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Banana Peel: A Green and Economical Sorbent for Cr(III) Removal

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Abstract

Banana peel, a common fruit waste has been investigated to remove and preconcentrate Cr(III) from industrial wastewater. It was characterized by FT-IR spectroscopy. The parameters pH, contact time, initial metal ion concentration and temperature were investigated and the maximum sorption was found to be 95%. The binding of metal ions was found to be pH dependent with the optimal sorption occurring at pH 4. The retained species were eluted using 5mL of 2 M HNO_3. The mechanism for the binding of Cr(III) on the banana peel surface was also studied in detail. The Langmuir and Dubinin-Radushkevich (D-R) isotherms were used to describe the partitioning behavior for the system at different temperatures. Kinetic and thermodynamic measurements of the banana peel for chromium ions were also studied. The method was applied for the removal and preconcentration of Cr(III) from industrial wastewater.

Keywords:*Banana peel; Chromium; Sorption; Kinetics; Adsorption Isotherms; Thermodynamics.*

Introduction

Chromium is the common contaminant in wastewater from electroplating, leather tanning and metal-finishing plants. The physiological effects of chromium on the biological system depend upon its oxidation state i.e. Cr(III) and Cr(VI). Cr(III) may be considered as an essential trace element for the proper functioning of living organisms (mammals) e.g. for the maintenance of "glucose tolerance factor"; it is thought to be a cofactor for the insulin action and to have a role in the peripheral activity of this hormone. The toxicity of metal ions comes to play when their concentration values exceed than the threshold value. Chromium is toxic, corrosive and irritant. The maximum allowable limit for total chromium in drinking water as recommended by the World Health Organization (WHO) is 0.05 mg L^{-1} [1]. The conventional chromium treatment method consists of following three steps.

1. The precipitation of Cr(III) as $Cr(OH)_3$ at high pH.
2. The settling of the insoluble metal hydroxide.
3. The disposal of the dewatered sludge.

The major shortcoming of conventional treatment includes the high cost of safely disposing the sludge. Wastewater containing Cr(III) is usually treated with ion-exchange resins which offer the advantage of the recovery of chromic acid but at a high cost brought about mainly by the use of expensive resins. During the past two decades, extensive research has been carried out to identify new sorbents for the removal of chromium which are both effective and economical. The following materials have been assessed for chromium uptake including coconut husk [2], sawdust [3], saltbush (*Atriplex canescens*) [4], sunflower stem [5], activated carbon fibers [6].

In the present work, we describe the use of an effective and inexpensive banana waste material for the removal and preconcentration of chromium species from industrial effluent. The chromium enrichment capability of the sorbent is ascertained by applying the method to a commercial wastewater treatment plant.

Experimental
Materials

All chemicals used in the current study were purchased from Fluka, Germany and were of analytical

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grade. A stock standard solution of Cr(III) was prepared by dissolving the appropriate amounts of $CrCl_3 . 6H_2O$ in 0.5 M HCl. pH 4-6 was maintained by the buffer of acetic acid and sodium acetate, while pH 7-10 was adjusted by 0.1 M NH_3.

Methods
Preparation of sorbent

Slices of banana peel were cut into small pieces, dried, crushed and passed through 120 mesh sieve (125 µm). The banana peel was then washed thoroughly with de-ionized water to remove physically adsorbed contamination and dried in an air oven at 100 ^{o}C for a period of 8 h. The surface area of the dried material was measured using the BET method [7] and was found to be 13 m^2 g^{-1}. The dried banana peel was also analyzed for biological constituents such as: dry matter, moisture, fat, crude fiber, crude protein and ash following the procedure reported in the literature [8] and was found to be 90.4%, 9.6%, 5.0%, 11.0%, 10.1% and 19.0% respectively [9].

Esterification

Modification of the carbonyl groups on the surface of the banana peel (esterification) was achieved using acidic methanol. 9 g of washed and dried banana peel was suspended in 633 mL of 99.9% methanol to which 5.4 mL of concentrated hydrochloric acid was added (0.1 M HCl final concentration). Then the solution was heated at 60°C and stirred continuously for 48 h. The solid material was then separated and washed three times with cold deionized water in order to halt the esterification reaction [9].

Chemical analysis

A Varian AA-10 atomic absorption spectrophotometer (AAS) was used to determine the concentration of chromium in the solution.

The pH measurements were made with a digital (InoLab pH level I) pH meter equipped with a calibrated combined pH glass electrode. A Gallenkamp thermostated automatic shaker model BKS 305–010, UK was used for the batch experiments.

