot 7H_2O$ were used for these ions. The initial Cr(III) concentration and biosorbent weight were, respectively, 25 mg/L and 5 g/L. The experimental method followed for Cr(VI) was also the same, except that the effect of different interfering anions (instead of cations), viz. Cl^-, NO_3^-, and SO_4^{2-} were examined and the biosorbent weight was 10 g/L.

Desorption of Bound Chromium

Desorption of bound Cr(III) and Cr(VI) from, respectively, orange peel and banana peel, was tested using demineralized water and 0.1 M NaOH as the eluants. Experiments were

conducted by agitating plastic bottles containing the loaded biosorbents and the eluants at 150 rpm for 2 h. Cr(III) and Cr(VI) loaded biosorbents were initially obtained by contacting 2.5 and 5 g of orange peel and banana peel, respectively, with 500 mL aqueous solutions containing 25 mg/L chromium for 24 h. Desorption efficiencies for Cr(III) and Cr(VI) were calculated from the ratio (%) of the amount desorbed to that initially sorbed onto the biosorbent.

Analytical Methods

Cr(III) and Cr(VI) concentrations in the sample filtrates were measured using an atomic absorption spectrometer (AAS, PerkinElmer, model AAnalist200), equipped with an air-acetylene flame as described by Balasubramanian and Pugalenthi [22]. The detection limit of the AAS for chromium was 1 mg/L.

The solution pH was measured with a SenTix21 pH electrode (WTW model pH323). The pH meter was calibrated using buffer solutions with pH values of 4.00, 7.00, and 10.00.

Results

Chromium Sorption Kinetics

Cr(III) removal by the different biosorbents initially occurred quickly and increased only gradually after 50 min (Fig. 1a). *S. quadricauda* displayed the highest Cr(III) removal efficiency (97 %) followed by orange peel, banana peel, and reed (Fig. 1a).

Cr(VI) sorption kinetics were similar to those of Cr(III) with the maximum removal taking place in the first 50 min, followed by a gradual increase until equilibrium was reached after ~120 min (Fig. 1b). Banana peel showed the best Cr(VI) removal efficiency (30 %) compared to the other biosorbents examined, which is, however, still not very high.

The equilibrium rate constants of the pseudo second-order kinetics for Cr(III) sorption were determined from the plot of t/q_t versus time (Fig. 2). The initial sorption rate (h), the rate constant (k_2), and the correlation coefficient (R^2) of this model for the sorption of Cr(III) by orange peel, reed, banana peel, and *S. quadricauda* and the sorption of Cr(VI) by banana peel were calculated from Fig. 2 and presented in Table 3. The results showed a very good fit ($R^2>0.98$) for Cr(III) removal by all these sorbents and Cr(VI) removal by banana peel. However, orange peel and banana peel gave the best fit ($R^2=1$) for Cr(III). The model fit for Cr(VI) removal by banana peel was also accurate ($R^2=0.999$).

Figure 3 presents the intraparticle diffusion model plot for Cr(III) and Cr(VI) sorption onto orange peel, banana peel, *S. quadricauda*, and reed. All the plots showed multiple linear phases, which is an indication of the existence of a boundary layer diffusion effect (i.e., external film resistance) as well as an intraparticle diffusion stage. The intraparticle diffusion rate constants (Table 3) were calculated from the slope of the second phase of the plots.

Effect of Biosorbent Dose on Chromium Removal

The Cr(III) removal efficiencies by *S. quadricauda* and orange peel increased with an increase in their dose (Fig. 4). In contrast, the Cr(III) sorption capacity decreased with their dosage. Figure 4 also shows the effect of a different dose of banana peel on Cr(VI) sorption, confirming the trend as observed with Cr(III) sorption by *S. quadricauda* and orange peel.

