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Sorptive potential of sunflower stem for Cr(III) ions from aqueous solutions and its kinetic and thermodynamic profile

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Abstract

The sorptive potential of sunflower stem (180–300 μm) for Cr(III) ions has been investigated in detail. The maximum sorption (≥85%) of Cr(III) ions (70.2 μM) has been accomplished using 30 mg of high density sunflower stem in 10 min from 0.001 M nitric and 0.0001 M hydrochloric acid solutions. The accumulation of Cr(III) ions on the sorbent follows Dubinin–Radushkevich (D–R), Freundlich and Langmuir isotherms. The isotherm yields D–R saturation capacity $X_m = 1.60 \pm 0.23$ mmol g^{-1}, $\beta = -0.00654 \pm 0.00017$ kJ^2 mol^{-2}, mean free energy $E = 8.74 \pm 0.12$ kJ mol^{-1}, Freundlich sorption capacity $K_F = 0.24 \pm 0.11$ mol g^{-1}, $1/n = 0.90 \pm 0.04$ and of Langmuir constant $K_L = 6800 \pm 600$ dm^3 mol^{-1} and $C_m = 120 \pm 18$ μmol g^{-1}. The variation of sorption with temperature (283–323 K) gives $\Delta H = -23.3 \pm 0.8$ kJ mol^{-1}, $\Delta S = -64.0 \pm 2.7$ J mol^{-1} K^{-1} and $\Delta G_{298k} = -4.04 \pm 0.09$ kJ mol^{-1}. The negative enthalpy and free energy envisage exothermic and spontaneous nature of sorption, respectively. Bisulphate, Fe(III), molybdate, citrate, Fe(II), Y(III) suppress the sorption significantly. The selectivity studies indicate that Cr(III), Eu(III) and Tb(III) ions can be separated from Tc(VII) and I(I). Sunflower stem can be used for the preconcentration and removal of Cr(III) ions from aqueous medium. This cheaper and novel sorbent has potential applications in analytical and environmental chemistry, in water decontamination, industrial waste treatment and in pollution abatement. A possible mechanism of biosorption of Cr(III) ions onto the sunflower stem has been proposed.

Keywords: Sorption; Cr(III) ions; Sunflower (*Helianthus annus*) stem; Sorption isotherms; Kinetics; Thermodynamics

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1. Introduction

The increasing awareness of health hazards of toxic metal ions in biosphere and their ultimate reach to human body and exorbitant cost of their removal has accelerated efforts to find out the most economical ways to control environmental pollution. The toxicity of metal ions based on their adverse and harmful effects on humans is determined by its specific dose. The threshold limit for chromium(III) uptake in air is 0.1 mg m^{-3} and in water is 0.05 mg dm^{-3} [1]. Chromium is carcinogenic, corrosive and irritant. The chromium metal and its compounds have wide applications in making alloys, chrome plating, leather tanning, batteries, refractories, dyes, paints, welding, catalysis and in wood preservatives [1,2] and its use at present may not be curtailed. However, its removal from industrial waste is essential before discharging into hydrosphere. Cr(III) ions may be removed using ion exchange, solvent extraction, chemical precipitation, reverse osmosis, dialysis, electrolysis and adsorption [3]. Removal through adsorption is effective, economical, time saving and easy in manipulation in stagnant and flowing effluents of industries, municipalities and in natural water [4].

The agricultural waste, the cheaper sorbents have been extensively exploited for the recovery of trace metal ions from aqueous solutions. Such sorbent–sorbate systems employed are: alfalfa (*Medicago sativa*) sprouts and cattail (*Typha latifolia*) roots—Al(III), Au(III) and Cu(II) [5]; apple

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waste—Cu [6]; bark of black oak, douglas fir and red wood, orange peel, senna leaves and pine needles—Hg(II) [7]; coconut (*Cocos nucifera*) husk—Cd(II), Pb and Zn(II) [8] and Hg(II) [9]; datura innoxia—Cd(II) [10], Eu(III) [11], U(VI) [12] and Al(III), Au(III) and Cu(II) [5]; groundnut (*Arachis hypogea*) husk—Cd(II) and Pb(II) [13]; mango (*Mangifera indica*) and neem (*Azadirachta indica*) bark—Cd(II), Cr(III) and Hg(II) [14] and Sr(II) [15]; onion skins—Hg(II) [16]; palm (*Elaesis guineensis*) kernel husk—Pb(II) and Zn(II) [17]; peanut skins—Cu(II) [18]; pine bark—Cd(II), Cu(II) and Ni(II) [19]; rice hulls (*Oryza sativa*)—Cr(III) and Hg(II) [20]; silage effluent and molasses—Cd(II), Cu(II) and Zn(II) [21]; sugarcane bagasse—Pb(II) [22] and sawdust—Hg(II) [23]. No report has appeared concerning the removal of chromium(III) ions using sunflower stem. The present communication represents Cr(III) ions sorption onto cost effective sunflower stem in detail.