The dried banana peel was analyzed by FTIR using a ZnSe SB-ATR accessory. The IR spectra were acquired using a Thermo Nicolet Avatar 330 FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and KBr optics and controlled by OMNIC software (Thermo Nicolet Analytical Instruments, Madison, WI) with spectra collected by co-addition of 32 scans at a resolution of 8 cm^{-1}. The spectrum of sample was rationed against a fresh background spectrum recorded from the bare ATR crystal cleaned with propanol to remove any residues and the residual solvent evaporated in a stream of nitrogen gas.

Equilibrium metal sorption experiments

The sorption behavior of chromium on the banana peel surface was investigated using batch equilibrium experiments. 10 mL aliquot of chromium solution (1.92×10^{-5} M) adjusted to pH 4 was added to a polyethylene flask containing 0.1 g of dried and sieved banana peel. The mixture was then stirred for a specified time (0-30 min) and temperature (20-40^{o}C) to allow selective sorption of Cr(III) ions. Finally, the mixture was filtered and adsorbed metal ions were then desorbed by shaking with 5 mL of 2 M HNO_3 solution and analyzed by flame atomic absorption spectrophotometer at 357.9 nm and a slit width of 1 nm using an air–acetylene flame. Experiments were conducted in triplicate and the results are the average of triplicate measurements. Precision in all cases is close to ~ ± 1%.

Results and Discussions
FT-IR spectra

FT-IR spectra of banana peel were obtained in order to understand the nature of the functional groups present in banana peel. FT-IR spectra (Fig. 1a) displayed a number of peaks, indicating the complex nature of the adsorbent. Bands appearing at 3313.4, 2920.3, 2850.6, 1734, 1613.6, 1317.4, 1035.2 and 884.6 cm^{-1} in Fig. 1a were assigned to OH stretching, C-H stretching of alkane, C-H and C=O stretching of carboxylic acid or ester, COO^- anion stretching, OH bending, C-O stretching of ester or ether and N-H deformation of amines respectively [10]. Out of these, carboxylic and hydroxyl groups played a major role in the removal of Cr(III) ions. As expected a significant reduction in the intensity of other groups especially OH and COOH group peak (absorbance intensity reduced from 0.0447 and 0.0659 to 0.0266 and 0.0314) along with peak shifting from 3336 and 1613.6 to 3313.4 and 1622.9 cm^{-1} were recorded in the spectra of esterified banana peel (Fig. 1b) [9].

Effect of pH

As pH of the system controls the sorption capacity through its influence on the surface properties of the adsorbent and species of adsorbate in solution, sorption experiments were carried out a pH range of 1–9, whilst maintaining all other parameters as constant.

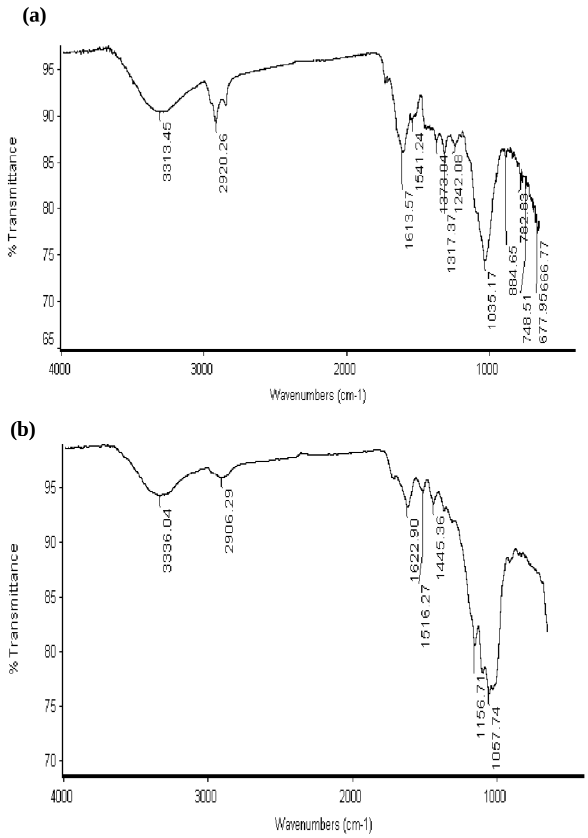

Figure 1. **FT-IR spectra of (a) Banana peel and (b) Esterified banana peel**

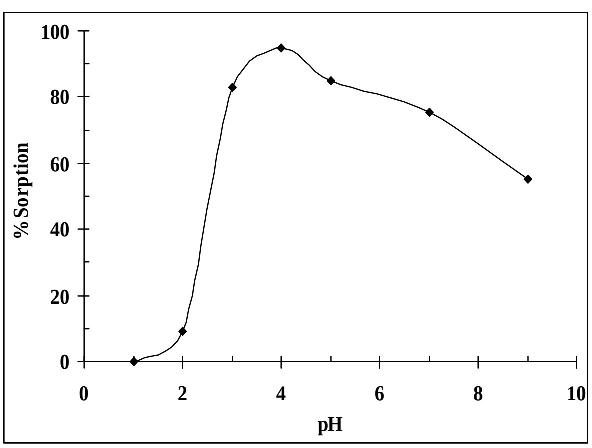

Figure 2. **Effect of pH for the removal and preconcentration of Cr(III) ions onto banana peel.**

