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Chromium Removal from Industrial Effluent by *Eucalyptus tereticornis* Bark

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Abstract : Removal of chromium from industrial effluent was investigated using *Eucalyptus tereticornis* bark with various parameters including amount of biomass, pH of solution and contact time. Biomass (2%) was able to remove 88% and 91.5% of chromium at pH 4.0 and pH 5.0, respectively from solution amended with 50 mg of Cr^{6+} l/L. Maximum chromium removal capacities of treated bark biomass were 70% and 94% from tannery effluent and chrome plating effluent, respectively in column mode. The adsorption parameters were determined using both Langmuir and Freundlich isotherms model. Calorific values of native bark biomass, tannery effluent and chrome plating effluent treated biomass were 2227, 3885 and 4003 kcal/kg, respectively with increases in chromium laden biomass. The results revealed that chromium loaded bark biomass can be disposed off by incineration or used in furnace as a fuel.

Key words : Adsorption isotherms, Bark biomass, Calorific values, Chromium, *Eucalyptus tereticornis*, Industrial effluent

Introduction

Chromium and its compounds are widely used in various industries such as metal finishing, electroplating, leather tanning, textile and wood preservation (Aoyama and Tsuda, 2001; Romero-Gonzalez *et al*., 2006). Chromium occurs in different oxidation states such as Cr^{6+} and Cr^{3+} of which Cr^{3+} is required for normal carbohydrate and lipid metabolism whereas Cr^{6+} is more toxic form of chromium (Anderson, 1998; Bahijri and Mufti, 2002; Feng *et al.*, 2003). Conventional physico-chemical remediation of chromium from industrial effluent involves chemical reduction and precipitation, ion exchange, reverse osmosis and carbon adsorption (Yan and Viraraghavan, 2001; Meena and Rajagopal, 2003).

Biosorption is a selective and effective method for the removal of heavy metals from industrial effluent (Ahluwalia and Goyal, 2005). Biomaterials such as saw dust (Ajay and Rajagopal, 2000; Baral *et al.*, 2006), *Tamarindus indica* seeds (Agrawal *et al.*, 2006), rice straw, coconut husks, peat moss, bangal gram (Bishnoi *et al.*, 2004; Ahalya *et al.*, 2005) food industrial waste (Selvaraj *et al.*, 2003); different biowaste material (Joshi *et al.*, 2003) and paper mill sludge (Ahluwalia and Goyal, 2004). Similarly, waste tea leaves (Ahluwalia and Goyal, 2005; Amir *et al.*, 2005), tree leaves (Aoyama *et al.*, 1999) and tree bark (Japanese ceder, larch, *Eucalyptus*) (Aoyama *et al.*, 2004; Aoyama and Tsuda, 2001; Sarin and Pant, 2006) are inexpensive and available in a great quantity. They contain various components such as polyphenolics, plant pigments and protein, which would provide active sites for heavy metal binding. *Eucalyptus* sp. is an economically important multipurpose tree and is grown extensively throughout the world to meet the requirement of the pulp and paper industry. Bark is available as a by product and is of less economic importance and can be used as an inexpensive bioadsorbent material. The present study was carried out to investigate the ability of bark from *E. tereticornis* to remove chromium from aqueous solution and chromium containing industrial effluents.

Materials and Methods

Potassium dichromate was used as source of hexavalent chromium. All other chemicals were of analytical grade.

Collection and characterization of industrial effluent:

Chrome and tannery effluents were collected from Goetze (India) Ltd., Bhadurgarh, Dist. Patiala, Punjab and Messers A.V. Tanneries, Kapurthala, Punjab, India, respectively. Characterization of both effluents was performed as per procedure described elsewhere (Clesceri *et al.*, 1998; APHA, 1995).

Preparation of bioadsorbent:

Eucalyptus tereticornis bark was collected, washed with water, oven dried at 80ºC for two days; ground in a blender and sieved to pass through a 0.2 mm sieve in order to obtain uniform particle size. To avoid, the release

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Table 1: Characterization of tannery and chrome effluent

Parameters	Tannery effluent	Chrome effluent
pH	3.73	2.77
Temperature	22.8 ºC	17.7 ºC
Electrical conductivity	65.5 mS	8.03 mS
Salinity	43.4‰	-
Cr (Total)*	1700	4805
Cr(VI)*	-	4069
Ca*	154.1	-
Cu*	0.1	3.93
Cd*	0.01	-
Co*	0.81	0.08
Fe*	110.11	150.3
K*	57	
Mg*	115.52	14.93
Mn*	0.88	
Na*	42.55	-
Ni*	1.15	0.09
Pb*	15.3	0.88
Zn*	0.79	1.14
Bacterial count CFU ml-1	261.6×10^{3}	128×10^{3}

**- Values represented in mg/L*

of functional groups and hence binding sites at the surface of dead cells due to which the percentage of adsorption increases. In the present study, the pretreated bark biomass reduced the colour of the treated effluent during bioadsorption. The purpose of removing soluble organic compounds, eliminating tanning colouration from the biomass thereby increasing efficiency of metal adsorption have been reported earlier (Gupta and Ali, 2004; Park *et al.,* 2004; Horsfall *et al.,* 2006).

