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Use of low-cost biological wastes and vermiculite for removal of chromium from tannery effluent

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Abstract

Biological wastes (sawdust, rice husk, coirpith and charcoal) and a naturally occurring mineral (vermiculite) have been tested for their effectiveness in removing Cr from tannery effluent through batch and column experiments. The adsorption capacities of the substrates were also evaluated using isotherm tests and computing distribution co-efficient. The sawdust exhibited a higher adsorption capacity ($k = 1482$ mg kg^{-1}), followed by coirpith ($k = 159$ mg kg^{-1}). The biosorbent and mineral vermiculite in columns were found very effective in removing Cr from tannery effluent. About 94% removal of Cr was achieved by a column of coirpith, and equally (93%) by a column containing a mixture of coirpith and vermiculite. This study showed that biological wastes are potential adsorbents of Cr, which could be successfully used to reduce the Cr concentrations in tannery effluent.
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Keywords: Chromium; Low-cost biological wastes; Biosorbents; Vermiculite; Freundlich adsorption isotherm; Distribution co-efficient; Tannery effluent

1. Introduction

Chromium (Cr), a heavy metal, is extensively used in tanning industries to obtain leather of desirable quality. Therefore, the resulting wastewater (effluent) is rich in Cr. Chromium generally exists in different forms, mostly as trivalent (Cr(III)) and hexavalent (Cr(VI)) forms. The trivalent Cr is non-toxic and relatively immobile in nature, whereas the hexavalent Cr is readily soluble in water, highly toxic and mobile and is known to be toxic with potential carcinogenic effects. Cr containing effluents find their way in the environment at disposal sites where Cr undergoes oxidation reactions and forms Cr(VI) (Bartlett and James, 1979). It has always been claimed that the oxidation of Cr(III) to Cr(VI) is a rare phenomena in soil. However, the presence of MnO_2 and microbial strains in soil may oxidize Cr(III) to Cr(VI). As Cr(VI) is readily soluble in water, it leaches down in the soil profile and could contaminate groundwater.

Mostly removal of Cr is achieved by various physico-chemical processes such as oxidation/reduction, precipitation/filtration, coagulation, ion-exchange and membrane separation. But high costs and process complexity have limited their use in industries. In recent years, use of low-cost adsorbents have been considered to reduce the Cr concentration from tannery effluent. Several such adsorbents have been examined by many scientists. Zhipei et al. (1984) reported the use of Chinese peat for the adsorption of Cr(VI) from solution. The use of sawdust (Srivastava et al., 1986), waste tea, exhausted coffee, nut and walnut shells (Orhan and Buyukgungor, 1993) and coconut husk and palm pressed fibres (Tan et al., 1993) in removing Cr from aqueous solutions has also been reported. The objective of the study was to evaluate certain adsorbents such as sawdust, rice husk, coirpith and charcoal and a mineral sorbent—vermiculite for their effectiveness in removing Cr from tannery effluent.

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Table 1
Some important characteristics of adsorbents

Adsorbents	pH	EC ($dS\,m^{-1}$)	Moisture content (%)	Exchangeable acidity (cmol (+) kg^{-1})	Total chromium ($mg\,kg^{-1}$)
Sawdust	5.97	0.62	4.06	131.1	BDL
Rice husks	6.68	0.86	4.82	30.0	BDL
Coirpith	7.33	0.57	2.88	110.0	3.375
Charcoal	10.04	3.80	4.28	10.0	BDL
Vermiculite	8.92	0.09	0.01	5.0	34.4

BDL—below detectable limit.

2. Materials

2.1. Adsorbents

The sawdust of teak (*Teclona grandis* Linn. f) was collected from St. Johns Saw Mill, Coimbatore. The rice husk was collected from a modern rice mill and the coirpith, a by-product from coconut coir industry, near Coimbatore. The charcoal was obtained manually by burning the prosopis tree wood (*Prosopis julifera* Linn.). The vermiculite, a 2:1 type aluminosilicate clay mineral obtained from Tamil Nadu Minerals Ltd., Dharmapuri was used as a mineral sorbent. All these materials were oven dried at 80 °C for 24 h, powdered and sieved through a 2 mm sieve to achieve uniform particle size. The sieved materials were stored in sealed polyethylene bags until further use. Characteristics of the materials are presented in Table 1.

Chrome tan effluent was collected from a private leather tanning industry in Vaduganthangal in Vellore district of Tamil Nadu, India, where cluster of tanneries exist. Characteristics of the chrome tan liquor are presented in Table 2.

All the chemicals used in the study were of analytical grade. A stock solution of Cr(VI) at a concentration of 1000 $mg\,l^{-1}$ was prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) in double distilled water. Further working solutions were made by appropriate dilution.

Table 2
Some important characteristics of chrome tan liquor

Characteristics	Values
l. pH	4.43
2. EC ($dS\,m^{-1}$)	7.55
3. Total dissolved solids ($mg\,l^{-1}$)	4832
4. Total chromium ($mg\,l^{-1}$)	184.9
5. Sodium ($mg\,l^{-1}$)	2900
6. Sulphate ($mg\,l^{-1}$)	1680
7. Chloride ($mg\,l^{-1}$)	2410

3. Methods

3.1. Batch experiment

Batch experiments were carried out in screw capped polypropylene shake bottles (50 ml capacity) at ambient temperature. Chromium adsorption as a function of equilibrium time, initial concentration and pH were studied. Two grams of each adsorbent were shaken with 50 ml of Cr(VI) solution (60 $mg\,l^{-1}$) for different time intervals viz., 0, 1, 6, 12, 24, 36 and 48 h. At the end of the shaking period the samples were centrifuged at 8000 rpm for 10 min and filtered through Whatman no. 1 filter paper. The concentrations of Cr in the extract were determined using a spectrophotometer at 540 nm.

In another set each 50 ml of Cr(VI) solutions at varying concentrations viz., 0, 20, 40, 60, 80 and 100 $mg\,l^{-1}$ were introduced into bottles containing 2 g of each adsorbent. The extract was analysed for Cr(VI) concentration after 24 h shaking.

The effect of pH (3–9) on Cr adsorption was examined. Adsorbent (2 g) was equilibrated with 50 ml of 60 mg $Cr\,l^{-1}$ by shaking for 1 h. The initial pH was adjusted to different pHs viz., 3, 4, 5, 6, 7, 8 and 9 using either 0.2 M NaOH or HCL. After shaking, the extracted solution was centrifuged at 8000 rpm for 10 min, filtered through Whatman no. 1 filter paper and analysed for pH and Cr(VI) ions.

3.2. Column experiment

The column experiment was carried out using locally fabricated glass columns of 50 cm height and 5 cm internal diameter. The wiremesh (0.1 mm) and filter paper (Whatman no. 1) were placed at the bottom of each column as shown in Fig. 1. The head space of the column was closed using a rubber cork with a glass tube insert for an air outlet. The bottom of the column had a closed end. The outlet was connected to a conical flask for the collection of treated effluents.

In the first set, two columns for each adsorbent were gently packed to a height of 30 cm with saw dust, rice husks, coirpith and vermiculite. Due to variations in the

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