2. Experimental

2.1. Sunflower stem

The sunflower (*Helianthus annus*) stem, collected from National Agriculture Research Centre, Islamabad, Pakistan, is washed with water and dried in air. Its inner soft tissue is removed and outer hard tissue (oht) are chopped up to ∼1 cm length, washed with deionized water (DW), dried in an oven at 105 ± 5 °C and ground in a blade mill. The powder is sieved into different fractions <180, 180–300, 300–425, and 425–600 μm. Fraction (180–300 μm) is utilized in this study. For better separation of sorbent from liquid phase, it is poured into deionized water and mixed. Frequently settled powder of higher density is separated, dried, stored and used as a sorbent. The surface area of the fraction utilized, using BET method [24] is found to be <2 $m^2 g^{-1}$. The analysis of higher density sunflower stem is carried out as per procedures [25] and the results cited in Table 1, are in agreement with the results reported for sunflower seed hulls [26].

2.2. Radiotracers

The radiotracer of ^{51}Cr is prepared by irradiating specpure chromium metal in the Pakistan Research Reactor (PARR-I) of Pakistan Institute of Nuclear Science and Technology (PINSTECH), Islamabad at a thermal neutron flux of 7×10^{13} $cm^{-2} s^{-1}$. The irradiated metal is dissolved in concentrated HCl. For the removal of excessive acid, the content is diluted with DW and heated near to dryness. This procedure is repeated thrice. The tracer, along with washings, is stored in 10 ml volumetric flask and further dilutions are made from this stock solution. The radiochemical purity of the tracer is checked on a 4 k Canberra series 85 multichannel analyzer, USA, coupled with a 25 cm^3 Ge (Li) detector. The other radiotracers utilized (^{46}Sc, ^{60}Co, ^{99m}Tc, ^{110m}Ag, ^{115m}Cd, ^{124}Sb, ^{128}I, ^{134}Cs, $^{152+154}$Eu, ^{160}Tb, ^{170}Tm and ^{203}Hg) are prepared by irradiating metals or their suitable compounds as mentioned above.

Table 1
Proximate analysis of higher density sunflower stem (180–300 μm) in percent

Dry matter	91.5
Crude fibre	47.2
Crude protein	5.3
Ash	1.9
Neutral detergent fibre	79.0
Acid detergent fibre	64.0
Cellulose	53.0
Hemicellulose	14.6
Acid detergent lignin	10.7

2.3. Reagents/buffer solutions

All reagents used are specpure or of analytical grade. The buffer solutions of pH 1–10 (ionic strength of 0.1 M) are prepared by mixing appropriate volumes of 0.1 M of KCl and HCl (pH 1–3), sodium acetate and acetic acid (pH 4–6); and boric acid and sodium hydroxide (pH 7–10) solutions.

3. Procedure

A known concentration of Cr(III) radiotracer is pipetted out and mixed uniformly with 20 cm^3 of a standard acid or known pH buffer solution. One-milliliter solution is pipetted into each of at least three counting glass vials for its initial gross gamma activity (A_i) and 4.5 ml into each of three (teflon lined screw-type polythene capped) glass vials, containing specific amount (10–500 mg) of sunflower stem. The contents are shaken for 10 min (or as specified) with a Stuart Scientific Wrist-Action Mechanical Shaker and centrifuged for 3 min for phase separation. One milliliter of supernatant aqueous solution from each vial is pipetted into three counting vials.

The activities of Cr(III) ions in solution before and after (A_e) equilibration are assayed on a Tennelec gross Gamma Scintillation Counter (USA), coupled with a 30 cm^3 well-type NaI (TI) crystal. The batch technique is carried out at 26 ± 2 °C.

The distribution ratio, R_d, and percentage sorption are determined using following equations:

$$R_d\,(\mathrm{cm^3\,g^{-1}}) = \frac{\text{amount of metal ion onto sunflower stem}}{\text{residual amount of metal ion in solution at equilibrium}} \times \frac{\text{volume of solution, } V(\mathrm{cm^3})}{\text{mass of sunflower stem, } W(\mathrm{g})} \quad (1)$$

$$\text{sorption}\,(\%) = \frac{R_d}{(R_d + V/W)} \times 100 \quad (2)$$

the results are the average of at least triplicate measurements and precision in most cases is ±2%.