The uptake of metal ions onto banana peel as a function of pH is shown in (Fig. 2). The maximum uptake of Cr(III) was achieved at pH 4 and this behavior can be explained by taking into account the p*K*a value of the carboxylic groups which is 3.3–4.8. At pH > 4, the carboxylic groups is deprotonated and became negatively charged hence increasing the availability of binding sites for positively charged metal ions. The predominant species of Cr(III) at pH 4 are $Cr_2(OH)_2^{4+}$ (~5%), $Cr_3(OH)_4^{5+}$ (~22%), $Cr(OH)^{2+}$ (~31%) and Cr^{3+} (~42%) [11]. At pH values below 3, the carboxylic groups become protonated and thus unavailable for binding with metal ions in solution.

Sorption of chromium on esterified banana peel

In an attempt to identify the nature of the functional groups responsible for chromium sorption, sorption experiments were carried out on esterified banana peel. Results from the sorption experiments showed that the amount of Cr(III) bound was reduced from 99% to 22%. Thus the sorption of Cr(III) was attributed to complexation with carboxylic groups and at a lesser extent to interaction with vicinal hydroxyl groups.

Recovery of chromium

Desorption of chromium ions from Cr(III) reacted banana peel was studied by shaking the contaminated material with different concentrations of HNO_3, H_2SO_4 and HCl. The amount of chromium recovered is given in Table 1. Elution was found to be quantitative using 5 mL of 2 M HNO_3.

Table 1. **Recovery of Cr(III) from the banana peel surface.**

*Solvent/Reagent	Concentration (M)	Recovery (%)
HNO_3	0.1	17
HNO_3	1	31
HNO_3	2	99.3
H_2SO_4	0.5	9
H_2SO_4	1	10
H_2SO_4	2	14.5
HCl	0.5	6
HCl	1	6

*Volume of each reagent used = 5 mL

Kinetics of sorption

Kinetic study was carried out at optimized conditions from 0 to 30 min. The sorption was observed to be very fast, equilibrium attained within a 10 min. The removal was > 95% with very little increase in sorption after 10 min of contact time. In order to avoid the experimental error, a reaction time of 30 min was adopted for further studies. The recorded kinetic data were fitted to different equations namely, Morris–Weber and Lagergren. The adsorbed concentration q_t (µmol g^{-1}) at time t, was plotted against $\sqrt{t}$ to test the Morris-Weber equation [12] in the following form:

$$q_t = R_d \sqrt{t} \qquad (1)$$

Where, R_d is the rate constant of intraparticle transport. Up to 10 min Eq (1) held well with a regression coefficient of 0.99 but deviated as the agitation time increased. From the slope of the plot in the initial stage, the values of R_d, was found to be 5.13 ± 0.25 µmol g^{-1} $min^{-1/2}$. The Lagergren equation [13]

$$\log(q_e - q_t) = \log q_e - \frac{kt}{2.303} \qquad (2)$$

was tested by plotting $\log(q_e\text{-}q_t)$ versus time t, where q_e is the adsorbed concentration of chromium on banana peel (mol g^{-1}) at equilibrium. The overall value of rate constant (k) was estimated to be 0.3 ± 0.001 min^{-1} from the slope of the plot with a regression coefficient of 0.99.

Sorption isotherms

The sorption of Cr(III) ions was also investigated as a function of concentration at room temperature in the range of 0.5-100 mg L^{-1} using 0.1 g of adsorbent and 10 mL of adsorbate solution, and 30 min shaking time at a shaking speed of 100 rpm. The uptake of metal ions is 80-99% at lower adsorbate concentrations (0.5-8 mg L^{-1}) and 60-79% at higher adsorbate concentrations (10-100 mg L^{-1}). These results reflected the efficiency of banana peel for the removal of chromium ions from aqueous solution over a wide range of concentrations.

