Cr (VI) and Fe (III) removal using *Cajanus cajan* husk

N. Ahalya[1], R.D. Kanamadi[2] and T.V. Ramachandra*[1]
*cestvr@ces.iisc.ernet.in

[1]Energy and Wetlands Research Group, Centre for Ecological Sciences
Indian Institute of Science, Bangalore-560 012, India
[2]Department of Zoology, Karnataka University, Dharwad-580 005, India

Abstract: Husk of tur dal (Cajanus cajan) was investigated as a new biosorbent for the removal of Fe (III) and Cr (VI) ions from aqueous solutions. Parameters like agitation time, adsorbent dosage and pH were studied at different initial Fe (III) and Cr (VI) concentrations. The biosorptive capacity of the Tur dal husk was dependent on the pH of the chromium and iron solution, with pH 2 and 2.5 respectively being optimal. The adsorption data fit well with Langmuir and Freundlich isotherm models. The practical limiting adsorption capacity (q_{max}) calculated from the Langmuir isotherm was 96.05 mg of Cr(VI)/ g of the biosorbent at an initial pH of 2.0 and 66.65 mg/g at pH 2.5 . The infrared spectra of the biomass revealed that hydroxyl, carboxyl and amide bonds are involved in the uptake of Cr (VI) and Fe (III) ions. Characterisation of tur dal husk has revealed that it is an excellent material for treating wastewaters containing low concentration of metal ions.

Introduction

Mobilisation of heavy metals in the environment due to industrial activities is of serious concern as these metals are toxic to all forms of life including humans. Chemical oxidation-reduction, precipitation, adsorption, solidification, electrolytic recovery and ion exchange are some of the commonly adopted physico-chemical wastewater treatment processes for heavy metal removal. However, technical or economical constraints restrict wide application of such processes. In this regard, biosorption or biological metal removal has distinct advantages over conventional methods. These techniques are non-polluting, highly selective, more efficient, easy to operate and hence cost-effective for treatment of large quantities of wastewater containing low concentration of heavy metals. Low cost adsorbents like seaweeds, molds, yeast, bacteria, crabshells, agricultural products such as wool, rice, straw, coconut husks, peat moss, exhausted coffee (Macchi *et al.*, 1986; Baran *et al.*, 2005; Akinala and Ekiyoyo, 2006), waste tea leaves (Tee and Khan, 1988), walnut skin, coconut fibre (Espinola *et al.*, 1999), polymerized corn cob (Odozi *et al.*, 1985), melon seed husk (Okieimen and Onyenkpa, 1989), defatted rice bran, rice hulls, soybean hulls and cotton seed hulls (Marshall and Champagne, 1995; Marshall *et al.*, 1993) wheat bran, hardwood (*Dalbergia sissoo*) sawdust, pea pod, cotton and mustard seed cakes, petiolar felt sheath of palm (Iqbal and Saeed, 2002; Iqbal *et al.*, 2002; Saeed *et al.*, 2002) have been attempted in recent years for heavy metal removal. In the present study, tur dal husk (TDH) (*Cajanus cajan*), which is a low cost, milling agrowaste available in plenty in a tropical country like India, is used for the removal of Cr (VI) and Fe (III) ions from synthetic solutions.

Materials and Methods

Tur dal (*Cajanus cajan*) husk (seed coat) was collected from a legume seed-splitting mill. The tur dal husk (TDH) was thoroughly washed in running tap water to remove dirt and other particulate matter. This was later subjected to colour removal through washing and boiling in distilled water repeatedly. Subsequently the husk was oven dried at 105°C for 24 hr, stored in a desiccator and used for biosorption studies in the original piece size.