4. Results and discussion

4.1. Optimization of sorption

The nature of electrolyte, amount of sorbent and sorbate, equilibration time between the two and temperature play significant role on the sorption of trace metal ions onto solid surfaces [27]. Therefore, the sorption of Cr(III) ions onto sunflower stem is monitored step by step as a function of a parameter, keeping others constant. Initially, the nature and concentration of electrolytes such as deionized water, HCl, HNO_3 and buffer solutions of pH 1–10, are examined at arbitrarily chosen amount of sorbent (50 mg/4.5 cm^3) of electrolyte, concentration of sorbate (70.2 μM) and equilibration time of 20 min. The results are recorded in Table 2. The maximum sorption ≥85% is achieved from 0.001 M HNO_3 and 0.0001 M HCl. However, 0.001 M nitric acid solution is selected as the most suitable sorptive medium for further investigations. The dominant species of Cr(III) present in this acidic solution (pH 3) would be Cr^{3+} (95%) and $Cr(OH)^{2+}$ (5%) [28].

The effect of agitation time (1–60 min) for the partitioning of Cr(III) ions (70.2 μM) between solid and liquid phases of sunflower stem (50 mg) and 4.5 cm^3 of 0.001 M HNO_3, respectively, is investigated. The distribution ratio (R_d) and % sorption increased with an increase in agitation time (Fig. 1). The equilibration is accomplished in 20 min. However, 10-min shaking time is selected for further experiments.

Table 2
The sorptive behaviour of Cr(III) ions (70.2 μM) onto sunflower stem (50 mg) from different electrolytes using 20-min shaking time

Sorptive medium	% Sorption	R_d ($cm^3\ g^{-1}$)
Deionized water	82.3	422
0.01 M HCl	45.2	74
0.001 M HCl	81.0	384
0.0001 M HCl	84.4	487
0.1 M HNO_3	0.2	0.2
0.01 M HNO_3	35.7	50
0.001 M HNO_3	85.2	518
0.0001 M HNO_3	83.3	448
pH 1[a]	1.1	1.0
pH 2[a]	0.4	0.3
pH 3[a]	32.3	43
pH 4[b]	78.6	330
pH 5[b]	65.8	173
pH 6[b]	44.3	72
pH 7[c]	40.7	62
pH 8[c]	4.9	4.6
pH 9[c]	21.4	24.6
pH 10[c]	0.4	0.3

[a] pH 1–3: 0.1 M KCl + 0.1 M HCl.
[b] pH 4–6: 0.1 M sodium acetate + 0.1 M acetic acid.
[c] pH 7–10: 0.1 M boric acid + 0.1 M sodium hydroxide.

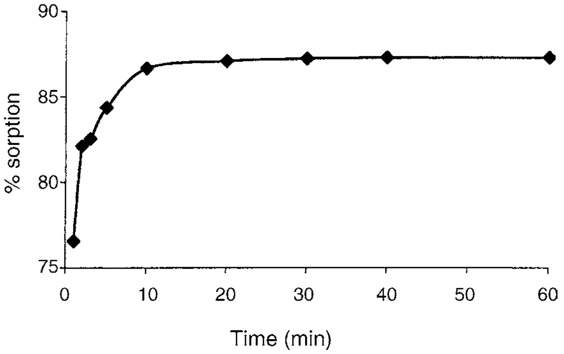

Fig. 1. The sorption of Cr(III) (70.2 μM) onto sunflower stem (50 mg) from 0.001 M HNO_3 as a function of equilibration time.

The influence of dosage of sunflower stem (10–500 mg)/4.5 cm^3 of 0.001 M nitric acid for Cr(III) (70.2 μM) ions, is studied. The results are shown in Fig. 2. The distribution ratio of sorbate increases with an increase in the mass of sorbent and attains a maximum value around 20 mg and then declines with increasing amount of sorbent. Thirty milligrams of sunflower stem is selected for further studies.

The effect of Cr(III) ions concentration over a 43-fold range (9.8–421 μM) on its own uptake by sunflower stem is examined under optimized conditions chosen. The variation in the Cr(III) ions sorption as a function of its own concentration is depicted in Fig. 3. Nevertheless, 70.2 μM Cr(III) ion concentration is selected for further exploration unless specified otherwise.

4.2. Kinetic studies

The kinetics of sorbed Cr(III) ions concentration onto sunflower stem is subjected to different equations, namely, Reichenberg, Lagergren and Morris–Weber. The effectiveness of the diffusion of the two exchanging ions within sorbent particles of radius '*r*' and control of film diffusion in sorption may be deduced from the linear fit of the data to the Reichenberg equation [29]:

$$Q = 1 - \frac{6e^{-B_t}}{\pi^2} \quad (3)$$

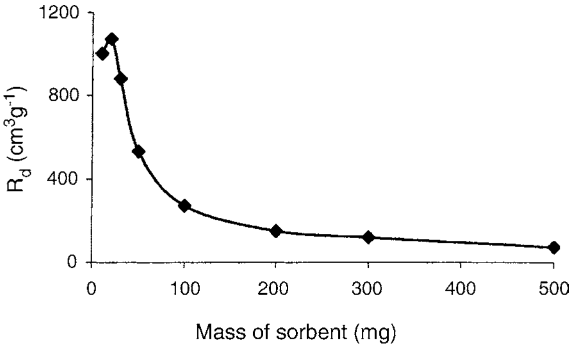

Fig. 2. The variation of sorption of Cr(III) (70.2 μM) as a function of dosage of sunflower stem from 0.001 M HNO_3 solution using 10-min shaking time.

