

## ADSORPTION OF CR (III) IONS THROUGH EFFICIENT AND ECO-FRIENDLY ADSORBENTS

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### ABSTRACT

Biosorption technology has evoked tremendous interest to manipulate natural resources as an alternative to expensive and cautionary chemical based procedures opted as purification treatment for industrial effluents. Feasibility of *Ficus bengalensis* L. (banyan), *Ficus religiosa* L. (pippal), *Helianthus annus* L. (sun flower) leaves and *Oryza sativa* L. (rice) straw were tested for removal of chromium(III) ions from the aqueous solution. Batch trials showed these four adsorbents hold 70-80% adsorption efficiency at dose of 0.5 g, pH 4.5, and at 35 mg L<sup>-1</sup> of metal concentration. Fourier Transform Infrared Spectroscopy (FTIR) explored amine (-NH<sub>2</sub>) and hydroxyl (-OH) as a predominant contributor in binding of Cr(III) on to adsorbents biomass. Both Langmuir and Freundlich sorption isotherms fitted data well at concentrations of 20, 40, 60, 80 and 100 mg L<sup>-1</sup> and showed physico-chemical type of adsorption. pH optimization trials at values of 2, 4, 6, 8 and 10, revealed the maximum adsorption efficiency of 80-84% at pH 4 by all adsorbents. The study concluded that the biomass of *F. religiosa*, *F. bengalensis*, *H. annus* and *O. sativa* could be utilized as naturally abundant, easily available and low cost adsorbents for the removal of Cr(III) ions from dilute aqueous solution (20-100 mg L<sup>-1</sup>).

**Keywords:** Biosorption, Cr(III), FTIR, low cost sorbent, metal isotherm, pH.

### INTRODUCTION

Many countries including Pakistan are facing problems of soil and water contamination with Cr from different sources including electroplating, tanning industries and textiles (Shoaib *et al.*, 2013) and its concentration above 0.05 mg L<sup>-1</sup> is considered to be toxic (Suwalsky *et al.*, 2008). Utilization of Cr(III) primarily as a tanning agent seriously deteriorating groundwater qualities around the tanneries in Pakistan (Musjtaq and Khan, 2010). Although Cr(III) is less mobile and less noxious than Cr(VI) but former species could be toxic to plants through persistence bonding to organic matter in soil and aquatic environment (Becquer *et al.*, 2003).

Removal of heavy metal by biosorption technology has been comprehensively evaluated during the last 20-30 years. Variety of adsorbents (microbes, agricultural waste and natural material) has been tested for their metal uptake ability in economic and environmental friendly way (Akhtar and Shoaib, 2012). In Pakistan, the biosorption protocols have gained considerable attention after 1995 and find focal point amongst many engineers, chemists and biologists after 2002. Till date, biosorption technology is graded as the appropriate substitute for detoxification of metal bearing waste from the dilute solution (Javaid and Bajwa, 2008). Natural materials or agricultural waste are the options to be used as low price, widely available and environmentally friendly adsorbents (Subhan and

Pardeep, 2011). Variety of adsorbents like wheat straw (Farooq *et al.*, 2010), rice husk (Subhan and Pardeep, 2011), *Araucaria* leaves (Shukla and Vankar, 2012) and orange peel (Lugo-Lugo *et al.*, 2012) were reported in literature for sequestering of Cr from aqueous medium. Current investigation was conducted to explore Cr(III) removal potential of various types of inexpensive, easily and locally accessible plant biomass/s. Preliminary batch biosorption trials were performed to assess potential biosorbents for Cr(III) ions followed by FTIR analyses of the biosorbents. Isotherm assessments and optimum pH was determined as key parameter of biosorption process.

### MATERIALS AND METHODS

The stock solutions of Cr(III) were prepared by dissolving 7.70 g Cr(NO<sub>3</sub>)<sub>2</sub>.9H<sub>2</sub>O (Merck Germany) in one liter of distilled water and desired dilutions of 20, 40, 60, 80 and 100 mg L<sup>-1</sup> were made from the stock solution with double distilled water.

*F. bengalensis*, *F. religiosa* and *H. annus* leaves were collected from local environment of the Punjab University, while *O. sativa* straw was acquired from local markets of Lahore, Pakistan. These biosorbents were washed with tap water, oven dried at 100 °C for 24 hours and pass through sieve to obtain fine mesh size particle (<0.25-1.00 mm). Each of the natural biosorbent material was kept in separate airtight bottles for later utilization in biosorption experimentations.