Batch mode adsorption studies using processed TDH were carried out to determine the adsorption of Cr (VI) and Fe (III). The synthetic stock solution (1000 ppm) of ferrous ammonium sulphate and potassium dichromate prepared in the laboratory was diluted to different concentrations and to each 100 ml; 1 g of the biosorbent (husk of *Cajanus cajan*) was added and agitated in a rotary shaker at 150 rpm for pre-determined time intervals. The adsorbate and the adsorbent were separated using whatman no. 1 filter paper. The residual metal concentration was determined spectro-photometrically using standard procedures of Eaton *et al.*, 1995 for Cr (VI) and Snell and Snell, 1961 for Fe (III). Infrared spectroscopic studies of TDH before and after treatment with Cr (VI) and Fe (III) was carried out to determine the functional groups responsible for adsorption.

Results and Discussion

The distribution of nutrients in the seed coat of tur dal is as follows: crude protein – 5.6%, ether extractives – 0.3%, crude fibre – 31.9%, ash – 3.5% and carbohydrates – 58.7% (Morton, 1976; Singh *et al.*, 1968).

The results indicated that increase in the contact time increased the metal uptake but remained constant after an equilibrium time. The uptake of Cr (VI) was rapid and the equilibrium was attained within 15 minutes of contact between the biosorbent and the metal solution. The equilibrium time remained constant for all the initial metal concentrations measured. Equilibrium time varied with the metals due to the difference in initial metal concentration and affinity of the adsorbent for the particular metal ion.

The equilibrium time for an initial Fe (III) concentration of 10 ppm and 20 ppm was 30 minutes, for 50 ppm and 100 ppm it was 60 and 240 minutes respectively. In the case of Fe (III), the percentage of heavy metal adsorbed decreased with increase in metal concentration (Fig. 1). The 100 ppm solution took longer to attain equilibrium due to the presence of proportionally high amount of Fe (III). Mameri *et al.* (1999), reported that the available adsorption sites on the biosorbent are the limiting factor for metal uptake. The equilibrium time required by the adsorbent to remove Cr (VI) is very less, compared to other adsorbents. This is significant as equilibrium time is one of the important considerations for economical water and wastewater applications.

The experiment was carried out with different adsorbent dosage up to the equilibrium time. It was noted that after an adsorbent dosage level of 1g/100 ml, adsorption of Cr (VI) and Fe (III) was very low or constant (Fig. 2). However, the percentage of metal removed increased with increasing initial metal concentration and increasing adsorbent dosage.

The biosorption of Cr (VI) and Fe (III) was dependent on pH. Maximum adsorption of Cr (VI) was seen at pH 2 and Fe (III) at pH 2.5. The percentage of Cr ions adsorbed at pH 2.0 decreased with increasing metal concentration. The adsorption of metal ions depends on solution pH, which influences electrostatic binding of ions to corresponding metal groups. At the optimum sorption pH 2.0, the dominant species of Cr ions in solution are $HCrO_4^-$, $Cr_2O_7^{2-}$, $Cr_4O_{13}^{2-}$ and $Cr_3O_{10}^{2-}$ (Dakiky *et al.*, 2002; Namasivayam and Yamuna, 1995). These chromate anions interact strongly with the negatively charged ions of the tur dal husk matrix. The experiments were carried out below pH3 for Fe (III) ions as Fe (III) precipitated as their hydroxides above pH 3. Ozer *et al.* (1999) and Sag and Kutsal (1996), obtained similar results. The optimum conditions for removal of heavy metals were standardized based on the results.

Langmuir isotherm was applied to the present study to estimate the adsorption capacity of tur dal husk. Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites (Langmuir, 1918). It is represented by the following equation:-

$$C_{eq}/q \; = \; 1/q_{max}.b + C_{eq}/q_{max} \quad\text{----------------}\quad (1)$$

where q is milligrams of metal accumulated per gram of the biosorbent material; C_{eq} is the metal residual concentration in solution; q_{max} is the maximum amount of the metal ion per unit weight of the biosorbent to form a complete monolayer on the surface bound at high C_{eq}. q_{max} represents a practical limiting adsorption capacity when the surface is fully covered by metal ions and assists in the comparison of adsorption performance. b is the constant related to the affinity of the binding sites. The linear plots of C_{eq}/q vs C_{eq} for Cr (VI) and Fe (III) show that adsorption follows the Langmuir adsorption model (Fig. 3i and 3ii).