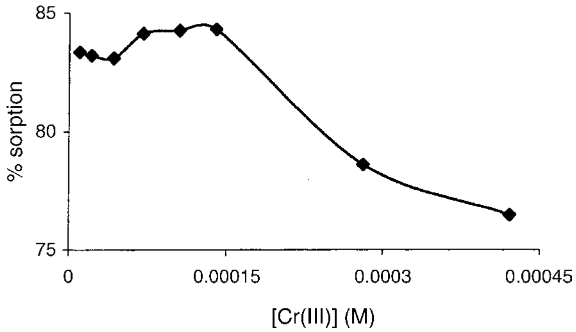

Fig. 3. The sorption of Cr(III) ions as a function of its concentration onto sunflower stem (30 mg) from 0.001 M nitric acid solution after 10-min agitation time.

where $Q = q_t/q_m$, $B_t = \pi^2 D_i/r^2$ and q_t and q_m are sorbed concentration at time t and the maximum sorption capacity of the sorbent and D_i is the effective diffusion coefficient of the two exchanging ions inside the sorbent particle. The value of B_t, which is a mathematical function of Q, can be evaluated for each value of Q, using following equation:

$$B_t = -0.4977 - \ln(1 - Q) \tag{4}$$

The plot of B_t versus time (Fig. 4) follows linearity from 1 to 60 min which indicates the diffusion of the Cr(III) ions within particles of the sunflower stem. The order of the sorption of Cr(III) ions onto sunflower stem is evaluated by subjecting the data to the linear form of Lagergren equation [30]:

$$\ln(q_e - q_t) = \ln q_e - kt \tag{5}$$

where k is the first-order rate constant of sorption, q_t the amount of Cr(III) ions sorbed at time t and q_e the maximum amount sorbed at equilibrium. The linear fit of $\ln(q_e - q_t)$ versus t shown in Fig. 5 (see Table 3) indicates the kinetics of sorption is of first order. The value of k from slope and regression analysis is $0.17 \pm 0.01\ \text{min}^{-1}$. The data is applied to the Morris–Weber equation [31]:

$$q_t = R_{idr}\sqrt{t} \tag{6}$$

where R_{idr} is the intraparticle diffusion rate constant, q_t the amount sorbed at time, t. The linearity applies only in the range of 2–10 min as designated in Fig. 6, which indicates the partial intraparticle diffusion. The value of R_{idr} comes out to be $0.17\ \mu\text{mol g}^{-1}\ \text{min}^{-1/2}$.

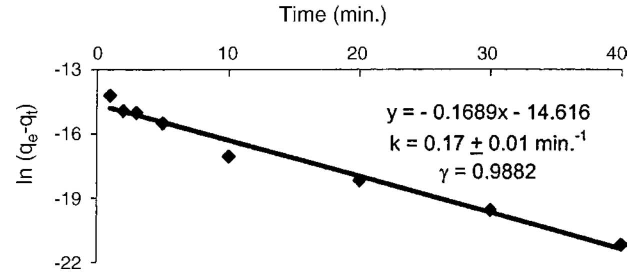

Fig. 5. Test of Lagergren equation for the retention of Cr(III) ions onto sunflower stem (50 mg) from 0.001 M nitric acid solution.

Table 3
Calculations for Fig. 5

Time (min)	q_t (mol g^{-1})	$\ln(q_e - q_t)$
1	4.8377E−06	−14.204E+01
2	5.1883E−06	−1.4932E+01
3	5.2155E−06	−1.5019E+01
5	5.3311E−06	−1.5506E+01
10	5.4771E−06	−1.7072E+01
20	5.5030E−06	−1.8187E+01
30	5.5125E−06	−1.9573E+01
40	5.5150E−06	−2.1182E+01
60	5.5156E−06	–

4.3. Sorption isotherms

The sorption data are subjected to different sorption isotherms namely D–R, Freundlich and Langmuir. The characteristic parameters from slope and intercept of the plots are determined using regression analysis. The data is subjected to following linear form of D–R isotherm [32]:

$$\ln C_{sorb} = \ln X_m - \beta\varepsilon^2 \tag{7}$$

where C_{sorb} is the amount of Cr(III) ions sorbed onto sunflower stem (mol g^{-1}), X_m represents the maximum sorption capacity of the sorbent (mol g^{-1}), β a constant related to sorption energy and ε Polanyi sorption potential, the amount of energy required to pull a sorbed molecule from its sorption