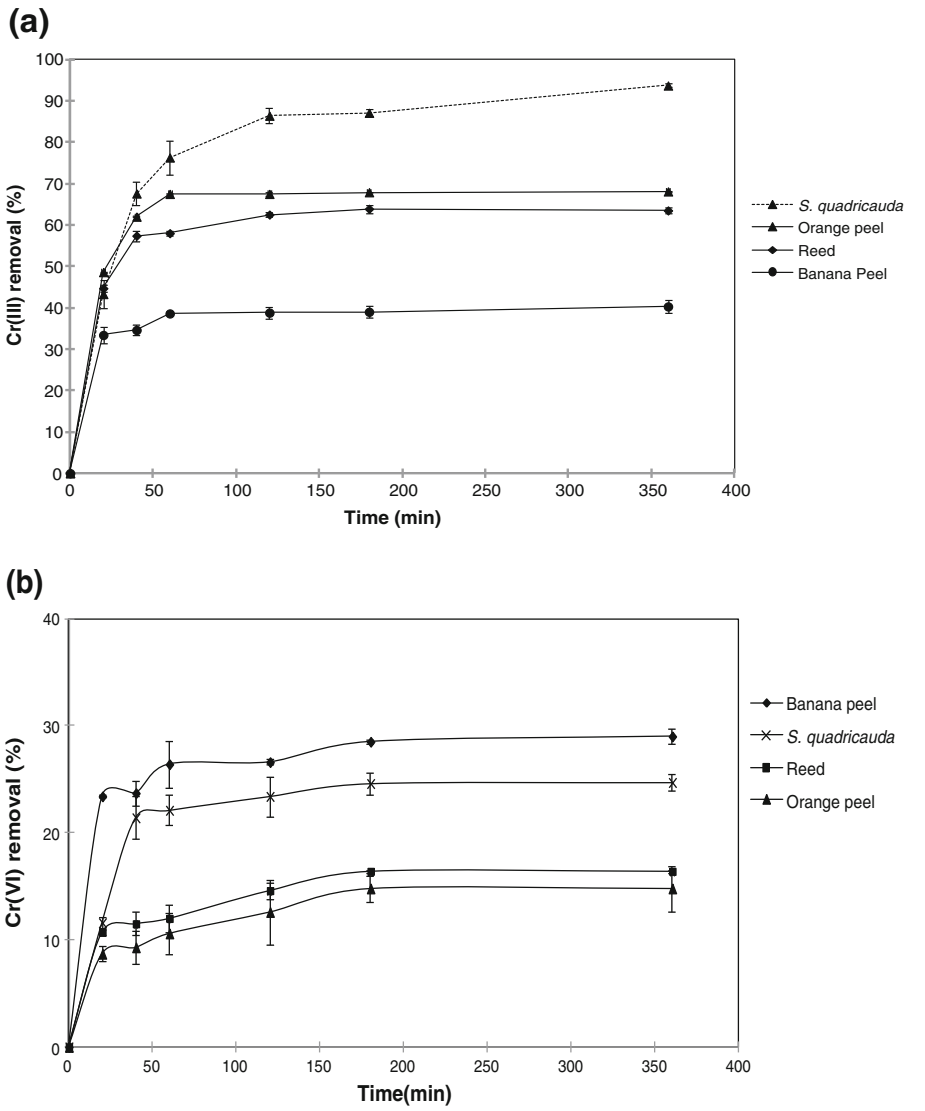

Fig. 1 Kinetics of **a** Cr(III) and **b** Cr(VI) removal by the different biosorbents. Sorption conditions: initial chromium concentration=20 mg/L, unadjusted solution pH, and 0.8 g/L biosorbent concentration

However, the Cr(VI) removal by banana peel was only high after adding a relatively large dose (10 g/L).

Effect of Initial Chromium Concentration on Its Removal

For both *S. quadricauda* and orange peel, the Cr(III) sorption capacity increased with an increase in the initial chromium concentration (Fig. 5). For orange peel, an initial Cr(III) concentration of 25 mg/L is found to be optimum. A similar trend was observed for the effect of initial Cr(VI) concentration on its removal by banana peel (Fig. 5).