An increase in the uptake of Cr(III) with increasing temperature was also observed indicating the nature of process to be endothermic. The sorption data was followed the Langmuir and Dubinin-Radushkevich (D-R) isotherms. The sorption data was analyzed using the Langmuir ($(C_e/C_{ads}) = (1/Qb) + (C_e/Q)$) and D-R ($\ln C_{ads} = \ln Xm - \beta\varepsilon^2$) and $\varepsilon = RT \ln[1 + (1/C_e)]$ equations, where C_{ads} is the amount of metal ions adsorbed per unit mass of sorbent and C_e is the amount of metal ions in the liquid phase at equilibrium. Q, b, Xm and β are Langmuir and D–R constants, respectively [14]. The Langmuir and D–R constants were evaluated from the slopes and intercepts of the linear plots studied at different temperatures. The results are listed in Table 2. The essential characteristic of the Langmuir isotherm, separation factor (R_L) was calculated using equation $R_L = 1/(1 + bCi)$, where Ci is the initial concentration of metal ions and b is Langmuir constant. R_L describes the type of Langmuir isotherm [15] to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The values of R_L calculated were between 0.07 and 0.99 (Table 2), indicating highly favorable sorption of chromium on banana peel at all temperatures. The values of E evaluated from the slope (β) of the D–R curve using the equation ($E = \frac{1}{\sqrt{-2\beta}}$) lied in between 9.10–9.43 kJ mol^{-1} and were out of the range (8–16 kJ mol^{-1}) indicated the ion exchange mechanism of sorption for Cr(III) [16]. It was observed that the values of the sorption capacities increased with the rise of temperature. This is because of the endothermic nature of the reaction.

Table 2. **Langmuir and D-R constant of Cr(III) ions onto sorbent surface at different temperatures.**

T (°C)	Langmuir				Dubinin-Radushkevich			
	Q (mmol g^{-1})	b ×10^3 (L g^{-1})	R_L	R^2	X_m (mmol g^{-1})	β ×10^{-3} (kJ^2 mol^{-2})	E (kJ mol^{-1})	R^2
20	1.31 ± 0.09	4.2 ± 0.34	0.11 - 0.96	0.98	10.10 ± 1.11	-6.19 ± 0.10	9.10 ± 0.10	0.99
25	1.53 ± 0.09	5.55 ± 0.39	0.09 - 0.95	0.98	10.73 ± 1.62	-6.18 ± 0.25	9.10 ± 0.20	0.99
30	1.70 ± 0.05	6.01 ± 0.36	0.08 - 0.94	0.99	11.50 ± 1.66	-5.74 ± 0.19	9.10 ± 0.20	0.99
35	1.79 ± 0.06	6.63 ± 0.40	0.07 - 0.94	0.99	15.1 ± 2.92	-5.81 ± 0.16	9.10 ± 0.20	0.99
40	2.22 ± 0.07	6.42 ± 0.26	0.08 - 0.94	0.99	24.42 ± 4.21	-5.67 ± 0.21	9.43 ± 0.19	0.99

R^2 regression coefficient, R_L dimensionless constant

Thermodynamics of sorption

The effect of temperature on the sorption of Cr(III) ions onto banana peel was studied in the range of 20–40°C at the optimized conditions. ln $K_c = F_e/(1 - F_e)$ where F_e is the fraction sorbed at equilibrium, was plotted against 1/*T* (Fig. 3). The values of ΔH, ΔS and ΔG were estimated using the relationships from the slope and intercept of the linear plot.

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (3)$$

and

$$\Delta G = - RT \ln K_c \quad (4)$$

The values of ΔH = 46 ± 2.82 kJ mol^{-1}, ΔS = -0.13 ± 0.01 kJ mol^{-1} K^{-1} and ΔG = [-(6.9-4.4) kJ mol^{-1}] were estimated with a regression coefficient of 0.99..The positive value of ΔH indicated the endothermic and the negative values of Δ*G* were obtained showing the spontaneous nature of the sorption process.

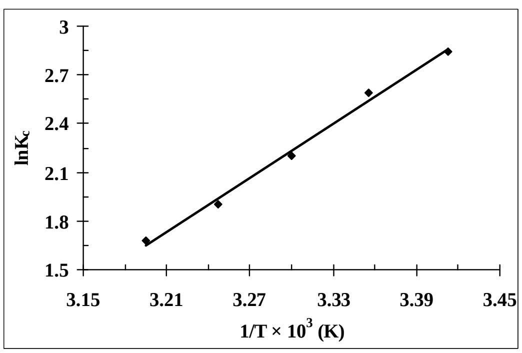

Figure 3. **Effect of temperature on the sorption of Cr(III) ions onto banana peel.**

Reusability of banana peel

In order to check the reusability of sorbent, banana peel was subjected to several loading and elution experiments. The capacity of the sorbent was found to be practically constant (variation of 1-3%) after 10 times repeated use; thus multiple use of sorbent was seen to be feasible.