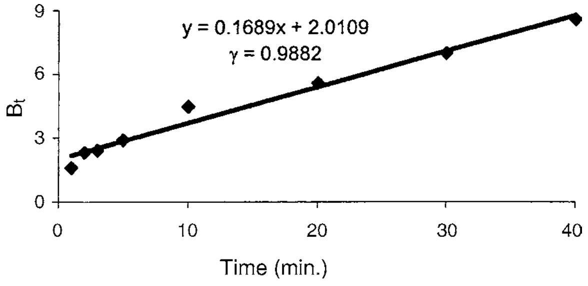

Fig. 4. Reichenberg plot for the sorption of Cr(III) (70.2 μM) ions onto sunflower stem (50 mg) from 0.001 M HNO_3 solution.

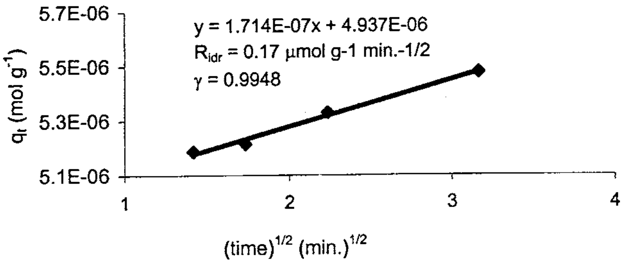

Fig. 6. Validity of Morris–Weber equation for the sorption of Cr(III) ions onto sunflower stem.

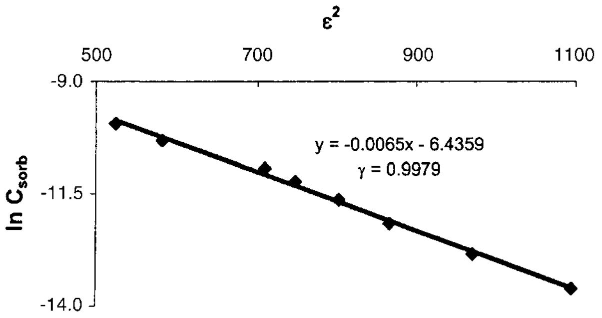

Fig. 7. D–R sorption isotherm of Cr(III) ions onto sunflower stem (30 mg) from 0.001 M HNO_3 solution at 25 °C.

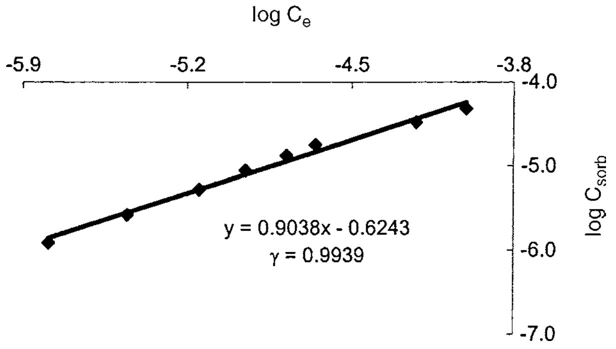

Fig. 8. Freundlich sorption isotherm of Cr(III) ions onto sunflower stem.

site to infinity which is equal to [33]:

$$\varepsilon = RT \ln\left(1+\frac{1}{C_\mathrm{e}}\right) \tag{8}$$

where R is the gas constant in kJ mol^{-1} K^{-1}; T the temperature in Kelvin and C_e the equilibrium concentration in solution (mol dm^{-3}). The Polanyi adsorption theory postulates [33] fixed volume of sorption site close to sorbent surface and existence of sorption potential over these sites. The sorption potential is related to an excess of sorption energy over the condensation energy and is independent of temperature. The plot of $\ln C_\mathrm{sorb}$ versus ε^2 (Fig. 7) follows linearity throughout the concentration range (9.8–421.2 μM) with a correlation factor of 0.9979, close to unity. The value of $X_\mathrm{m} = 1.60 \pm 0.23$ mmol g^{-1} is determined from the intercept and the value of $\beta = -0.00654 \pm 0.00017$ kJ^2 mol^{-2} is derived from the slope. The sorption energy, $E = 8.74 \pm 0.12$ kJ mol^{-1} for Cr(III) ions onto sunflower stem calculated using the expression [34]:

$$E = (-2\beta)^{-1/2} \tag{9}$$

is in the range of 8–16 kJ mol^{-1} designated for ion exchange mechanism [35]. The D–R sorption isotherm is more general than Langmuir isotherm, as its derivation is not based on ideal assumptions such as equipotential of the sorption sites, absence of steric hindrance between sorbed and incoming particles and surface homogeneity on microscopic level. The Freundlich isotherm [36] is tested using its linearized form:

$$\log C_\mathrm{sorb} = \log K_\mathrm{F} + \frac{1}{n}\log C_\mathrm{e} \tag{10}$$

where $1/n$ is a characteristic constant related to sorption intensity, C_sorb, C_e and K_F represent sorbed amount (mol g^{-1}), residual concentration of sorbate in solution at equilibrium (mol dm^{-3}) and sorption capacity of sorbent (mol g^{-1}), respectively. It is an empirical expression that accounts for the surface heterogeneity, exponential distribution of active sites of sorbent and their energies towards sorbate [37]. The plot of $\log C_\mathrm{sorb}$ versus $\log C_\mathrm{e}$ (Fig. 8) gives a straight line with a correlation factor of 0.9939. The slope and intercept yield the values of $1/n = 0.90 \pm 0.04$ and $K_\mathrm{F} = 237 \pm 113$ mmol g^{-1}, respectively. Comparing respective sorption capacities, this sorbent is more effective than rice hulls [20] for the sorption of Cr(III) ions. The sorption data is also applied to the following form of Langmuir isotherm:

$$\frac{C_\mathrm{e}}{C_\mathrm{sorb}} = \frac{C_\mathrm{e}}{C_\mathrm{m}} + \frac{1}{K_\mathrm{L}C_\mathrm{m}} \tag{11}$$

where C_m and K_L represent sorption saturation capacity of sunflower stem (mol g^{-1}) and Langmuir equilibrium constant (dm^3 mol^{-1}), respectively, and C_sorb and C_e are as defined earlier. The Langmuir equation assumes that all sorption sites are alike and uniform on microscopic scale. There are no interactions between the sorbed molecules, no steric hindrance between sorbed molecules and incoming ions and sorption can not proceed beyond monolayer surface coverage [38]. The plot of $C_\mathrm{e}/C_\mathrm{sorb}$ versus C_e follows linearity over 43-fold concentration range investigated as shown in Fig. 9. The values of $C_\mathrm{m} = 120 \pm 18$ μmol g^{-1} and $K_\mathrm{L} = 6800 \pm 700$ dm^3 mol^{-1} are determined from slope and intercept of the plot shown in Fig. 9, respectively, by regression analysis. A dimensionless equilibrium parameter, R_L, [39] is calculated using the relationship:

$$R_\mathrm{L} = \frac{1}{(1 + K_\mathrm{L}C_\mathrm{i})} \tag{12}$$

where K_L is Langmuir constant, C_i the initial concentration of Cr(III) ions in solution. The value of R_L is in the range 0.9373–0.2602. This large value of R_L indicates significant sorption of Cr(III) ions onto sunflower stem.

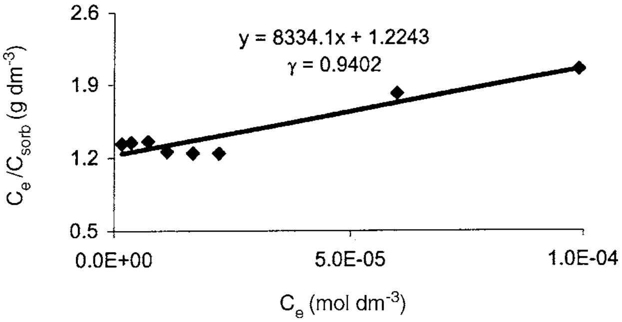

Fig. 9. Langmuir sorption isotherm of Cr(III) ions onto sunflower stem.

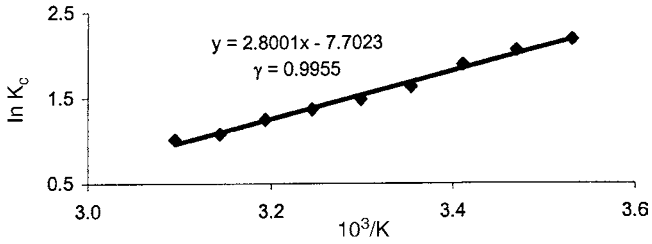

Fig. 10. The variation of equilibration constant for the sorption of Cr(III) ions onto sunflower stem as a function of temperature.