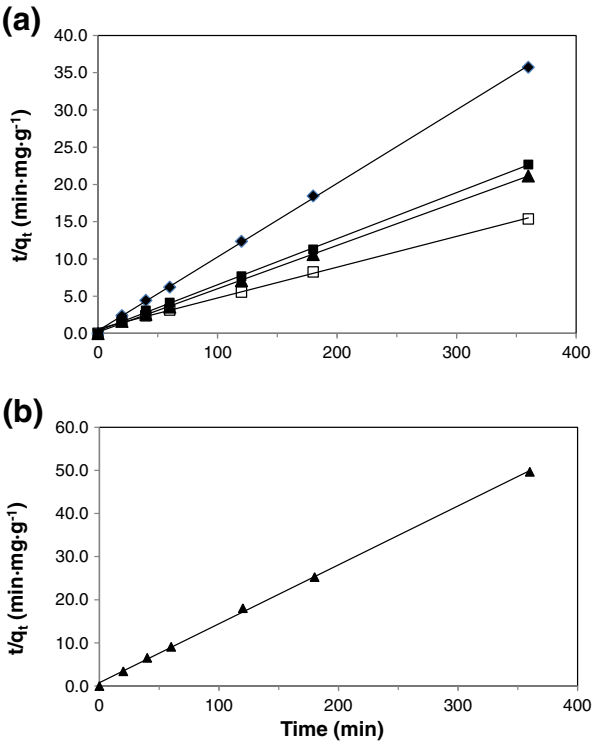

Fig. 2 Pseudo second-order kinetics plots for sorption of **a** Cr(III) and **b** Cr(VI) using orange peel (*filled diamond*), reed (*filled square*), banana peel (*filled triangle*), and *S. quadricauda* (*unfilled square*). Sorption conditions: initial chromium concentration=20 mg/L, unadjusted solution pH, and 0.8 g/L biosorbent concentration

Table 4 presents the estimated model parameters and accuracy of fitness of the Langmuir, Freundlich, and SIPS isotherm models to the experimental data. Between the two most popularly known two-parameter isotherm models, the high R^2 values obtained due to the Langmuir model for all three biosorbents indicate its better applicability over the Freundlich model in explaining the experimental data. Further, the estimated n' values from the three-parameter SIPS isotherm model for these biosorbents are close to unity, confirming that the data followed more monolayer sorption theory-based Langmuir model than the Freundlich model [17]. The value of the Freundlich constant n obtained for Cr(III) sorption by *S. quadricauda* and orange peel, which is greater than one, also indicates favorable sorption of Cr(III) onto the biosorbents [23]. Similarly, Cr(VI) sorption by banana peel was found favorable, as indicated by the value of its Freundlich constant n (Table 4).

Effect of Solution pH and Biosorbent Size on Chromium Removal

The removal efficiencies of both Cr(III) and Cr(VI) decreased only slightly with an increase in particle size of both orange peel and banana peel (Fig. 6). Cr(VI) removal by banana peel at varying pH showed that its uptake increased at a decrease in solution pH and the maximum removal is observed at pH 3 (Fig. 7). At a pH value below 3, the removal

Table 3 Summary of the kinetic model parameters for Cr(III) and Cr(VI) sorption

Kinetics parameter	Biosorbent			
	Orange peel	Reed	Banana peel	*S. quadricauda*
Cr(III)				
Pseudo second-order				
q_e (mg g^{-1})	10.132	16.129	17.212	24.155
k_2 (g mg^{-1} min^{-1})	2.421×10^{-2}	1.385×10^{-2}	1.807×10^{-2}	2.808×10^{-3}
h (mg g^{-1} min^{-1})	10.123	16.139	17.210	24.158
R^2	1	0.999	1	0.996
Intraparticle diffusion				
k_{id} (mg g^{-1} $min^{-0.5}$)	0.395	1.461	1.014	0.975
R^2	0.993	0.974	0.999	0.969
Cr(VI)				
Pseudo second-order				
q_e (mg g^{-1})			7.331	
k_2 (g mg^{-1} min^{-1})			2.226×10^{-2}	
h (mg g^{-1} min^{-1})			12.046	
R^2			0.999	
Intraparticle diffusion				
k_{id} (mg g^{-1} $min^{-0.5}$)			0.225	
R^2			0.945	

efficiency was less. Figure 7 shows that the Cr(III) removal efficiency by both *S. quadricauda* and orange peel increased with an increase in pH from 3 to 5, and the removal was found to be less outside this pH range. Between the two biosorbents, *S. quadricauda* again showed the higher Cr(III) removal efficiency with a maximum of 88 % at pH 5.

Effect of Competing Ions on Chromium Removal

Figure 8 shows the effect of competing ions on the Cr(III) and Cr(VI) removal efficiency by orange peel and banana peel, respectively. Cr(III) removal was mainly affected by Mg^{2+} (Fig. 8a) that resulted in maximum 20 % reduction in the Cr(III) removal efficiency. Whereas less than 20 % reduction in the Cr(III) removal efficiency is observed in the presence of Na^+, K^+ had an almost negligible effect. Figure 8b shows that compared to Cl^- and SO_4^{2-}, NO_3^- slightly (less than 10 %) inhibited the removal of Cr(VI) by banana peel, but only at a high concentration (100 mg/L).