Batch tests were performed at pH 4.5 by adding each 0.5 g of biosorbent biomass in 100 mL of 35 mg L<sup>-1</sup> of metal concentration in 250 mL flask kept at constant mixing rate in an orbital shaker at 150 rpm for 2 hours. Remaining Cr concentration of the triplicate samples was analyzed through Atomic absorption spectrophotometer (AAS). Samples were also analyzed from experimental control, which contained no biomass. pH assessment trials were performed at values of 2, 4, 6, 8 and 10 at the similar parameters as mentioned above. Isotherms assessment for Cr(III) adsorption onto four adsorbents was carried out over the range of 20-100 mg L<sup>-1</sup> at constant adsorbent dose, pH and temperature.

Fourier Transform Infrared Spectroscopy (FTIR) of control and metal-loaded biomass was carried out using KBr and the spectral range varying from 4000 to 400 cm<sup>-1</sup>.

The amount of chromium accumulated by biomass and efficiency of biosorbents were calculated by formula described by Barros *et al.* (2003).

## RESULTS AND DISCUSSION

**FTIR spectroscopy:** Adsorption efficiency of the four adsorbents varies with the type of adsorbents. Difference in the structures and organic components of adsorbent exhibited following order of adsorption efficiency: *F. religiosa* & *F. bengalensis* leaves (80%) > *H. annuus* leaves (77%) > *O. sativa* straw (74%) (Akhtar and Shoaib, 2012). The assignment of the major identified bands in four adsorbent after IR spectroscopy is presented in Table I and relevant spectra are shown in Fig. I A-D. IR spectrum of all four adsorbents comprising of both crude and metal laden biomass showed well-define bands in the range of 3336-3300 cm<sup>-1</sup>. This region is corresponded to O-H stretching groups due to inter- and intra-molecular hydrogen bonding of polymeric compounds, such as alcohols, occasionally phenols, and carboxylic acids present in the cellulose and lignin. The region 3300-3000 cm<sup>-1</sup> is characteristic for C-H stretching vibrations of C=C, C=C and Ar-H, while the region from 3000-2700 cm<sup>-1</sup> is dominated by the C-H stretching vibrations of CH<sub>3</sub>, CH<sub>2</sub>, CH and CHO functional groups (Awwad and Salem, 2012). In metal-laden biomass, change in peak to low wave number indicate bounding of free O-H stretching vibrations with metal due to negatively charged on O-H groups thus facilitated in metal binding to a substantial level (Munagapati *et al.*, 2010).

Protein spectra is specified at region between 1800-1500 cm<sup>-1</sup>, whereas 1700 to 1600 cm<sup>-1</sup> is specific for amide-I bands mainly due to C=O stretching vibrations of peptide bond. The bands in the amide I region provide insight into the protein secondary structure. It is evident from the Table II that after

treatment with metal, bands showed their shifting to low wave number indicated attachment of metal with these groups (Akhtar and Shoaib, 2012). Area between 1715-1775 cm<sup>-1</sup> is a distinct series for the carbonyl and double-bond region provided additional binding sites in metal laden biomass of *F. bengalensis* and *F. religiosa*. Vibrational shifting of various functional groups such as C-C, C-O, C-O-C and C-O-P stretching vibrations of polysaccharides to various mode of higher and low stretching frequencies signified their involvement in Cr(III) bonding onto treated biomass (Zvinowanda *et al.*, 2010; Munagapati *et al.*, 2010; Shoaib *et al.*, 2013). Although, significance of these functional groups in metal uptake by the adsorbent depends on the sites capacity, its approachability and chemical state (Alam *et al.*, 2009).

