

## Biosorption of hexavalent chromium using tamarind (*Tamarindus indica*) fruit shell-a comparative study

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**Abbreviations:** CTFS: crude tamarind fruit shells  
H-TS: HCl treated shells  
O-TS: oxalic acid treated shells

The adsorption of chromium (VI) ions from aqueous solutions has been investigated on crude tamarind fruit shell, HCl treated and Oxalic acid treated shells at room temperatures. The biosorbents are characterized by FT-IR, EDXRF and porosimetry. The biosorption experiments are conducted through batch system. The influence of different experimental parameters such as pH, effect of initial metal ion concentration and effect of dosage of adsorbent on biosorption are evaluated. The adsorption followed first order kinetics. The data are fitted well to Langmuir and Freundlich isotherm models. A comparison is drawn on the extent of biosorption between untreated and treated forms of the tamarind shells. Due to their outstanding adsorption capacities, tamarind shells are excellent sorbents for the removal of chromium ions.

Increased knowledge about toxicological effects of heavy metals on the environment is well recognized and therefore, it is inevitable to search for different methods to reduce water pollution (Mahvi et al. 2005). The major sources of heavy metal contaminations are the industrial effluents. Due to their persistence in nature, it becomes essential to remove them from wastewaters (Klimmrk et al. 2001). Conventional techniques have limitations (Ozdemir et al. 2004) and often are neither effective nor economical especially for the removal of heavy metals at low concentrations. New separation methods are effective and environmentally acceptable at affordable cost (Volesky, 1994).

An alternative method for the removal of heavy metals is considered based on the biological methods of metal

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removal and recovery. The ability of microorganisms to remove heavy metals from aqueous solutions has been known for some decades (Volesky, 1990). The removal of the metals occur actively only with living cells and/or passively at the surface of dead cells. This is known as biosorption. Biosorption is a fast and reversible reaction of the heavy metals with microorganisms or biomass. The by-products obtained from biomaterial production are a cheap source of biosorbents. Therefore biosorption is potentially cost effective way of removing heavy metals from industrial wastewaters. The process is effective even if the concentration is as low as 200 µg/ml. Several approaches have been studied and developed for the effective removal of heavy metals using biosorbents like peat (Brown et al. 2000; Ricou-Hoeffler et al. 2001), fly ash (Ho and Mckay, 2000), microbial biomass (Texier et al. 1999) and other agricultural by products (Laszlo and Dintzis, 1994), soya bean hulls (Marshall et al. 2000) walnut hulls (Wartelle and Marshall, 2000), cotton seed hulls and corn cobs (Reddad et al. 2002). It has also been observed that these biosorbents need further modifications to increase the active binding sites and also made them readily available for sorption. Huang and Huang (1996) stated that pre-treatment of biomass removes the surface impurities on the biosorbents and expose the available binding sites for metal sorption (Cabuk et al. 2005).

The aim of the present study is to investigate the biosorption of chromium (VI) on crude tamarind fruit shells (CTFS), HCl treated shells (H-TS) and oxalic acid treated shells (O-TS) and compare their performance. In the present work, adsorbents are prepared from tamarind shells and treated with acids and utilized for the removal of hexavalent chromium from synthetic solutions. The effect of time, initial concentration of the metal, solution pH and adsorbent dosage on the biosorption at room temperature are also studied and compared. The kinetic data is checked for the pseudo first order reaction and the rate constants are evaluated. The equilibrium data are fitted with Langmuir and Freundlich isotherms equations. Further the biosorbents are characterized by FT-IR, to examine the metal accumulation due to the presence of different functional groups on biosorbent, EDXRF for elemental analysis and porosity.

## MATERIALS AND METHODS

### Biosorbent

Tamarind fruit shells, a waste product of tamarind pulp, are used for the removal of Cr(VI) ions from aqueous solutions. These shells are collected from tamarind fruit pods in Tirupati town, A.P., India, and are powdered and sieved to get uniform size (60-80) mesh particle size. They are washed thoroughly with distilled water and dried in the oven for 2 hrs at 60°C. It is used as a biosorbent (CTFS).

### Pre-treatment of the biosorbent

The pre-treatment of tamarind shells is carried out to increase the metal uptake efficiency. 10 g of the tamarind shells are treated with 100 ml 1N HCl and 1N Oxalic acid for 24 hrs separately and kept on the water bath (70°C) for half an hr. It is cooled and is neutralized with 50 ml of 1N NaOH. The filtrates are separated and are dried in the oven for 4 hrs at 60°C. Thus the pretreated tamarind fruit shells H-TS, and O-TS are used as a second and third biosorbent.