Desorption of Bound Chromium

NaOH was found to be a better eluant over demineralized water, which resulted in 60 and 27 % release of the bound Cr(III) from orange peel and Cr(VI) from banana peel, respectively. Using demineralized water as the eluant, only 25 and 4 % desorption of Cr(III) from orange peel and Cr(VI) from banana peel, respectively, were obtained.

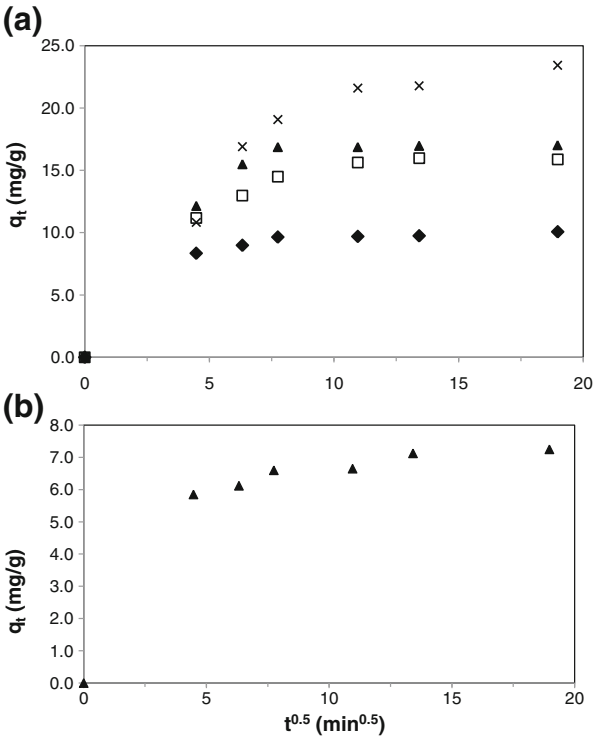

Fig. 3 Intraparticle diffusion plot for sorption of **a** Cr(III) and **b** Cr(VI) using orange peel (♦), *S. quadricauda* (×), banana peel (▲), and reed (□). Sorption conditions: initial chromium concentration=20 mg/L, unadjusted solution pH, and 0.8 g/L biosorbent concentration

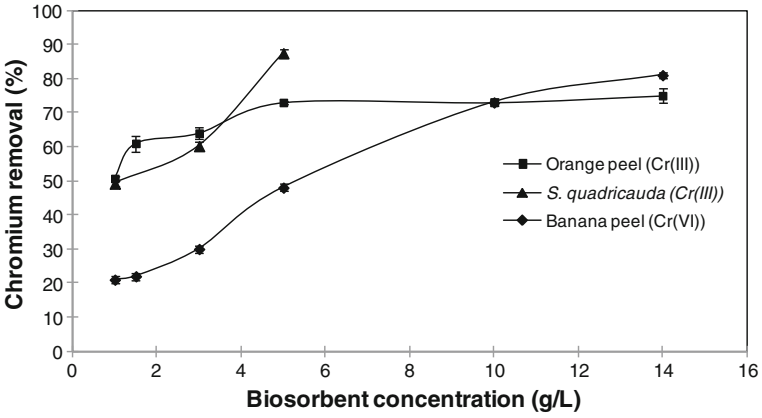

Fig. 4 Effect of biosorbent dose on Cr(III) and Cr(VI) removal. Biosorption conditions: initial chromium concentration=25 mg/L and solution pH=5

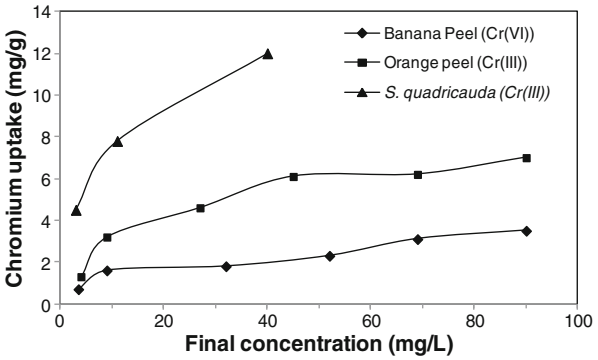

Fig. 5 Effect of initial concentration on Cr(III) and Cr(VI) biosorption. Biosorption conditions: biosorbent concentration (g/L)=10 (banana peel), 5 (orange peel), 2.5 (*S. quadricauda*); and solution pH=5