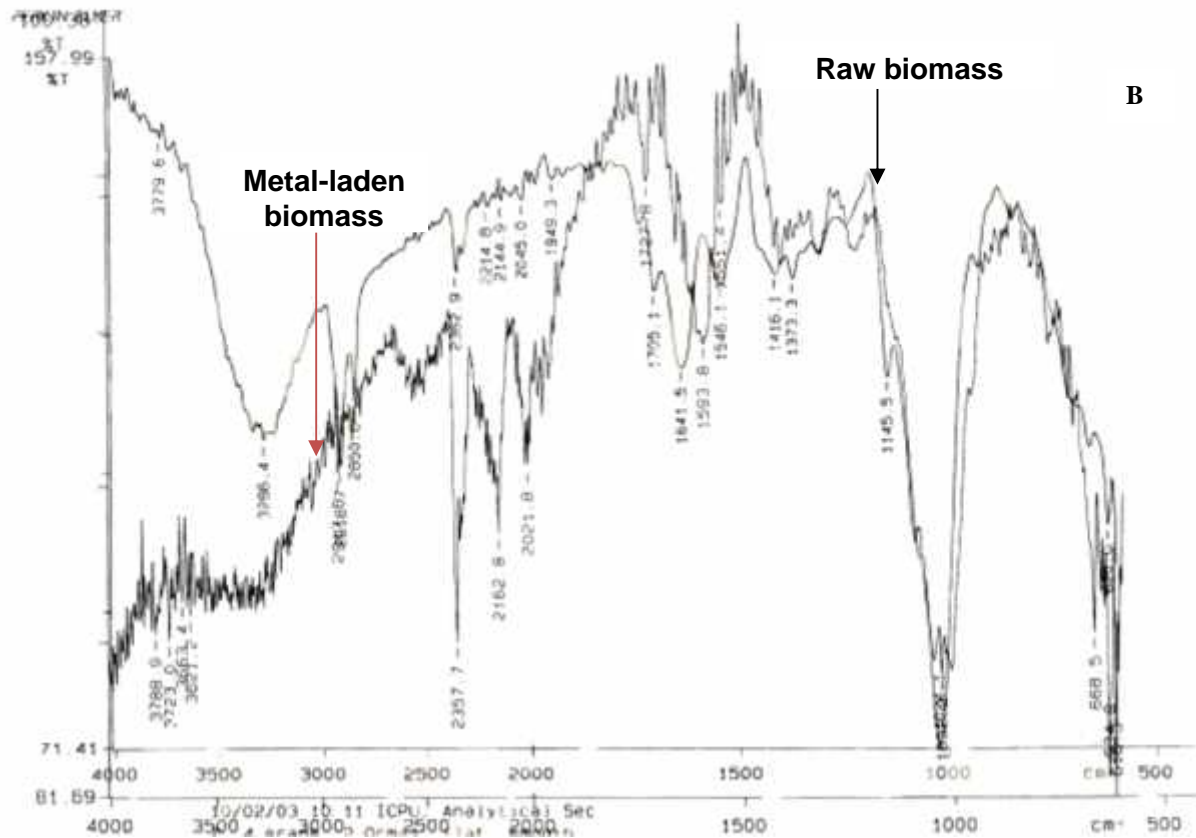
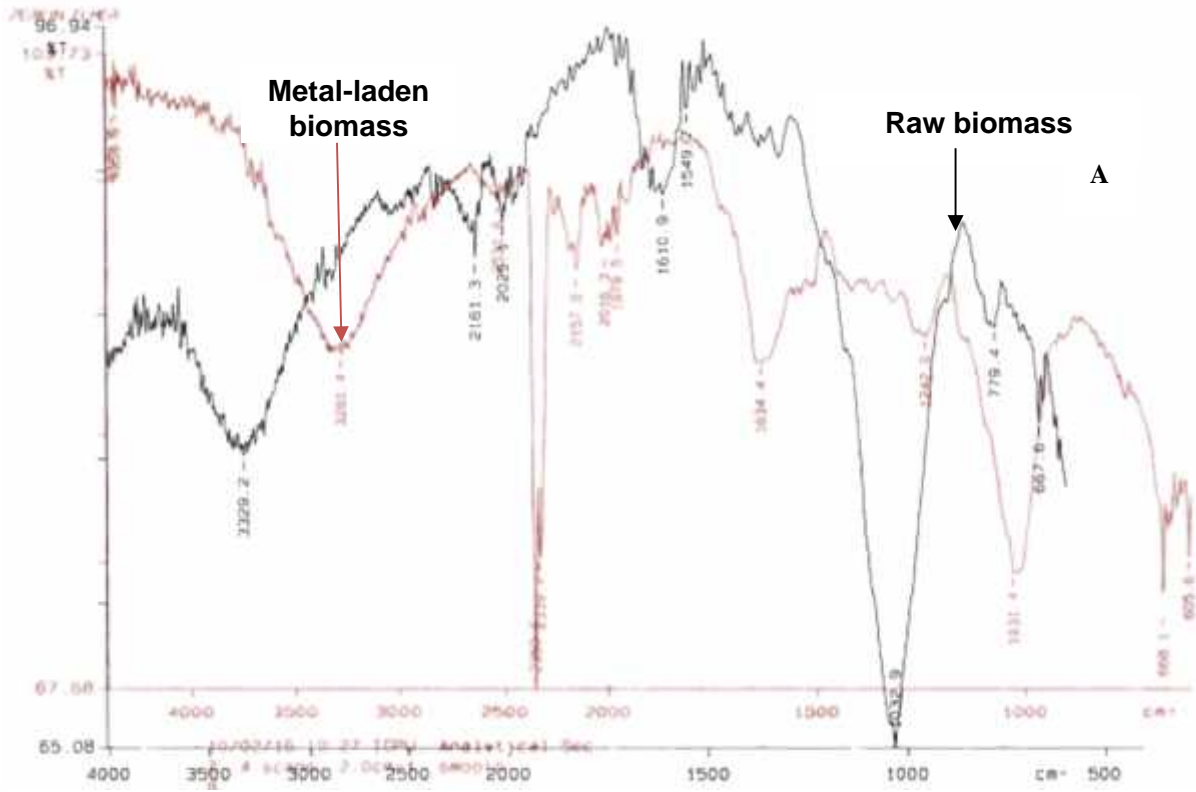
**Isotherm studies:** Experimental data acquired through biosorption experiments with four adsorbents at different initial concentration of Cr(III) was described by Langmuir or L-type (1916) and Freundlich or F-type (1906) isotherms.