Table 1. Conversion of Cr(VI) to Cr(III) at different pH.

pH	Reduction of Cr(VI) to Cr(III) (mg/L)
1	6.183
2	3.039
3	1.013
4	0.021
5	0.000
6	0.000

### Effect of pH

The effect of pH on chromium biosorption on CTFS, H-TS, O-TS are studied at room temperature by varying pH of chromium solution. The pH of the solutions is adjusted with 0.05N HCl and 0.05N NaOH by making use of digital pH meter (Hanna Instruments, Italy).

### Batch studies

An adsorbate stock solution of 1000 mg/l of Cr(VI) is prepared by dissolving 2.829 g of potassium dichromate in double distilled water. Batch adsorption experiments are carried out by shaking 100 mg of biosorbent mixed with 100 ml of potassium dichromate solution of known concentration in 200 ml Erlenmeyer bottles at room temperature in a rotatory mechanical shaker at 80 rpm. The effect of contact time, metal ion concentration, pH are studied. The bottles are removed after the desired contact time and the filtrates are analyzed using atomic adsorption spectrophotometer (Perkin Elmer 280) and UV-Visible spectrophotometer (Elico-180). All chemicals used are of analytical grade obtained from Glaxo, India, Ltd. Double distilled water is used in preparing the stock solutions and also throughout the experimental analysis.

Four samples of chromium ion concentrations varying from 50-200 mg/L were treated with 100 mg of the biosorbent. In acidic media some part of chromium (VI) was reduced to the trivalent state when it contacts with organic substance. Cr(III) was oxidized to Cr(VI) by potassium permanganate and sodium azide and analyzed by spectrophotometrically (Systronics-118) at wavelength 540 nm using diphenyl carbozide as complexing agent (Prakasham et al. 1999).