The adsorption capacity (q_{max}) was calculated to be 96.05 and 66.63 mg/g for Cr (VI) and Fe (III) respectively. The adsorption capacity of Cr (VI) and Fe (III) by TDH with other adsorbents is compared in Table 1, which indicates that tdh has better capability than some of the biosorbents used previously.
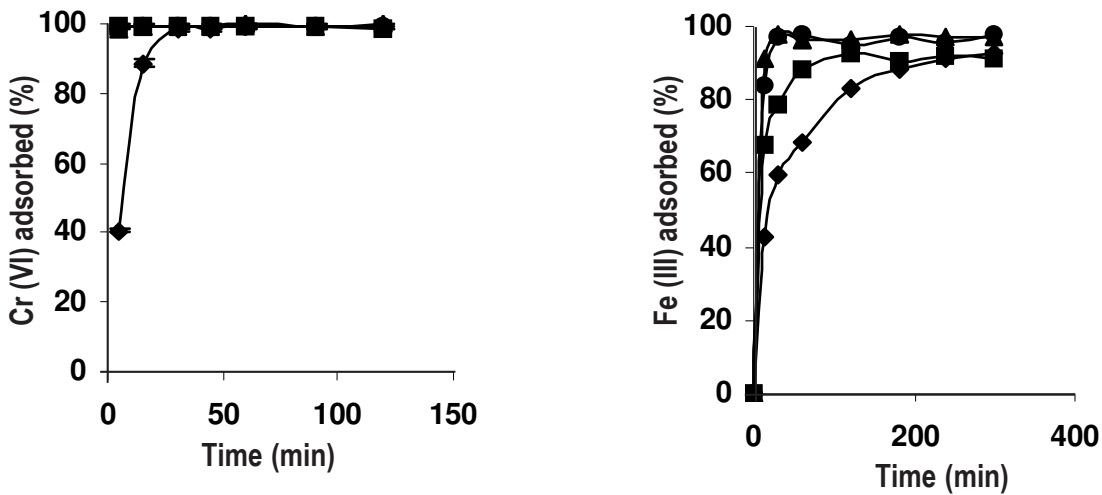

Fig. 1: Effect of contact time on removal of metals at increasing metal concentrations
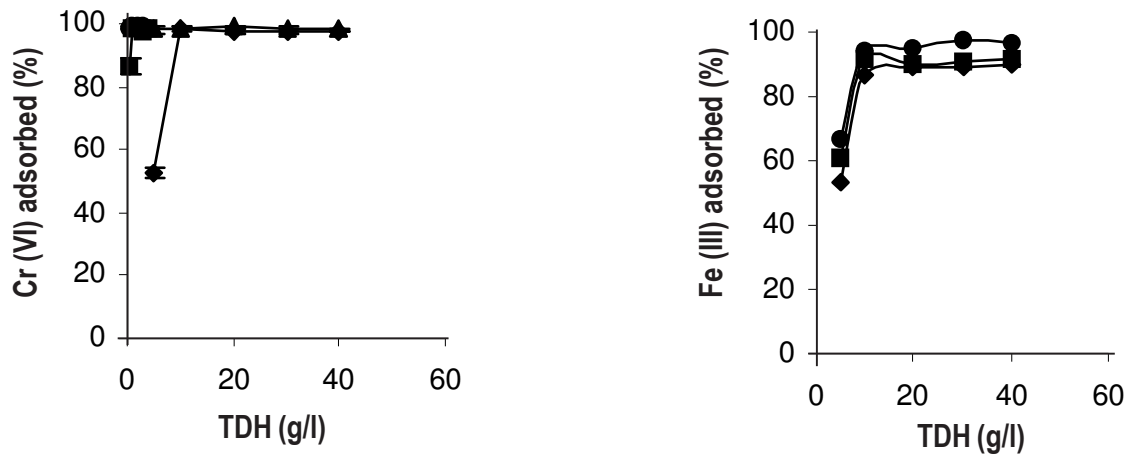(▲ 10 ppm, ● 20 ppm, ■ 50 ppm, ◆ 100ppm)