Discussion

Effect of Process Parameters on Chromium Removal

Chromium biosorption was well described by the two-parameter Langmuir isotherm model. The estimated n' values from the three-parameter SIPS isotherm model for these bisorbents (Table 4) also confirmed that the chromium sorption followed the Langmuir sorption theory. The equilibrium sorption capacity of the biosorbent increased with increase in the initial concentration of chromium (Fig. 5), as was also reported for tea waste [24]. This can be attributed to the increased availability of the metal ions at high initial concentration that provides the necessary driving force for its effective mass transfer and also binding with the available functional groups on the biosorbent surface [25]. From the second-order kinetics model fitting of the data (Fig. 2 and Table 3), both Cr(III) and Cr(VI) biosorption followed a second-order reaction pathway. To further deduce the diffusion mechanism and rate-controlling steps affecting the chromium sorption kinetics, the experimental results were further analyzed by the intraparticle diffusion model, which revealed that the rate-limiting step was the intraparticle diffusion rather than film diffusion (Fig. 3 and Table 3). To further identify the functional groups and binding mechanisms involved in the chromium sorption process, structural details of the biosorbents as well as the speciation of the sorbed chromium need to be determined using Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, or high-resolution nuclear magnetic resonance [17].

Table 4 Estimated model parameters on Cr(III) biosorption by *S. quadricuada* and orange peel (OP) and on Cr(VI) biosorption by banana peel (BP)

Biosorbents	Isotherm model and estimated values of the parameters									
	Langmuir			Freundlich			SIPS			
	q_{max} (mg/g)	b (L/mg)	R^2	K_f (mg/g)	N	R^2	q'_{max} (mg/g)	b (L/mg)	n'	R^2
S. quadricuada	12	0.224	0.9801	2.30	2.77	0.9278	24	0.123	0.566	0.9399
Orange peel	9	0.043	0.9839	3.20	1.98	0.9271	8	0.063	0.953	0.8496
Banana peel	3	0.05	0.9584	2.83	2.21	0.9106	63	0.007	0.474	0.9357

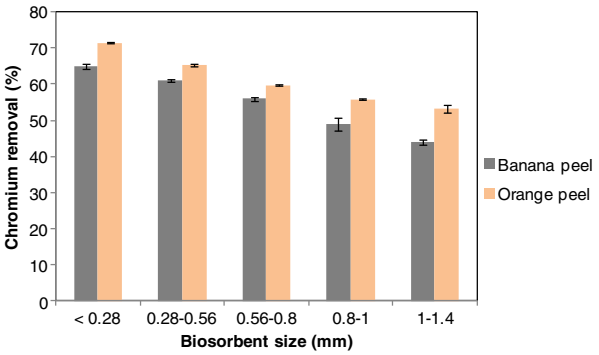

Fig. 6 Effect of biosorbent size on chromium removal efficiency. Biosorption conditions: initial chromium concentration=25 mg/L, solution pH=5, and biosorbent concentration (g/L)=10 (banana peel), 5 (orange peel), and 2.5 (*S. quadricauda*)

An increase in chromium removal efficiency at high biosorbent dose (Fig. 4) revealed that chromium binding sites on the biosorbents were plenty but the amount of chromium available for binding was limited. However, the Cr(III) removal efficiency by orange peel at a dose above 5 g/L remained the same, probably due to limitation in Cr(III) mass transfer from solution to the biosorbent binding site, particularly due to the flux required to drive the sorption process [26]. In contrast, a slight decrease in both Cr(III) and Cr(VI) removal efficiency with an increase in size of the biosorbents (Fig. 6) is easily explained based on the reduced availability of chromium binding sites due to relatively small surface area of larger-sized biosorbents [27].