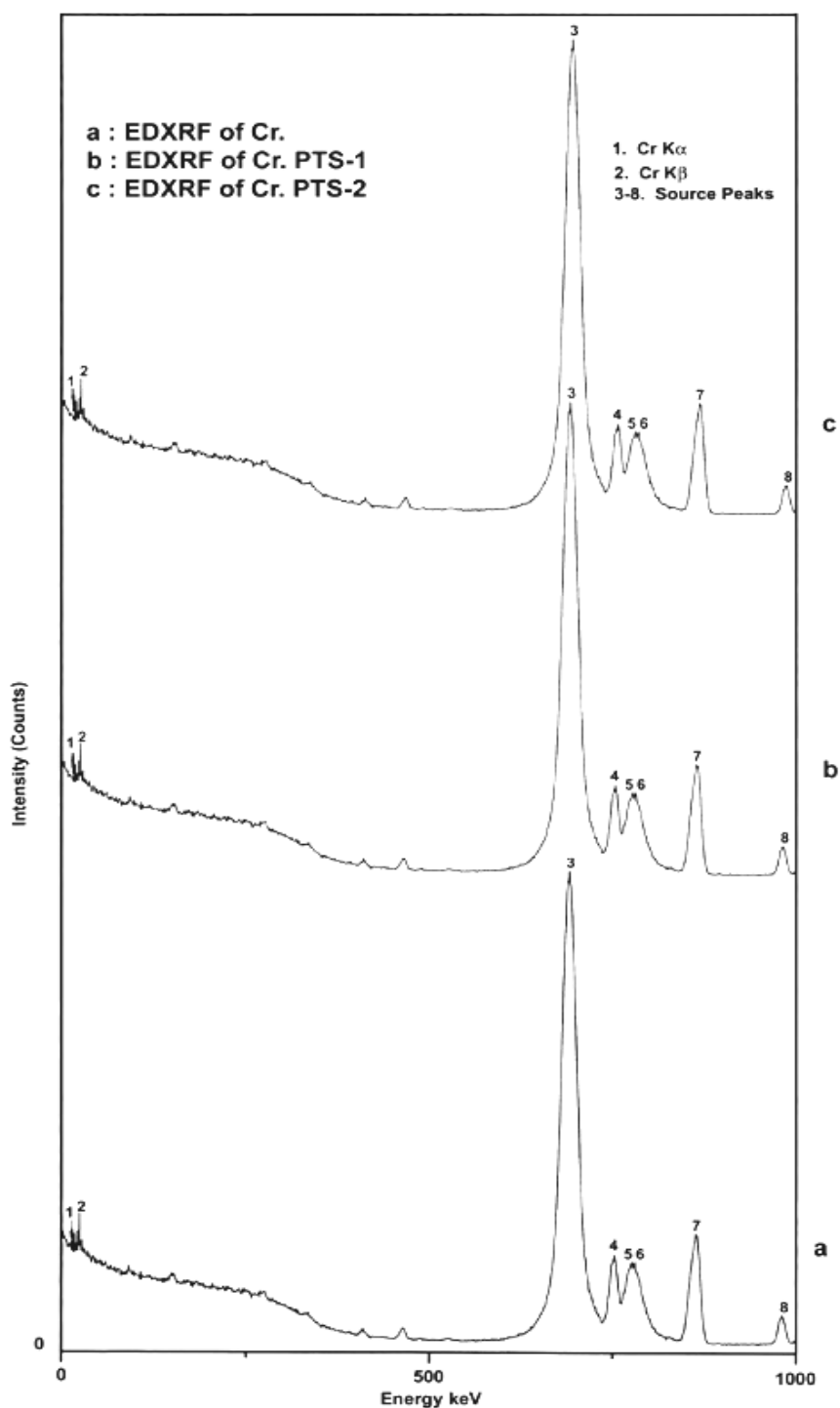


Figure 1. EDXRF spectra of tamarind shell.

With increasing pH, reduction of chromium from hexavalent state to trivalent state is also decreases. In the present work, the optimum pH for chromium adsorption was found to be 3.0 and at this pH reduction of chromium (VI) to chromium (III) was less. Detailed description of the

paper. The data of the reduction of chromium from hexavalent state to trivalent was depicted in Table 1. Total unadsorbed chromium (VI) was calculated by taking the difference of initial concentration and total hexavalent chromium concentration in the filtrate.

$$\text{Cr(VI) adsorbed} = \left( \text{Initial chromium concentration} \right) - \left( \text{chromium concentration in the filtrate} + \text{chromium reduced from VI to III} \right)$$

After the equilibrium is attained by each system, the metal uptake capacity for each sample is calculated according to mass balance on the metal ion using

$$q_e = \left( \frac{C_i - C_e}{m} \right) \cdot v \quad [1]$$

where  $C_i$  and  $C_e$  are initial and equilibrium concentrations of Cr(VI) respectively,  $m$  is the mass of adsorbent and  $V$  is volume of solution in litres.

### Characterization

The biosorbents are characterized using pycnomatic ATC (microstructures) -It is designed for the analysis of solids and extremely fine powders. The real density of the solid is calculated from the ratio of the dried sample weight and the volume is measured by the pycnomatic. From these values of pore volume, specific volume is calculated from which percent porosity of each sample is obtained.

Energy dispersive X-ray fluorescence spectrophotometer is an instrument used to determine the presence of an element both qualitatively and quantitatively. The solid pieces, loose powders and granules are directly paced on to the XRF instrument and analyzed with a single calibration. Thermo Electron Corporation, EDXRF spectra analysis (ED 2000 model), used in the detection of chromium is designed specifically for heavy metal analysis in environmental samples.

Infrared spectroscopy detects the vibrations of chemical function groups in a given sample. A Fourier transform infrared spectrometer, (Nicolet IR-200 spectrometer), used in this analysis gives the information of the spectra of the compounds being analyzed. The spectra collected are within the range 4000-450  $\text{cm}^{-1}$  using a KBr window. The background obtained from the scan of pure KBr is automatically subtracted from the sample spectra. The spectra plotted are having the same scale on the transmittance axis.

## RESULTS AND DISCUSSION

### Characterization of biosorbents

**Pycnomatic ATC.** Porosity is defined as the fraction of pore volume  $V_p$  of the adsorbent that is attributed to the pores detected (Rouquerol et al. 1994)

$$\epsilon = V_p/V \quad [2]$$

where  $\epsilon$  is porosity,  $V_p$  = pore volume and  $V$  = apparent volume.

Porosity is one of the factors that influence the chemical reactivity of solids and physical interaction of solids with liquids and gases. Percent porosity is measured by taking one gram of the biosorbent and these values are presented in Table 2. Pretreated biosorbents showed increased pore volume, decreased density and high percentage of porosity indicating more pores are available for adsorption of metal ions after the pretreatment.

Table 2. Porosity values of biosorbents.