Effect of biosorbent dosage:

The maximum Cr removal efficiency was 95% at the dosage of 2 g/L, 87.1% at 1 g/L and minimum removal was recorded (58.33%) at 0.25 g/L (Fig. 1). It was observed that, removal efficiency of chromium was directly proportional to the dosage of biomass. This is expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites for the ions. The literature survey also revealed that, the higher biomass dose could be attributed to interference between binding sites. Similarly, removal of Cr by low cost sorbents such as coconut fiber and palm pressed fibres were reported earlier (Tan *et al.,* 1993; Fiol *et al.,* 2003). The higher Cr removal efficiency of *Eucalyptus* bark (Sarin and Pant, 2006), *Pinus sylverstris* (Alves *et al.,* 1993) and cedar bark (Aoyama *et al.,* 2004) were reported earlier.

Effect of pH:

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionisation of the adsorbate during reaction. The chromium removal was efficient in acidic pH rather than alkaline condition (Fig.2). The uptake of free ionic Cr depends on pH, 99.6% of Cr ions were adsorbed from a solution of 50 mg/L at pH 5.0, whereas, 86% reduction in Cr removal was determined as the pH shifted

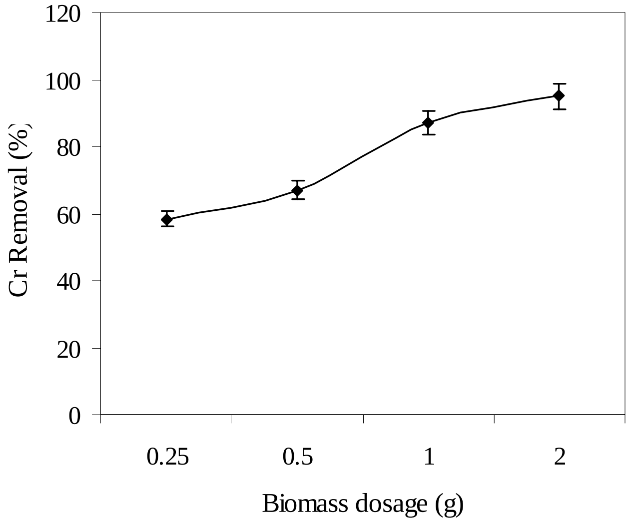

Fig. 1: Effect of bioadsorbent dosage on removal of Cr aqueous solution

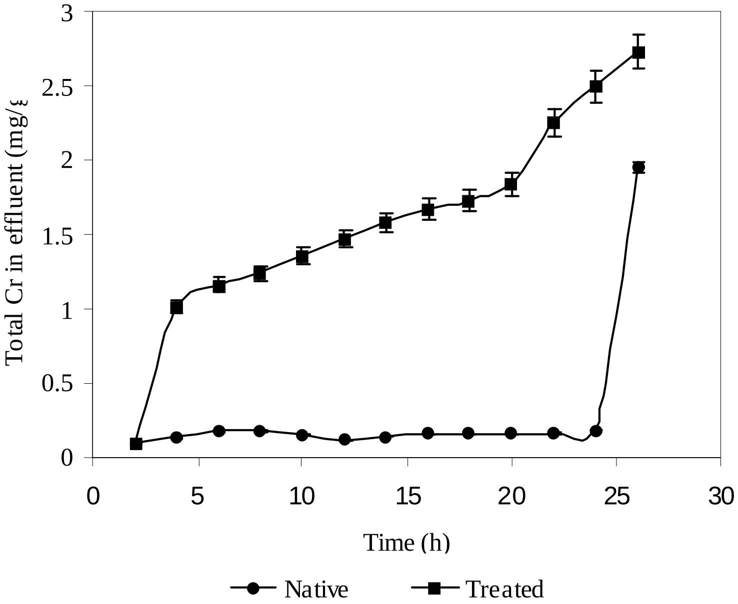

Fig. 4: Removal of Cr from chrome effluent in sorption column packed with native and treated *Eucalyptus* bark

the undesirable leaching of soluble substances from the substrate could be eliminated after the pretreatment, a slight increase in the adsorption capacity was observed. The literature survey clearly indicated that the native biomass has the shows potential for chromium adsorption rather than the treated biomass (Aoyama and Tsuda, 2001).

Adsorption isotherms:

The Freundlich isotherm is a non-linear sorption model. This model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules (Romero-Gonzalez *et al.*, 2006).

(1)

where, q_e is the maximum uptake capacity, C_e is the equilibrium concentration and K_f(mg/g) stands for adsorption capacity and n for adsorption intensity.

The logarithmic form of Eq (1) is

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (2)$$

where K_f and n are Freundlich constant be determined from the linear plot of log(q_e) versus log(C_e). The correlation coefficient values obtained from the Langmuir and Freundlich isotherms are presented in Table 2. The Langmuir model represents one of the first theoretical treatments of nonlinear sorption and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The Langmuir isotherm is represented in the following equation:

$$q_e = K_f C_e^{\frac{1}{n}}$$

$$q_e = \frac{(Q_L b C_e)}{(1 + bC_e)} \qquad (3)$$

where Q_L (mg/g) and b are Langmuir constants related to adsorption capacity and the energy of adsorption, respectively. Eq. (3) is usually linearized to obtain the following form:

Table 2: Model parameters for the adsorption of chromium on *Eucalyptus* bark at different pH and adsorbent dose 28 °C

Model	**Freundlich**			**Langmuir**		
Parameters	K_f (mg/g)	n	R^2	Q_L	b	R^2
Adsobent size	1.17	1.37	0.93	0.08	1.48	0.93
pH	6.72	4.79	0.95	1.72	0.17	0.94

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