Fig. 2: Effect of adsorbent dosage on removal of metals at increasing metal concentrations
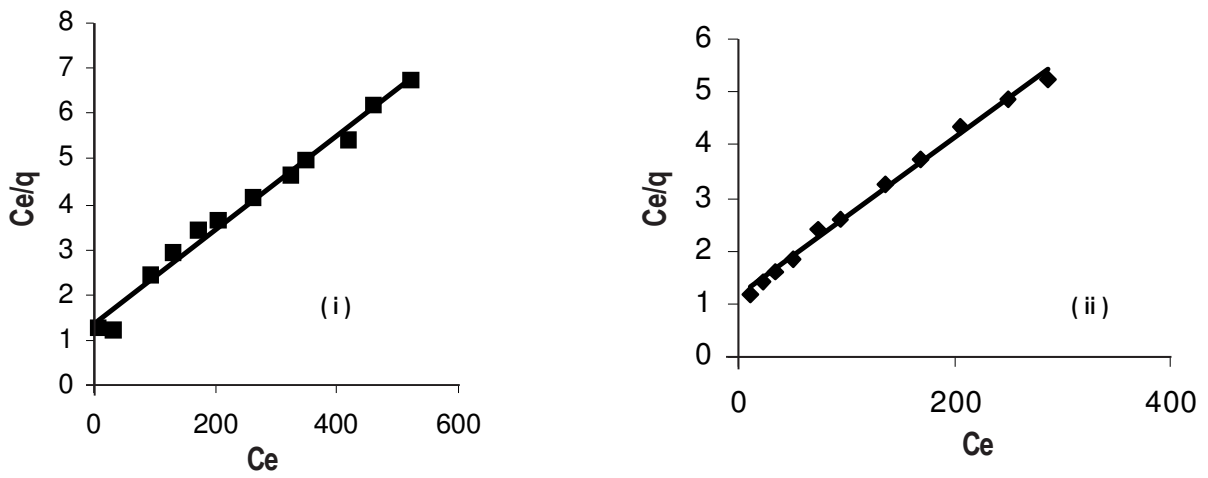(● 20 ppm, ■ 50 ppm, ◆ 100ppm)

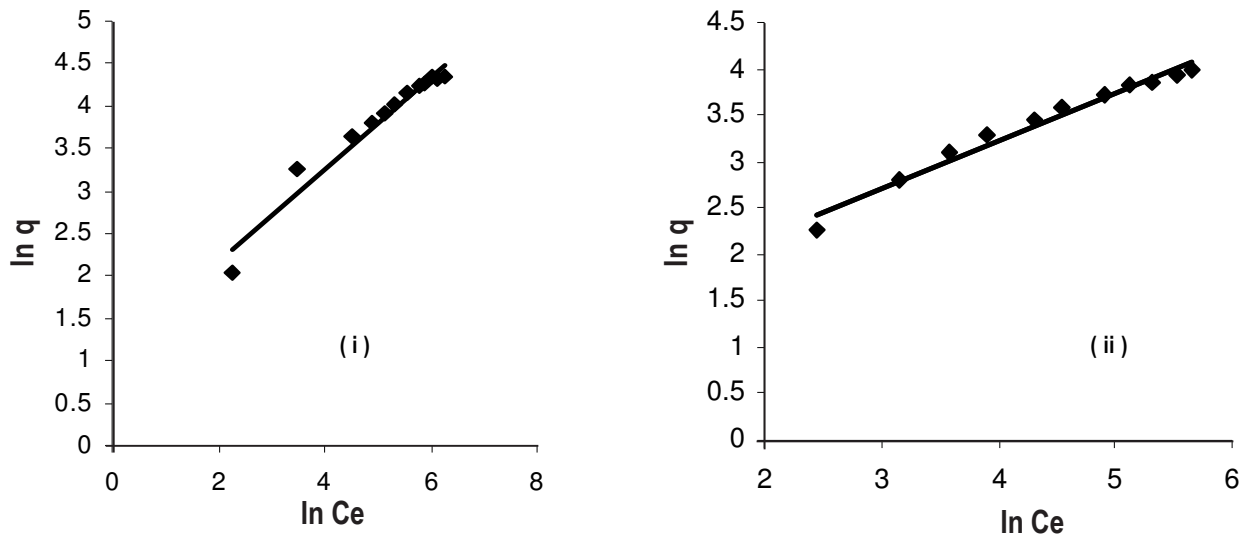**Fig. 3:** Langmuir plots for metal removal (i) Cr (VI) (ii) Fe (III)