4.4. Thermodynamics

The variation in temperature, influencing the distribution of sorbate between solid and liquid phases is examined in the range of 283–323 K, under optimized conditions mentioned earlier. The dependence of the equilibration constant $K_c = F_e/(1-F_e)$ where F_e is the fraction of percent sorption at equilibrium, with temperature is expressed by the equation:

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (13)$$

where ΔS is the entropy (J mol^{-1} K^{-1}) and ΔH the enthalpy (kJ mol^{-1}). The plot of $\ln K_c$ versus temperature in Kelvin as shown in Fig. 10 is linear with a correlation factor of 0.9955, in the entire range of temperature investigated. The values of $\Delta H = -23.3 \pm 0.8$ kJ mol^{-1} and of $\Delta S = -60.0 \pm 2.7$ J mol^{-1} K^{-1} are deduced from the respective slope and intercept of the plot (Fig. 10). The value of Gibbs' free energy $\Delta G_{298\mathrm{K}} = -4.04 \pm 0.09$ kJ mol^{-1} is estimated using the following equation:

$$\Delta G = -RT \ln K_c \qquad (14)$$

where R is a gas constant in kJ mol^{-1} K^{-1} and T is temperature in Kelvin. The negative values of ΔH and ΔG envisage the exothermic and spontaneous nature of the sorption, respectively. The increase in the value of ΔG with an increase in temperature indicates that the reaction slows down with a rise in temperature. Since the adsorbed molecules have at most two degrees transitional freedom on the surface and since the rotational freedom of adsorbed species must always be less than that of gas phase molecules, the entropy change on adsorption $\Delta S = S_{\mathrm{ads}} - S_{\mathrm{gas}}$ is necessarily negative. In order for significant adsorption to occur the free energy change on adsorption (ΔG) must also be negative and since $\Delta G = \Delta H - T\Delta S$ that requires ΔH negative or exothermic adsorption. This is generally true for adsorption from liquid phase also, although exceptions are possible [40]. This is in conformity with the observation of negative ΔH, ΔS and ΔG in the present investigation.

4.5. Influence of diverse ions

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.

Table 4
The effect of anions on the sorption of Cr(III) ions (70.2 μM) onto the sunflower stem (30 mg) from 0.001 M HNO_3 using 10-min agitation time

Anions of sodium ~0.01 M	% Sorption	R_d (cm^3 g^{-1})
Nil	85.4	881
Sulphide	84.2	801
Borate	83.5	760
Chlorate	82.6	715
Thiosulphate	79.8	594
Bromide	78.9	560
Chloride	78.0	542
Iodide	76.7	493
Thiocyanate	76.5	489
Sulphate	74.3	433
Iodate	60.4	229
Oxalate	59.6	221
EDTA	59.0	221
Acetate	58.4	211
Perchlorate	50.6	158
Nitrite	43.8	118
Bisulphite	31.6	69
Disulphite	29.6	63
Tartrate	24.6	49
Chromate	21.3	41
Ascorbate	19.3	36
Carbonate	17.4	32
Citrate	3.7	5.7
Molybdate	1.5	2.4
Bisulphate	0.8	1.2

The influence of common anions, cations and complexing agents on the sorption of Cr(III) ions onto sunflower stem has been investigated under optimized conditions. The sodium salts of anions and nitrates or chlorides of cations are added with sorbate in solution. The final concentration of common ions in solution is maintained at $\sim 10^{-2}$ M which is 143 times greater than Cr(III) ions concentration. The results are given in Tables 4 and 5. Bisulphate, Fe(III), molybdate, citrate, Fe(II) and Y(III) impede the sorption significantly. The ions, interfering in the sorption of Cr(III) need to be removed from the sorptive medium for better results. The ions which cause hindrance in the sorption of Cr(III) ions onto the solid surface may be explained in terms of stronger affinity for anionic complexes of Cr(III) and other cations which may replace Cr(III) ions sorbed already on the sorbent surface. The strong complexes of citrate, molybdate and bisulphate with Cr(III) ions have been reported in the literature [41,42].

4.6. Selectivity of the sorbent

The selectivity of sunflower stem is investigated by measuring the sorption of other metal ions representing different periods and groups of periodic table under optimized conditions chosen for the sorption of Cr(III) ions. The results

Table 5
The influence of cations on the sorption of Cr(III) ions (70.2 μM) onto the sunflower stem (30 mg) from 0.001 M nitric acid

Cations of nitrates ~0.01 M	% Sorption	R_d (cm^3 g^{-1})
Nil	85.4	881
Tl(I)[a]	85	864
Cs(I)	80	592
Na(I)	80	588
Li(I)[a]	68	319
K(I)	67	306
Mg(II)	52	163
Sn(II)[a]	41	105
Sr(II)	40	102
Cd(II)[a]	33	75
Mn(II)[a]	32	70
Ca(II)[a]	31	68
Ni(II)	31	68
Ag(I)	30	65
Co(II)	30	64
Ba(II)[a]	25	50
Al(III)	18.5	34
Pb(II)	12.7	21.8
Ce(III)	12.6	21.7
Y(III)	8.2	13.4
Fe(II)[a]	5.7	9.2
Fe(III)	0.8	1.2

[a] Added as chloride.

including separation factors with respect to Cr(III) ions are presented in Table 6. The difference in the affinity of sunflower stem towards other metal ions can provide a foundation for the effective separation of these ions from aqueous solutions. Eu(III) and Tb(III) reflected higher affinity, whereas, I(I) and Tc(VII) showed low affinity towards sunflower stem as compared to Cr(III). The value of separation factor 'α' for I(I) and Tc(VII) is >2000. It is evident that Cr(III), Eu(III) and Tb(III) can be separated from I(I) and Tc(VII).