Biosorbent	Pore volume (cc)	Density (g/cc)	% Porosity
CFTS	0.2053	4.869	30.85
H-TS	0.2232	4.480	33.70
O-TS	0.2466	4.055	37.4

**EDXRF studies.** An EDXRF analysis is a surface sensitive technique used to measure almost every element from Na to Pu in the periodic table. X-rays observed in fluorescent analyses typically have energies ranging from 1-100 KeV. These photons can only penetrate a few millimeters into substance so that it reflects the composition of the substance not the core or overall composition. Elemental analysis of biosorbents after biosorption is studied from the spectra of EDXRF and is shown in Figure 1. From the spectral data the three biosorbents show the presence of chromium at 5.4 ( $K\alpha$ ) and 5.98 KeV ( $K\beta$ ). The penetration of photons into the substance reflects the composition of the substance and this is seen from the peaks obtained at respective energies for chromium.

**FTIR spectral studies.** FT-IR spectra given in Figure 2 shows peaks at 3550-3400  $\text{cm}^{-1}$  indicating the presence of -OH or -NH groups. In Figure 2a, the presence of peaks at 1750-1730  $\text{cm}^{-1}$  correspond to C = O stretching *i.e.* aromatic ester groups in the crude form and these peaks do not appear in the pretreated forms (Figure 2b, Figure 2d and Figure 2e). The peaks present at 800-700  $\text{cm}^{-1}$  indicate the presence of aromatic orthodisubstituted heterocyclic molecules, but these peaks are also absent in the metal adsorbed spectra of chromium. This indicates that there is a possibility of ring cleavage after the biosorption of chromium. Thus the binding capacities of the pretreated forms are higher than the crude form. From the spectral data it is concluded that in the pretreated forms the ester groups are already converted into acid groups by the pretreatment and decarboxylation occurs after the adsorption of chromium. Peak at 2600  $\text{cm}^{-1}$  (Figure 1c) indicates the presence of O-H group obtained from conversion of ester into acid. It may be stated that the rate of hydrolysis and the rate of adsorption also influence the adsorption capacity of the biosorbent. Therefore, the adsorptive capacities of the pretreated biosorbents are greater than the crude form. Treatment of biomass with HCl implies the protonation which displaces the light metal ions from the binding sites (*i.e.*, carboxylic, sulfonic, and others). According to Huang