Fig. 4: Freundlich plots for metal removal (i) Cr (VI) (ii) Fe (III)

Table - 1: Comparison of adsorption capacity of tur dal husk for Cr (VI) and Fe (III) with other adsorbents

Biosorbent	Cr (VI)	Fe (III)	References
Exhausted coffee	1.42		Orhan and Buyukgungor (1993)
Nut shell	1.47		Orhan and Buyukgungor (1993)
Sawdust	10.1, 16.05, 4.44		Bryant *et al.* (1992), Dikshit (1989), Zarraa (1995)
Walnut shell	1.33		Orhan and Buyukgungor (1993)
Waste tea	1.55		Orhan and Buyukgungor (1993)
Anaerobic activated sludge	195.30		Aksu and Akpinar (2001)
Industrial biomass			
(*Aspergillus niger* grown on wheat bran)		19.2	Chandra Sekhar *et al.* (1998)
Streptomyces rimosus		125	Selatnia *et al.* (2004)
Chlorella vulgaris	27.27	24.49	Aksu *et al.* (1997)
Zoologea ramifera		65.49	Sag and Kutsal (1995)
Tur dal husk	96.05	66.63	Current study

Table - 2: Sorption isotherm constants and coefficients of determination for tur dal husk

	Langmuir equation			Freundlich equation		
	Q_{max} (mg/g)	b (l/mg)	R^2	K_F (mg/g)	n	R^2
Iron	66.63	0.01	0.99	1.446	1.82	0.97
Chromium	96.05	0.007	0.98	2.95	1.83	0.95

Table - 3: Infra red absorption bands and their corresponding groups

Wave numbers (cm^{-1})	Functional group
3431	-OH, -NH
2918.89	-CH
1442.89	-CH
1733	C=O
1621	C=C
1381	-CH

The Freundlich adsorption isotherm (Freundlich, 1907) was also applied for the adsorption of Fe (III) and Cr (VI) by husk of *Cajanus cajan*.

The Freundlich isotherm is represented by the equation

$$q = K_f C_{eq}^{1/n} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

where C_{eq} is the equilibrium concentration (mg/l), q is the amount adsorbed (mg/g) and K_f and n are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity respectively. The linearised forms of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$$\ln q = \ln K_f + 1/n \ln C_{eq} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(3)$$

Linear plots of ln Ce vs ln q show that the adsorption of metal ions onto the tur dal husk follows the Freundlich isotherm model (Fig. 4i and 4ii).

It also indicates that the average energy of adsorption decreases with increasing adsorption density. Values of K_f and n were calculated from the intercept and slope and are given in Table 2 along with the Langmuir constants. The values of n between 1 and 10 represent good adsorption of the adsorbate onto the adsorbent (McKay *et al.,* 1982).

The infrared spectra of tdh before and after treatment with Cr (VI) and Fe (III) reveal the functional groups that are responsible for binding the heavy metal ions. Table 3 gives the wavenumbers with the corresponding functional groups. The results indicate that several functional groups are available on the surface of tdh for binding Fe(III) and Cr(VI).