Table 6
The sorption of other metal ions onto sunflower stem (30 mg) after 10-min agitation time from 0.001 M nitric acid

Elements	% Sorption	R_d (cm^3 g^{-1})	$\alpha = R_d$ Cr(III)/R_d, (M)
Cr(III)	85.4	881	–
I(I)	0.23	0.259	3401
Tc(VII)	0.27	0.433	2035
Cs(I)	23.0	44.9	19.6
Sb(II)	41.6	107	8.25
Co(II)	54.0	176	5.00
Sc(III)	65.7	289	3.05
Tl(I)	74.6	440	2.00
Ag(I)	74.9	448	1.96
Cd(II)	75.4	459	1.92
Hg(II)	80.2	608	1.45
Tb(III)	86.9	991	0.89
Eu(III)	87.7	1072	0.82

4.7. Sorption mechanism

The plant cells have a diverse chemical composition, expected to vary among species [43]. The potential binding sites in the cells are carbohydrates, amine, hydroxyl, and other functional groups contained in the cell proteins and sugars [43]. The relationship between pH and Cr(III) sorption onto sunflower stem is shown in Table 2. This table shows a variation in the sorption with pH of the sorptive medium. This dependency although does not indicate a systematic pattern because of the change of the dominant species of Cr(III) ions present in solution [43]. Several hydroxy species of Cr(III) ions, namely, $Cr(OH)^{2+}$, $Cr(OH)_2{}^{+}$, $Cr(OH)_3$, $Cr(OH)_4{}^{-}$, $Cr_2(OH)_2{}^{4+}$ and $Cr_3(OH)_4{}^{5+}$ have been formed at different pH values. The sorption mechanism may be deduced from the involvement of different functional groups present on the sorbent surface such as –COOH, $-NH_2$, –OH, metal oxides (via ash content) and fibre carbonaceous C_xOH. These functional groups may be dissociated at different pH values as per their acidic dissociation constants and consequently take part in surface complexation/exchange of metal ions [44]. The surfaces are expected to be negatively charged, which may facilitate the sorption of positively charged metal ions (Cr^{3+} and $CrOH^{2+}$) onto these active groups via surface complexation.

$$-COOH \rightleftharpoons -COO^- + H^+$$

$$-NH_2 \rightleftharpoons -NH^- + H^+$$

$$-OH \rightleftharpoons -O^- + H^+$$

$$MOH \rightleftharpoons -MO^- + H^+$$

$$C_xOH \rightleftharpoons -C_xO^- + H^+$$

The results listed in Table 1 indicate that sunflower stem is composed of substantial amount of cellulose, hemicellulose, lignin and protein besides ash. These active sites may display different affinities for various metal ions [5]. Therefore, the quantity and nature of active sites in the cells of such biomaterials may be a major factor in the binding behaviour of metal ions at a given pH in sorptive solution. The lignin content may increase the biosorption of metal ions on the sorbents of botanical origin [45]. Moreover, phenolic group in the wood plays an important role through making a chelate complex to metal ions [19]. Salim et al. have attributed the loss of metal ions from aqueous solution in the presence of agricultural materials due to the complexation of constituents of these materials [46]. Furthermore, the exchange of metal ions is likely to take place depending upon the affinity of these ions towards the exchange sites [47]. The ion exchange mechanism is in conformity with the sorption energy of 8.74 ± 0.12 kJ mol^{-1} deduced from Eq. (9) for Cr(III) ions. Hence, a combination of ion exchange and surface complexation of Cr(III) ions is proposed as a possible mechanism of biosorption onto sunflower stem.

5. Conclusions

Cr(III) ions up to 85% can be sorbed by sunflower stem (30 mg/4.5 cm^3) in 10 min from 0.001 M nitric acid solution. Its kinetics follows Reichenberg and Lagergren equations over the entire agitation time investigated, while that of Morris–Weber follows partially up to 10 min. The sorption data obeys D–R, Freundlich and Langmuir isotherms. Bisulphate, citrate, molybdate, Fe(II), Fe(III) and Y(III) decrease the sorption significantly. The negative enthalpy and free energy reflect exothermic and spontaneous nature of sorption, respectively. Sunflower stem column can be used, as a selective scavenger for the removal of Cr(III) ions from Tc(VII) and I(I) and as a cheaper and novel sorbent for preconcentration and separation of Cr(III) ions from industrial waste and from its very dilute solutions.

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