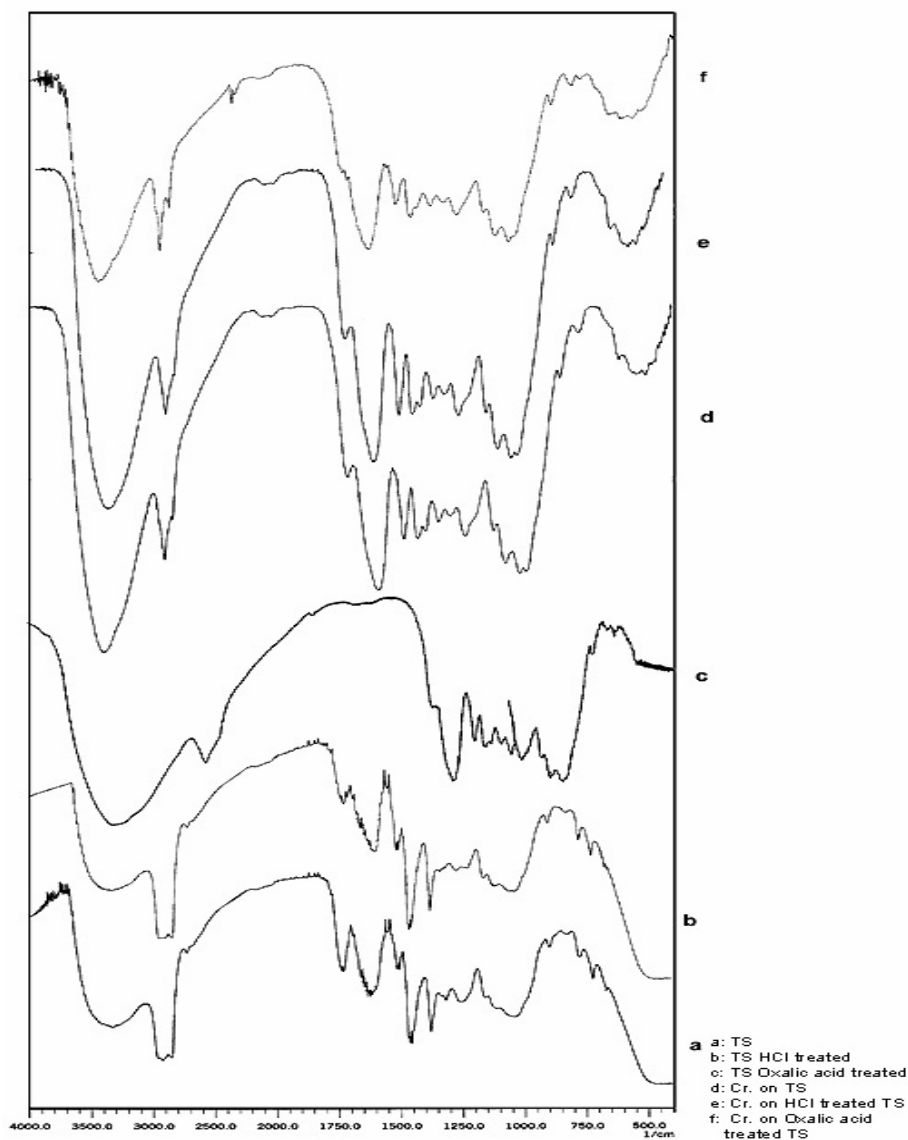


Figure 2. FTIR spectra of tamarind shell.

and Huang (1996), acid treated biomass contained a higher percentage of surface nitrogen. This indicates that acid treatment may dissolve polysaccharide compounds in the outer layer of the cell wall and therefore produce additional binding sites. Acid treatment results not only in a clean-up of the surface impurities, stabilization of the surface compounds, and increases the surface area by opening the available sites for metal adsorption.

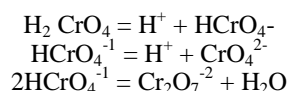
Table 3.  $K_{ad}$  values of the biosorbents for the adsorption of Cr(VI).

Concentration (mg/L)	CFTS	H-TS	O-TS
50	0.014	0.031	0.037
100	0.014	0.031	0.037
150	0.014	0.031	0.036
200	0.014	0.031	0.037

### Effect of pH

Since the solution pH can significantly influence the removal of heavy metals, it is therefore an important condition for adsorption of Cr(VI) ions. Experiments over a range of pH values (1-8) with 100 mg/L of chromium solution in Figure 3 reveal that biosorption capacity of chromium is maximum at pH 3. Agarwal et al. (2006) reported similar results in the biosorption of chromium (VI) by tamarind shell. Tamarind shells are a rich source of protein and amino acids (Marathe et al. 2002). Some functional groups, such as amines, are positively charged when protonated and may electrostatically bind with negatively charged metal complexes. At lower pH, the biosorbent is positively charged due to protonation and dichromate ion exists as anion leading to an electrostatic attraction between them (Boddu et al. 2003). As pH is increases, deprotonation starts and there by results

in decrease of adsorption capacity. Chromium (VI) forms stable complexes such as  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{HCrO}_4^{-1}$ ,  $\text{CrO}_4^{2-}$ , and  $\text{HCr}_2\text{O}_7^{-1}$  depending on the pH of the solution. The fraction of any particular species depends upon the chromium concentration and pH of the solution (Udaybhaskar et al. 1990; Kawamura et al. 1997). Speciation studies of Cr(VI) in aqueous solution, on the basis of spectrophotometry, electrochemistry, freezing point depression and NMR, indicates the existence of the following equilibria;



Equilibria are dependent on pH, with  $\text{HCrO}_4^{-1}$  and  $\text{Cr}_2\text{O}_7^{2-}$  existing primarily in acidic media and  $\text{CrO}_4^{2-}$  being the lone species of Cr(VI) above pH 7.0. At higher pH range, the fraction of  $\text{Cr}_2\text{O}_7^{2-}$  species rapidly decreases with increasing pH above 5. The chromium adsorption and pH curves imply that the  $\text{Cr}_2\text{O}_7^{2-}$  ion is the principal ion being adsorbed on the *tamarind* fruit shell.

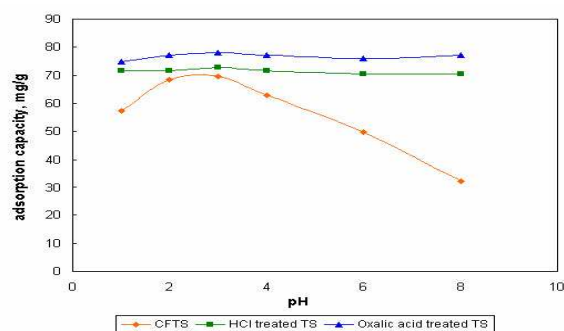
**Table 4. Langmuir and Freundlich constants for the biosorption of Cr(VI) on biosorbents.**