Langmuir model:  $q_{eq} = q_{max}bC_{eq}/1+bC_{eq}$ ,

Freundlich model  $q_e = K_F (C_e)^{1/n}$

$q_{eq}$ = metallic ions adsorbed per unit of weight of adsorbents at equilibrium (mg g<sup>-1</sup>);  $q_{max}$ = maximum adsorption capacity of metal (forming monolayer) per unit weight of the adsorbent (mg g<sup>-1</sup>);  $b$  = constant related to the affinity of binding sites for metal ions (L mg<sup>-1</sup>);  $C_{eq}$  = equilibrium concentration (mg L<sup>-1</sup>);  $K_F$  (L g<sup>-1</sup>) and  $n$  = Freundlich characteristic constants

A good correlation between experimental data and Langmuir (monolayer adsorption of solute) and Freundlich adsorptions (heterogeneous surfaces models) for chromium ( $R_2 > 0.9$ ) was recorded (Table II). However, Freundlich model relatively fitted well than Langmuir model throughout the concentration range (20-100 mg L<sup>-1</sup>). Langmuir assumption revealed simultaneous occurrence of both physisorption and chemisorption on the adsorbent surface (Shoaib *et al.*, 2012). There are two simple interpretable constants i.e.  $q_{max}$  and  $b$  of the Langmuir model which help in predicting the good adsorbent in general. A good biosorbent should hold low  $b$  and high  $q$  (Kratochvil and Volesky, 1998). Presently desirable affinity ( $b$ ) under specific experimental conditions demonstrated the small values i.e. 0-0.031 L mg<sup>-1</sup> for the adsorbents and high  $q$  values (27-30 mg g<sup>-1</sup>). In Freundlich model (Table II), value of  $n$  specifies the degree of non-linearity between solution concentration and adsorption. The value of  $n$  in Freundlich equation ranged between 1.2-2.0, that could be due to chemical type of adsorption along with extent of heterogeneity on the adsorbents surface. Further, value of  $n$  if greater than 1 describe favorable adsorption of Cr(III) on to biomass of adsorbents.