The study reveals that tur dal husk, an agro-milling waste available in plenty at low cost is efficient in the removal of Cr (VI) and Fe (III). In batch mode studies, adsorption was dependent on contact time, pH, initial metal ion concentration and biosorbent dosage. Adsorption followed Langmuir and Freundlich isotherm models. Consisting of approximately 31.9% crude fibre composed of cellulose, hemicellulose and lignin, the TDH biomatrix indicates the presence of many –OH and –COOH groups in the lignocellulosic moieties. Hydrogen of these groups is capable of ion exchange with metal cations. Protein content in TDH is less than 5.6%, which is advantageous over the protein rich algal and fungal biomass projected as metal biosorbents, since proteinious materials are likely to putrefy under moist conditions. These adsorbed heavy metal ions can be easily desorbed and the biomass be incinerated for final disposal. This biosorbent is of low cost, its utility will be economical and can be viewed as a part of a feasible waste management strategy.

Acknowledgments

References

Akinola, M.O. and T.A. Ekiyoyo: Accumulation of lead, cadmium and chromium in some plants cultivated along the bank of river Ribila at Odo-nla area of ikorodu, Lagos state, Nigeria. *J. Environ. Biol.*, **27**, 597-599 (2006).

Aksu, Z., A. Unsal and K. Tulin: Application of multicomponent adsorption isotherms to simultaneous biosorption of iron (III) and chromium (VI) on *C. vulgaris. J. Chem. Tech. Biotechnol.*, **70**, 368-378 (1997).

Aksu, Z. and D. Akpinar: Competitive biosorption of phenol and chromium (VI) from binary mixtures onto dried anaerobic activated sludge. *Biochem. Eng. Jou.*, **7**, 183-193 (2001).

Baran, Ayse, Senay Hamarat Baysal and Atakan Sukatar: Removal of Cr^{6+} from aqueous solution by some algae. *J. Environ. Biol.*, **26**, 329-333 (2005).

Bryant, P.S., J.N. Petersen, J.M. Lee, T. M and Brouns: Sorption of heavy metals by untreated red ®sawdust. *Appl. Biochem. Biotechnol.,* **34-35**, 777-788 (1992).

Chandra Sekhar, K., S. Subramanian, J.M. Modak and K.A. Natarajan: Removal of metal ions using an industrial biomass with reference to environmental control. *Int. J. Miner. Process.,* **53**, 107-120 (1998).

Dakiky, M., M. Khamis, A. Manassra and M. Meaeb: Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents. *Advin. Environ. Res.*, **6**, 533-540 (2002).

Dikshit, V.P.: Removal of chromium (VI) by adsorption using sawdust. *Nat. Acad. Sci. Lett.*, **12**, 419-421 (1989).

Eaton, A.D., L.S. Clesceri and A.E. Greenberg: Standard methods for the examination of water and wastewater. 19th Edn., American Public Health Association Washington, D.C. pp. 34-39 (1995).

Espinola, A., R. Adamian and L.M.B. Gomes: An innovative technology: Natural coconut fibre as adsorptive medium in industrial wastewater cleanup. *Waste Treat. Clean Technol. Proc.*, **3**, 2057-2066 (1999).

Freundlich, H.: Ueber die adsorption in loesungen. *Z. Physik Chem.*, **57**, 385-470 (1907).

Iqbal, M., A. Saeed and N. Akhtar: Petiolar felt-sheath of palm: A new biosorbent for the removal of heavy metals from contaminated water. *Biores. Technol.*, **81**, 153-155 (2002).

Iqbal, M. and A. Saeed: Removal of heavy metals from contaminated water by petiolar felt-sheath of palm. *Environ. Technol.*, **23**, 1091-1098 (2002).

Langmuir, I.: The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.*, **40**, 1361-1403 (1918).

Macchi, G., D. Macroni and G. Tiravarthi: Uptake of mercury by exhausted coffee grounds. *Environ. Technol. Lett.,* **7**, 431-444 (1986).