Biosorbent	Langmuir			Freundlich		
	Q <sup>o</sup>	b	r <sup>2</sup>	K <sub>F</sub>	n	r <sup>2</sup>
CFTS	74.62	0.005	0.99	3.00	0.90	0.98
H-TS	140.84	0.007	0.99	3.06	0.70	0.98
O-TS	151.51	0.035	0.99	4.87	0.80	0.98

The decrease in the adsorption with increase of pH may be due to the decrease in electrostatic force of attraction between the sorbent and sorbate ions. At lower pH ranges, due to the high electrostatic force of attraction, the percentage of Cr(VI) removal is high. At very low pH value, the surface of sorbent would also be surrounded by the hydronium ions which enhance the Cr(VI) interaction with binding sites of the biosorbents by greater attractive forces. A sharp decrease in adsorption above pH 4 may be due to occupation of the adsorption sites by anionic species like  $\text{HCrO}_4^{-1}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{CrO}_4^{2-}$ , etc., which retards the approach of such ions further toward the sorbent surface (Dönmez and Aksu, 2002). The decrease in adsorption at high pH values may be due to the competitiveness of the oxyanion of chromium and  $\text{OH}^-$  ions in the bulk. These results suggest that pH affects the solubility of metals and the ionization state of the functional groups like carboxylate, phosphate and amino groups of the cell walls of the biosorbent.

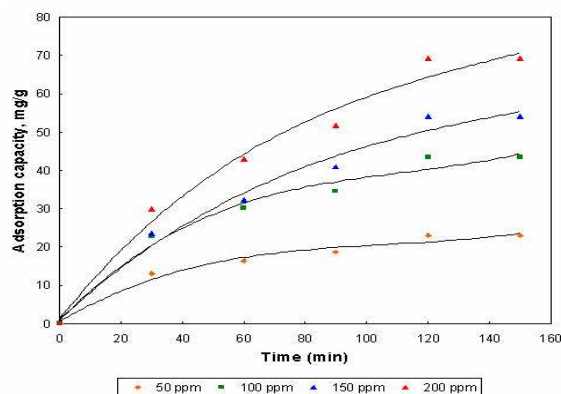
### Effect of contact time and initial concentration of chromium ions

The equilibrium time required for the biosorption of Cr(VI) on CFTS, H-TS, O-TS is studied at various initial concentrations (50-200 mg/L) and with 0.1 g of the biosorbent at different time intervals.



**Figure 3. Effect of pH on adsorption.**

Figure 4, Figure 5 and Figure 6 show that adsorption capacity sharply increases with increase in time and attains equilibrium in 120 min for (CFTS), 60 min for (H-TS), less than 50 min for (O-TS) respectively. The metal adsorption increased rapidly during the first 20 min and remained nearly the same afterwards. The rate of adsorption is higher in the beginning due to large available surface area of the biosorbent. After the capacity of the adsorbent gets exhausted, i.e. at equilibrium, the rate of uptake is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the biosorbent particles (Verma et al. 2006). The contact time is a very important consideration for the treatment of wastewater and accordingly, the contact time is fixed at a little more than the respective equilibrium times for each of the biosorbent.



**Figure 4. Effect of contact time on adsorption CFTS.**

### Adsorption kinetics

Although a range of models is available to study kinetics, Lagergren pseudo first order kinetic model is used for the biosorption of chromium. It should be emphasized that the nature of the metal-ion-sorbent interactions is likely to be different for different biosorbents so that biosorption of metal ions on a particular biosorbent could be a reaction kinetic controlled process, a diffusion controlled process or even a combination of the two (Cheung et al. 2003). The

rate constant of Cr(VI) adsorption on CTFS, H-TS and O-TS followed the first order rate expression given by Lagergren,

$$\log(q_e - q_t) = \log q_e - \left( \frac{K_{ad}}{2.303} \right) t \quad [3]$$

where  $q_e$  and  $q_t$  are amount of metal ion adsorbed per unit mass of adsorbent at equilibrium and at time  $t$  (min).  $K_{ad}$  is the rate constant of adsorption. The linear plots of  $\log(q_e - q_t)$  versus  $t$  for the metal ion studied at different concentrations indicate the approachability of the equation (Shekinaah et al. 2002). Ho and McKay (1999) obtained a similar equation, assuming that the rate limiting step of the reaction may be chemical sorption involving valence forces through sharing or exchange of electrons between the sorbent and the sorbate. From equation 3 the  $K_{ad}$  values are calculated and are presented in Table 3. The values of  $K_{ad}$  remains constant irrespective of initial concentration of Cr(VI) indicates that the adsorption process follows first order kinetics. Further, increase in  $K_{ad}$  values for acid-treated biosorbents relative to untreated form reveal that the rate of adsorption process increases upon treatment.