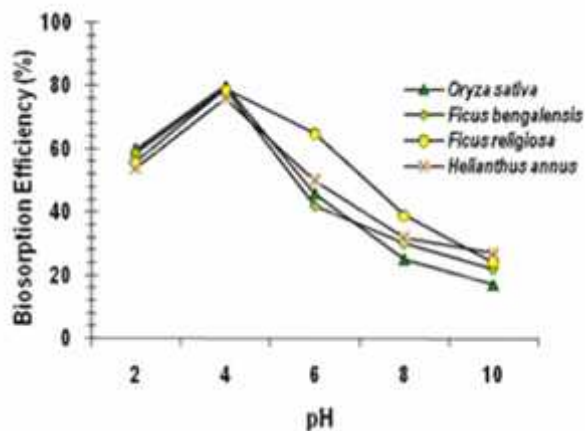
**Table I: Comparison of IR spectra of raw and Cr(III)-loaded biomass of different biosorbents.**

<i>Ficus religiosa</i>	<i>F. religiosa</i>	
3788, 3723, 3663, 3621	3779, 3286	Protein and carbohydrate (O-H), (N-H)(amide I)
1728	1705, 1641	C=O of ester group and C=N of amine
1593, 1551	1546	Protein amide II band mainly (N-H) and (C-N)
1032	1024, 1145	Carbohydrate (cellulose and pectin)
<i>Ficus bengalensis</i>	<i>F. bengalensis</i>	
3808, 3694, 3863, 3334	3280	Protein and carbohydrate (O-H), (N-H)(amide I)
1727	1742	C=O of ketones
1610, 1529	1632, 1539	Protein of amide-I and amide-II
1032	1032,1152	Carbohydrate (cellulose and pectin)
<i>Helianthus annuus</i>	<i>H. annuus</i>	
3769, 3268	3309	Protein and carbohydrate (O-H), (N-H)(amide I)
-	1633	Protein of amide-I mainly(C=O)
1596, 1552	-	Protein of amide-II mainly (N-H) and (C-N)
1241	-	P=O of phosphodiester group of nucleic acids and phospholipids
1015	1035	Carbohydrate (cellulose and pectin)
<i>Oryza sativa</i>	<i>O. sativa</i>	
3329	3281	Protein and carbohydrate (O-H), (N-H)(amide I)
1610, 1549	1602	Protein of amide-I mainly(C=O)
1032	1241	P=O of phosphodiester group
	1016	Carbohydrate (cellulose and pectin)

**Table II: Langmuir and Freundlich isotherms parameters for biosorption of Cr(III) ions onto biosorbents**

Biosorbents	Langmuir and Freundlich Isotherms						
	$q_{exp}$ ( $\text{mg g}^{-1}$ )	$q_{max}$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_f$ ( $\text{L g}^{-1}$ )	$n$	$R^2$
<i>Oryza sativa</i>	33	33	0.031	0.99	0.03	1.29	0.99
<i>Ficus bengalensis</i>	25	27	0.024	0.97	0.03	1.82	0.99
<i>Ficus religiosa</i>	25	26	0.023	0.97	0.15	1.23	0.99
<i>Helianthus annuus</i>	28	27	0.021	0.98	0.09	1.24	0.99

**pH studies:** Maximum uptake of Cr(III) by *H. annuus*, *F. religiosa*, *F. bengalensis* and *O. sativa* was recorded at moderately to slightly acidic medium (i.e. pH 4-4.5) (Fig. III). Adsorption efficiency of the adsorbents increased from ~50-80% at acidic pH values (2-4) and decreased from ~45-22% with increasing alkalinity of solution (pH 6-10). Solubility of metal ions is largely pH dependent. In the low pH range (2-3) adsorption sites are more protonated and they are less attractive against various cationic forms of metals i.e. electrostatic repulsion will be high. On increasing in pH (4-5), electrostatic repulsion decline, positive charge decrease thus metal uptake increase. While, at pH values 6-10, the amount of metallic ions taken up was decreased due to the formation of soluble complexes of the metal ions and their competition with the active sites (Shoaih *et al.*, 2013).

**Fig. II: Influence of pH on adsorption efficiency of the adsorbents.**

**Conclusions:** Biomass of *F. religiosa*, *F. bengalensis*, *H. annuus* leaves and *O. sativa* straw hold considerable metal removal efficiency (70-80%), thus could be utilized effectively to remove Cr(III) from industrial effluents in

ecofriendly and economic way. The FTIR spectral analysis revealed participation of amine (NH<sub>2</sub>) and hydroxyl (OH) groups in uptake of Cr(III) from aqueous solution. The Cr(III) biosorption data fitted well to Freundlich and Langmuir model well over the concentration range studied (20, 40-----100 mg L<sup>-1</sup>). Cr(III) ions uptake by the adsorbents was considerably affected by solution pH with maximum removal (80-84%) was observed at pH.

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