Mameri, N., N. Boudries, L. Addour, D. Belhocine, H. Lounici, H. Grib and A. Pauss: Batch zinc biosorption by a bacterial nonliving *Streptomyces rimosus* biomass. *Wat. Res.*, **33**, 1347-1354 (1999).

Marshall, W.E. and E.T. Champagne: Agricultural byproducts as adsorbents for metal ions in laboratory prepared solutions and in manufacturing wastewater. *J. Environ. Sci. Hlth.,* **A30**, 241-261 (1995).

Marshall, W.E., E.T. Champagne and W.J. Evans: Use of rice milling byproducts (hulls and bran) to remove metal ions from aqueous solution. *J. Environ. Sci. Hlth.,* **A28**, 1977-1992 (1993).

McKay, G., H.S. Blair and J.R. Gardener: Adsorption of dyes on chitin I. Equilibrium studies. *J. Appl. Polym. Sci.*, **27**, 3043-3057 (1982).

Morton, J.F.: The pigeon pea (*Cajanus cajan* Linn) - A high protein tropical bush legume. *Hortscience*, **11**, 11-19 (1976).

Namasivayam, C. and R.T. Yamuna: Adsorption of chromium (VI) by a low cost adsorbent: Biogas residual slurry. *Chemosphere,* **30**, 561-578 (1995).

Odozi, O., S. Okeke and R.B. Lartey: Studies on binding metal ions with polymerized corncob and a composite resin with sawdust and onionskin. *Agric. Wastes,* **12**, 13-21 (1985).

Ozer, A., D. Ozer and H.I. Ekiz: Application of Freundlich and Langmuir models to multistage purification process to remove heavy metal ions by using *Schizomeris leibleinii. Proc. Biochem.*, **34**, 919-927 (1999).

Okieimen, F.E. and V.U. Onyenkpa: Removal of heavy metal ions from aqueous solutions with melon (*Citrullus vulgaris*) seed husks. *Biol. Waste,* **29**, 11-16 (1989).

Orhan, Y. and H. Buyukgungor: The removal of heavy metals by using agricultural wastes. *Water Sci. Technol.*, **28**, 247-255 (1993).

Saeed, A., M. Iqba and M.W. Akhtar: Application of biowaste materials for the sorption of heavy metals in contaminated aqueous medium. *Pak. J. Sci. Ind. Res.,* **45**, 206-211 (2002).

Sag, Y. and T. Kutsal: Biosorption of heavy metals by *Zoogloea ramigera*: Use of adsorption isotherms and a comparison of biosorption characteristics. *The Chem. Eng. J.,* **60**, 181-188 (1995).

Sag, Y. and T. Kutsal: Fully competitive biosorption of chromium (VI) and iron (III) Ions from binary metal mixtures by *R. arrhizus:* Use of the Competitive Langmuir model. *Proc. Biochem.*, **31**, 573-585 (1996).

Selatnia, A., A. Boukazoula, N. Kechid, M.Z. Bakhti and A. Chergui: Biosorption of Fe^{3+} from aqueous solution by a bacterial dead *Strptomyces rimosus* biomass. *Proc. Biochem.,* **39**, 1643-1651 (2004).

Singh, Shalini, H.D. Singh and K.C. Sikka: Distribution of nutrients in the anatomical parts of common Indian pulses. *Cer. Chem.*, **45**, 12-19 (1968).

Snell, F.D. and C.T. Snell: Colorimetric Methods of Analysis, 3rd Edn., Van Nostrand, New York (1961).

Tee, T.W. and R.A.M. Khan: Removal of lead, cadmium and zinc by waste tea leaves. *Environ. Technol. Lett.*, **9**, 1123-1232 (1988).

Zarraa, M. A.: A study on the removal of chromium(VI) from waste solutions by adsorption on to sawdust in stirred vessels. *Adsorption Sci. Technol.*, **12**, 129-138 (1995).