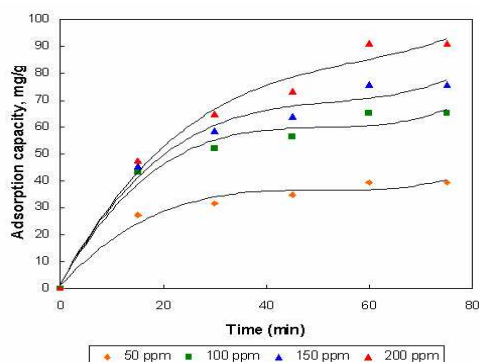


Figure 5. Effect of contact time on adsorption H-TS.

### Effect of dosage

The effect of biosorbent dosage on the removal of chromium is shown Figure 7. The results indicate that the percent removal of chromium (VI) increases with increase in the amount of adsorbent and capable of removing for CTFS, H-TS and O-TS are 93%, 96% and 98% of Cr(VI) respectively. The removal of metal ions increased with the increase in biosorbent concentration and attained equilibrium after 0.25 g of adsorbent dosage for the chromium (VI) ions. This is due to availability of more biosorbent as well as greater availability of surface area (Aoyama, 2003). The removal of Cr(VI) is highly favoured at pH 3 and the same pH is maintained through out the experiments.

### Adsorption isotherms

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. Classical adsorption models (Langmuir

and Freundlich) are used to describe the equilibrium between adsorbed metal ions on the algal cell ( $q_{eq}$ ) and metal ions in solution ( $C_{eq}$ ) at a constant temperature. The equilibrium established between adsorbed component on the biosorbent and unadsorbed component in solution can be represented by adsorption isotherms. The most widely used isotherm equation for modeling equilibrium is the Langmuir equation which is valid for monolayer sorption onto a surface with a finite number of identical sites which are homogeneously distributed over the sorbent surface. The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface suggesting that binding sites are not equivalent and/or independent. The linearized Freundlich and Langmuir adsorption isotherms of nickel (II) and copper (II) ions for both the forms of algae obtained at 33°C varying the concentration from 50-500mg/L was shown in Figure 8 and Figure 9.

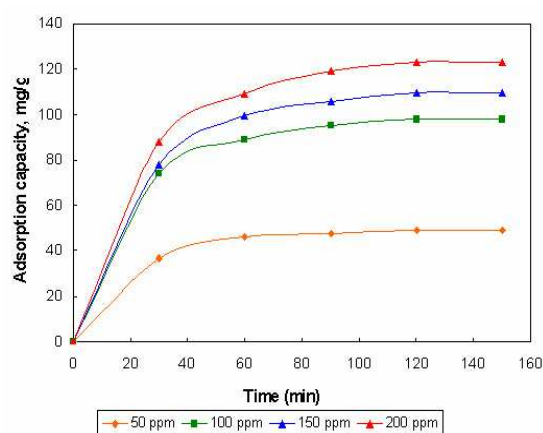


Figure 6. Effect of contact time on adsorption O-TS.

The linearized Langmuir and Freundlich models are used to describe adsorption of hexavalent Cr(VI) on crude and pretreated forms of the biosorbent.

The Langmuir isotherm takes the form,

$$q_t = \frac{Q^o b C_e}{1 + b C_e} \quad [4]$$

where  $Q^o$  is the maximum amount of the metal ion per unit weight of cell to form a complete monolayer on the surfaces at equilibrium concentrations and  $b$  is related to affinity of the binding site.  $Q^o$  and  $b$  are determined from the linear plots  $1/C_e$  vs.  $1/q_e$ . Langmuir constants,  $Q^o$  and  $b$  and correlation factor ( $r^2$ ) are presented in Table 4 and are shown in Figure 8. The values of  $Q^o$  appear to be significantly higher for Cr(VI) on treated TS. The adsorption capacity of O-TS is higher than that of H-TS, which in turn is greater than that of CFTS. This may be due to the fact that oxalic acid has strong metal chelating properties suggesting a ligand promoted mechanism, which