Chromium biosorption was largely affected by the solution pH (Fig. 7). This is mainly due to its well-known effect on chromium speciation and also due to its significant influence on the degree of ionization and surface characteristics of the biosorbents [25, 28]. At a low pH, whereas competition from H^+ ions caused a reduction in the removal efficiency of cationic Cr(III) species by both orange peel and *S. quadricauda*, the removal efficiency of predominantly anionic Cr(VI) species by banana peel improved due to the availability of positively charged protons and other protonated functional groups (e.g., amino groups). Thus, the Cr(III) removal efficiency by *S. quadricauda* and orange peel increased with an

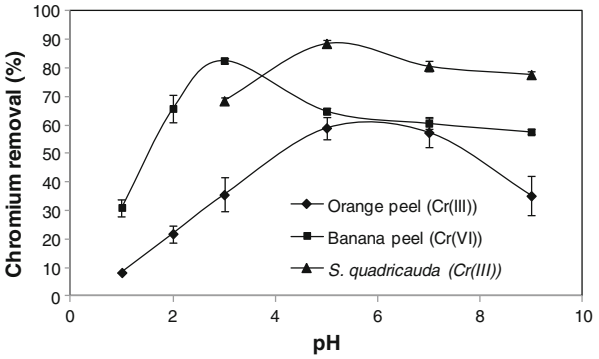

Fig. 7 Effect of solution pH on Cr(III) and Cr(VI) biosorption. Biosorption conditions: initial chromium concentration=25 mg/L and biosorbent concentration (g/L)=10 (banana peel), 5 (orange peel), and 2.5 (*S. quadricauda*)

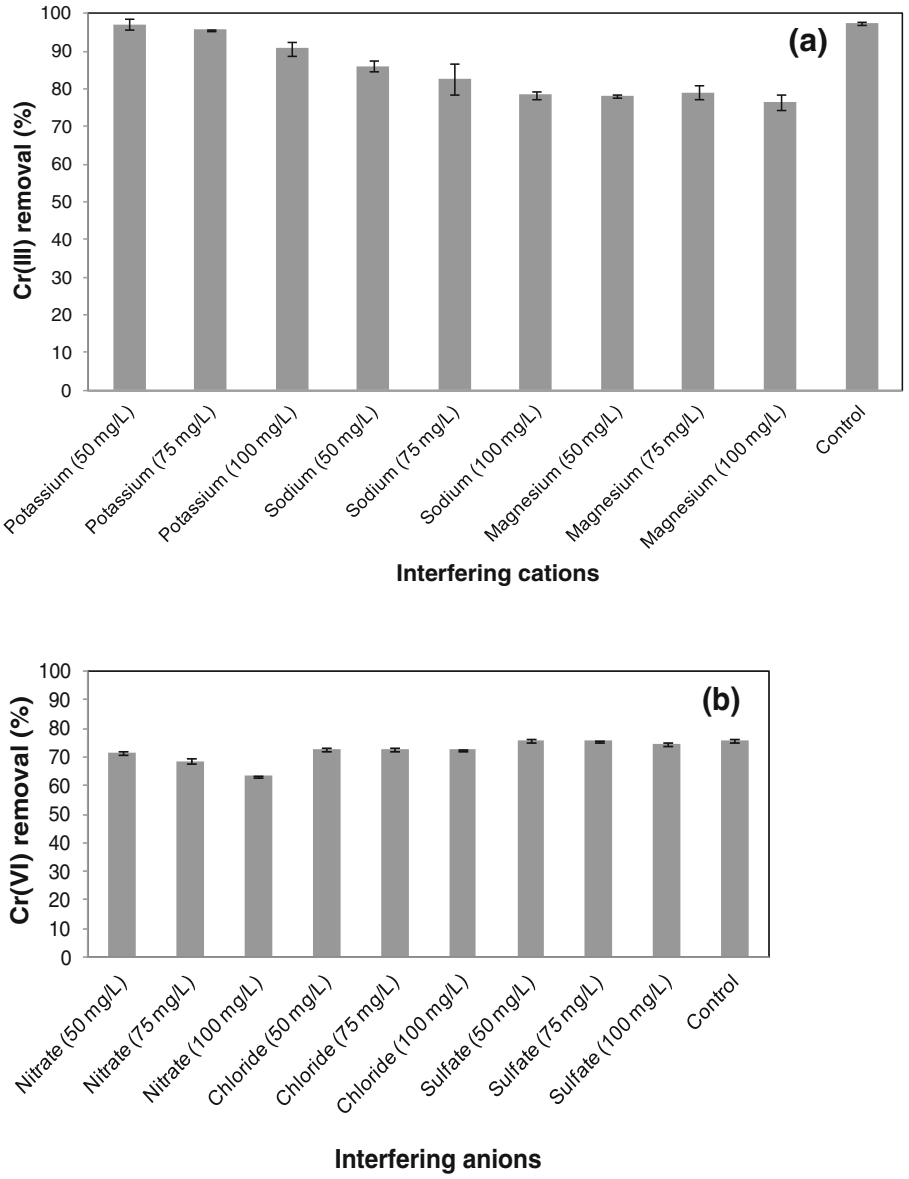

Fig. 8 Effect of competing ions on **a** Cr(III) removal by orange peel and **b** Cr(VI) removal by banana peel. Biosorption conditions: initial chromium concentration=25 mg/L, solution pH=5, and biosorbent concentration (g/L)=10 (banana peel) and 5 (orange peel)