Interference study

The sorption of metal ions in the presence of common ions or complexing agents may be affected due to precipitation, complex formation or competition for sorption sites. The sorption of Cr(III) ions onto banana peel in the presence of different cations and anions have been investigated under optimized conditions. The sodium salts of anions and nitrates or chlorides of cations were added with the sorbate in solution in the concentration ratios of 1:50 and 1:10, respectively. The results are given in Tables 3. In case of anions, PO_4^{3-} and $C_6H_5O_7^{3-}$ impede the sorption in the range of 53-56%. The interferences of these ions can be tolerated using concentration ratios of 1:10. With cations, Al(III), Cd(II), Bi(III), Ni(II) and Mn(II) impede the sorption in the range of 50-70%. The interferences of these ions can be tolerated using concentration ratios of 1:1. The ions which cause hindrance in the sorption of Cr(III) ions onto the solid surface may be explained in terms of their stronger affinity for anionic complexes of Cr(III) and other cations which may replace Cr(III) ions sorbed already on the sorbent surface.

Table 3. **Interferences of cations and anions on the sorption of Cr(III) onto banana peel**

Cr:Cation (Tolerance Limit = 1:10)	Sorption (%)	Cr:Anion (Tolerance Limit = 1:50)	Sorption (%)
Al(III)	25	PO_4^{3-}	39
Cd(II)	32	$C_6H_5O_7^{3-}$	42
Bi(III)	34	CO_3^{2-}	83
Ni(II)	41	HCO_3^-	85
Mn(II)	45	Br^-	87
Tl(III)	85	CH_3COO^-	90
Hg(II)	87	HPO_4^{2-}	90
Fe(II)	89	Cl^-	90
Ca(II)	90	$C_4H_4O_6^{2-}$	90
Pb(II)	90	NO_3^-	91
Cu(II)	91	SO_4^{2-}	91
K(I)	91	HSO_4^-	92
Tl(I)	91	$C_2O_4^{2-}$	93
Co(II)	92	SCN^-	93
Fe(III)	92	F^-	94
Zn(II)	93	NO_2^-	94
Mg(II)	94	SO_3^{2-}	94
Nil	95	Nil	95

Analytical application

The analytical applicability of banana peel was tested for removal and preconcentration of chromium ions from industrial wastewater samples collected from Karachi, Pakistan. A 50mL aliquot of water sample was filtered and adjusted to required pH. Another 50mL aliquot of water sample was spiked with Cr(III) at pH 4. The solutions were then agitated at optimum shaking speed for a period of 30 min. The metal ions were eluted and determined. The results are given in Table 4. The RSD was always within 2% which showed the suitability of banana peel for the removal of Cr(III) ions from industrial wastewater.

Table 4. **Determination and recovery of chromium ions from industrial wastewater**

Sample	Cr(III) ($\mu g\ mL^{-1}$)		
	SA [a]	Found	%Recovery
Mian M. Shafee Leather Tanning	0.0	5.72	100
	5	10.7	99.81
Fasto Leather Workers	0.0	ND [b]	-
	5	4.96	99.2
Alma Leathers	0.0	4.06	100
	5	9.0	99.34
Leather Tanning	0.0	4.33	100
	5	9.3	99.68
National Oil Refinery	0.0	ND	-
	5	4.95	99

[a] SA = Standard addition
[b] ND = Not detected

Conclusion

The present work explores a new cheaper, economical and selective adsorbent as an alternative to costly adsorbents for the removal of Cr(III) ions. The main advantages of procedure are:

1. Cost of process.
2. Ease and simplicity of preparation of the sorbent.
3. Sensitivity.
4. Rapid attainment of phase equilibration and good enrichment.

FT-IR analysis of banana peel showed the presence of various functional groups indicating the complex nature of the banana peel. The kinetics of sorption for chromium follows a pseudo first order rate equation. The positive value of ΔH and negative values of ΔG indicate the endothermic and spontaneous nature of the sorption process. For the sorption of Cr(III) ions, most of the cations and anions can be tolerated up to 1:10 and 1:50 concentration ratios except with Al(III), Cd(II), Bi(III), Ni(II), Mn(II), PO_4^{3-} and $C_6H_5O_7^{3-}$ ions, which can be tolerated up to ratios of 1:1 and 1:10. Study shows that the banana peel has the ability to extract Cr(III) from industrial wastewater.

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