**Table 5. Adsorption capacities of different adsorbents for Cr(VI).**

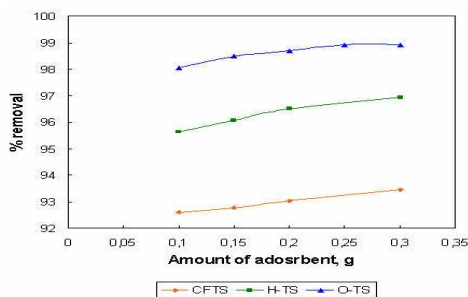
Adsorbent	Q° (mg/g)
Saw dust (Dikshit, 1989)	16.05
Leaf mould (Sharma and Forster, 1994)	43.00
Maize cob (Sharma and Forster, 1994)	13.80
Palm pressed fibres (Tan et al. 1993)	15.00
<i>Pinus sylvestris</i> bark (activated by 0.05 N NaCl) (Alves et al. 1993)	19.50
<i>O. anthropi</i> (Ozdemir et al. 2003)	86.20
CFTS (present work)	74.62
H-TS (present work)	140.84
PTS2 (present work)	151.51

is the main mechanism of mineral dissolution (Fomina et al. 2005).

The empirical Freundlich equation is written as

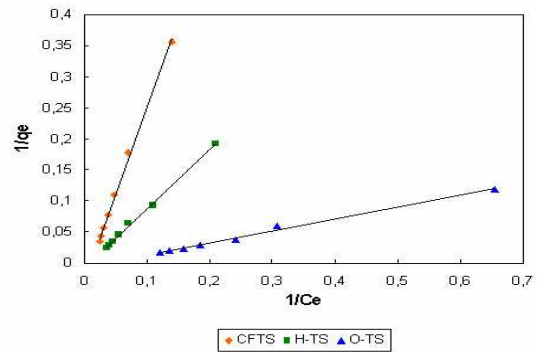
$$q_e = K_F C_e^{\frac{1}{n}} \quad [5]$$

where  $K_F$  and  $n$  are Freundlich constants and are indicators of adsorption capacity and intensity respectively. The values of  $K_F$ ,  $n$  and correlation coefficients ( $r^2$ ) are presented in Table 4 and are shown in Figure 9. In general,  $n$  values are less than unity indicating that the surface of the adsorbent is heterogeneous in nature (Lyubchik et al. 2004). The differences in the Freundlich parameters for each biosorbent are probably related to their molecular structures. The results of equilibrium of biosorption of hexavalent chromium thus fit to the equations. Both models were developed for a single-layer adsorption. However, the Freundlich model physically provides a more realistic description of adsorption by organic matter because it accounts for different binding sites. But, in most cases, both equations fit the data set reasonably well for the experimental data over moderate ranges of concentration. Furthermore, the value of Freundlich exponent  $n = 0.90$  in the range of 3-5, indicates a favourable adsorption (Ho and McKay, 1998). Also, high adsorption capacity indicates the strong electrostatic force of attraction between dye molecules and biosorbent binding-sites (Kaewsarn and Yu, 2001).



**Figure 7. Effect of adsorbent dosage on Cr(VI) adsorption.**

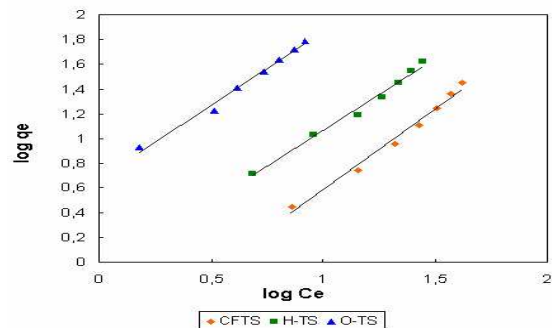
The extent of biosorption of chromium (VI) by tamarind shell and by different biosorbents is comparable with values found in literature and are presented in Table 5. The data in the table indicate that biosorbents CTFS, H-TS and O-TS have maximum adsorption capacity compared to many adsorbents.



**Figure 8. Langmuir isotherms for the adsorption of Cr(VI) on tamarind shell.**

### CONCLUDING REMARKS

The results obtained have shown that tamarind fruit shells both in its natural and acid treated forms are excellent biosorbents for the removal of chromium ions. The maximum uptake of chromium (VI) ions occurs at pH 3. Increase in the amount of biosorbent increases the percent removal of the metal ions. Further, the biosorbents are characterized by porosimetry, EDXRF spectra and FTIR spectral analyses. The data fits well to both Langmuir and Freundlich isotherms and the monolayer maximum adsorption capacities of CTFS, H-TS and O-TS are 74.62 mg/g, 140.84 mg/g, and 151.51 mg/g respectively. Therefore, the present study clearly demonstrates the possibility of usage of low cost biosorbent, tamarind fruit shells and pretreated tamarind fruit shells as suitable alternatives for the removal of chromium ions.



**Figure 9. Freundlich isotherms for the adsorption of Cr(VI) on tamarind shell.**



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