increase in the solution pH from 3 to 5. The removal was less outside this pH range for both biosorbents, which further supports the involvement of functional groups such as carboxylic acids on the biosorbent surface in its uptake [29]. However, at an initial solution pH above 6, because precipitation of Cr(III) cannot be neglected, the precise role of these biosorbents on Cr(III) removal needs to be ascertained further, e.g., by determining the amount of Cr(III) removed from solution in the form of precipitates both in the presence and in the absence of

biosorbents at an elevated solution pH. In case of Cr(VI), at low solution pH it predominates as the anions $HCrO_4^-$ and $Cr_2O_7^{2-}$ that can effectively bind with the protons and protonated functional groups on the biosorbent [24, 25].

Cr(III) Versus Cr(VI) Removal Mechanisms

The influence of solution pH on chromium sorption revealed the involvement of anionic functional groups in both orange peel and *S. quadricauda* for Cr(III) binding, which could, however, be neutralized or protonated under low pH condition to reduce the Cr(III) removal efficiency (Fig. 6). On the other hand, it is mainly the protein molecule containing amino groups of banana peel that play a major role in Cr(VI) sorption even under unadjusted pH conditions [28]. These two aspects were further validated from the influence of interfering ions on chromium sorption. Indeed, the interfering divalent Mg^{2+} competed more strongly than monovalent cations (Na^+ and K^+) with Cr(III) for binding with the biosorbent (Fig. 8). This competition was, however, independent of the Mg^{2+} concentration, suggesting that the tested lowest concentration was itself sufficient to interfere with Cr(III) sorption onto orange peel. Secondly, only NO_3^- among the other anions slightly inhibited Cr(VI) removal by banana peel (Fig. 8), particularly at its highest concentration tested confirming that at pH 5 (a) the anionic species of Cr(VI) is simply not available for competition with other strong interfering anions (SO_4^{2-} and Cl^-) for the same binding sites and (b) nitrate, which is a relatively weak anion, competes with undissociated Cr(VI) for binding with the same protein molecule containing amino groups on the biosorbent [30]. The desorption efficiency of Cr(III) and Cr(VI) from orange peel and banana peel, respectively, further confirmed the involvement of ionic forces in the case of Cr(III) binding with orange peel, whereas Cr(VI) binding with banana peel involves non-electrostatic forces [30].

Practical Implications

The biosorbents based on cheaply available fruit waste and algae investigated in this study can be used for effectively removing chromium from tannery wastewater. The maximum chromium sorption capacity of these biosorbents at an unadjusted pH was also better than most biosorbents reported in the literature (Table 1). For practical applications, these chromium-loaded biosorbent materials must be regenerated and reused allowing recovery of the sorbate. Additional work to optimize the regeneration step is necessary. Further, to evaluate the application of these biosorbents at industrial scale, laboratory column and subsequent pilot scale studies are required. In addition, the performance of the biosorbents to remove chromium from real tannery wastewater needs to be examined during the pilot study. Finally, for application at the industrial level, a detailed cost–benefit analysis and comparison of different processes with biosorption using these sorbents must be worked out.

Conclusions

This study showed that cheaply available fruit wastes and algae have an excellent potential for the removal of chromium from contaminated wastewaters. Among the biosorbents tested, banana peel proved to be efficient in removing Cr(VI), whereas orange peel and *S. quadricauda* showed an equally good potential to remove Cr(III). The chromium sorption kinetics by these biosorbents were governed by intraparticle diffusion mechanisms and the biosorption isotherms followed the Langmuir model that is based on the monolayer sorption

theory. The influence of solution pH, interference of various ions on chromium biosoprtion and desorption of bound chromium revealed the involvement of electrostatic forces for binding Cr(III) in contrast to non-electrostatic forces for binding Cr(VI) onto the waste fruit materials.

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