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Removal of chromium from industrial waste by using eucalyptus bark

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Abstract

Several low cost biomaterials such as baggase, charred rice husk, activated charcoal and eucalyptus bark (EB) were tested for removal of chromium. All the experiments were carried out in batch process with laboratory prepared samples and wastewater obtained from metal finishing section of auto ancillary unit. The adsorbent, which had highest chromium(VI) removal was EB. Influences of chromium concentration, pH, contact time on removal of chromium from effluent was investigated. The adsorption data were fitted well by Freundlich isotherm. The kinetic data were analyzed by using a first order Lagergren kinetic. The Gibbs free energy was obtained for each system and was found to be $-1.879\ \text{kJ}\,\text{mol}^{-1}$ for Cr(VI) and $-3.885\ \text{kJ}\,\text{mol}^{-1}$ for Cr(III) for removal from industrial effluent. The negative value of ΔG^0 indicates the feasibility and spontaneous nature of adsorption. The maximum removal of Cr(VI) was observed at pH 2. Adsorption capacity was found to be 45 mg/g of adsorbent, at Cr(VI) concentration in the effluent being 250 mg/l. A waste water sample containing Cr(VI), Cr(III), Mg, and Ca obtained from industrial unit showed satisfactory removal of chromium. The results indicate that eucalyptus bark can be used for the removal of chromium.

Keywords: Adsorption; Eucalyptus bark (EB); Hexavalent chromium; Lagregren kinetic; Freundlich isotherm

1. Introduction

Water pollution by chromium is of considerable concern, as this metal has found widespread use in electroplating, leather tanning, metal finishing, nuclear power plant, textile industries, and chromate preparation. Chromium exists in two oxidation states as Cr(III) and Cr(VI). The hexavalent form is 500 times more toxic than the trivalent (Kowalski, 1994). It is toxic to microorganism plants, animals and humans. Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage (US Department of Health and Human Services, 1991; Cieslak-Golonka, 1995). The tanning process is one of the largest polluters of chromium all over the world. Most of the tanneries in India adopt the chromium tanning process because of its processing speed, low costs, and light color of leather and greater stability of the resulting leather. In the chromium tanning process, the leather takes up only 60–80% of applied chromium, and the rest is usually discharged into the sewage system causing serious environmental impact. Chromium ion in liquid tanning wastes occurs mainly in trivalent form, which gets further oxidized to hexavalent Cr(VI) form, due to the presence of organics.

The maximum levels permitted in wastewater are 5 mg/L for trivalent chromium and 0.05 mg/L for hexavalent chromium (Acar and Malkoc, 2004). With this limit, it is essential for industries to treat their effluents to reduce the Cr to acceptable levels. Due to more stringent environmental regulations, most of the mineral processing plants, metal-finishing industries are facing nowadays the difficult problem of disposal of wastewater produced in huge quantities, laden with Cr.

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Chromium metal ions are usually removed by precipitation (Patterson, 1977), although ion exchange (Tiravanti et al., 1997) and adsorption (Dahbi et al., 1999; Orhan and Buyukgangor, 1993) are also used for its removal. The hydroxides of heavy metals are usually insoluble, so lime is commonly used for precipitating them. The most important factor in precipitation of heavy metal is the valence state of metal in water. Cr whose hexavalent form, chromate (CrO_4^{2-}), is considerably more soluble than trivalent form, Cr(III). In this case, the chromate, in which Cr is present as Cr(VI) must be reduced usually with SO_2 available from sodium metabisulphite at low pH for removal of chromium as Cr(III) by precipitation process. Another aspect of precipitation process is the zeta potential of the initial heavy metal colloidal precipitate. In many plants where heavy metals are being removed, one of the principal problems in reaching the desired effluent limits is the colloidal state of precipitated materials—they have not been properly neutralized, coagulated and flocculated. A final aspect of heavy metals is the possible formation of complex ions, which is common when dealing with wastewaters containing ammonia, fluoride, or cyanide ions along with heavy metals. Because of these important aspects in the precipitation of heavy metals, there is no way to predict the best solution of a specific problem without undergoing a series of bench tests to evaluate the alternative available (Kemmer, 1988).

The present study is aimed at selection of a low cost biosorbent, which can adsorb chromium from the wastewater. Detailed batch studies with the selected adsorbent, eucalyptus bark has been carried out in the present investigation. The effect of pH, contact time, adsorbent concentration, thermodynamics study, and metal ion/adsorbent ratio were also investigated.

2. Methods

2.1. Materials

All the chemicals used were of analytical grade. $K_2Cr_2O_7$, HCHO, NaOH, diphenyl carbizide, $KMnO_4$, HNO_3 and H_2SO_4 were procured from Merck. The adsorbents selected for the preliminary study were baggase, charred rice husk, activated charcoal, and eucalyptus bark (EB). These were grounded and washed with deionized water. The adsorbents were dried at room temperature, (32 ± 1 °C) till a constant weight of the adsorbent was achieved. A uniform particle size of the adsorbent was maintained between 120 and 500 μm.

2.2. Preparation of eucalyptus bark adsorbent

Eucalyptus bark of *Eucalyptus globulus* tree species was collected from the local area. The bark was grounded to small particles of size $120 < d_p < 500$ μm. It was washed with deionized water and then dried. To avoid, the release of color by bark in to the aqueous solution during adsorption, it was treated with formaldehyde (Randall et al., 1976). For this 5 mL of aqueous formaldehyde was added to 100 mL of 0.1 M H_2SO_4 and then 10 g of grounded and washed bark was added to this solution. The final mixture was stirred and heated at 50 °C for 24–48 h till the mixture became thick slurry. The slurry (treated bark) was washed with deionized water until the pH of the filtrate was more than 4.5.

Finally the bark was air-dried and sieved. Particles in the range of 120–500 μm size were collected as the final adsorbent. Surface area of the sorbent was determined, using BET apparatus, using liquid nitrogen as adsorbent.

Further, ultimate and proximate analysis of the EB adsorbent was also carried out. The detailed characteristics of EB obtained are shown in Table 1.

2.3. Determination of chromium content

The chromium concentration in raw and treated effluent was determined by UV (Varian, Australia) spectrophotometer. The wavelength of operation was kept at 540 nm. For this purpose, $K_2Cr_2O_7$ solutions of different concentrations were prepared and their absorbance recorded by using a UV-spectrophotometer. A calibration plots for Cr(VI) were drawn between '%' absorbance and standard Cr(VI) solutions of various strengths (APHA, 1992). Runs were made in triplicate. Cr(III) concentration was determined by measuring the difference between total chromium concentration and Cr(VI) concentration. Total Cr concentration was determined by oxidizing Cr(III) to Cr(VI) using $KMnO_4$ and then determining final Cr(VI) content in the sample (APHA, 1992).

2.4. Experimental

Stock solution of 1000 ppm of Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ (AR grade), in deionised, double-distilled water. All the batch adsorption studies

Table 1
Characteristics of eucalyptus bark (EB) adsorbent

Characteristics	Values
Surface area (m^2/g)	0.59 ± 0.05
Bulk density (g/cm^3)	0.25 ± 0.02
Moisture content (%)	10.1 ± 0.3
Ash content (%)	19.0 ± 0.5
Volatile matter (%)	65.7 ± 2.0
Fixed carbon (%)	15.3 ± 0.5
Carbon (%)	43.68 ± 1.3
Hydrogen (%)	8.14 ± 0.25
Nitrogen (%)	0.43 ± 0.01
Oxygen (%)	47.75 ± 1.4