

A comparative study of chromium(VI) removal using sawdust and eucalyptus bark

Abhinav Sharma, Aditya Tulsyan and Srinivas Motamarri

ABSTRACT

A comparative study on low cost biological adsorbents such as eucalyptus bark and sawdust has analyzed them for their effectiveness in the removal of hexavalent chromium. Batch experiments were carried out on synthetic solutions mimicking bore water collected from an industrial area contaminated with tannery effluent. The analysis on hexavalent chromium removal was carried out by varying experimental parameters such as pH, dosage and contact time. The study reveals that sawdust works best at pH 3 while eucalyptus shows better results at pH 2. Moreover, the optimum dosages determined for the adsorbents were in compliance with the Langmuir and Freundlich isotherms. The study highlights the benefits of eucalyptus bark in purification of Cr(VI) contaminated water supply.

Key words | biological adsorbent, chromium, eucalyptus bark, sawdust

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INTRODUCTION

In the tanning industries across India, chromium (Cr) is a widely used metal for obtaining leather of desired quality. The tannery effluent pollutes nearby water sources specially the ground water to a large extent thereby resulting in high chromium contamination. Chromium once released in the environment is found to exist in two stable oxidation states namely trivalent and hexavalent (Sarin & Pant 2006). Trivalent form is innocuous and non-toxic whereas its counterpart has been reported to be toxic, carcinogenic, mutagenic and highly soluble in aqueous solutions (Mahimairaja *et al.* 2005). Intake of Cr(VI) causes rupturing of nasal septum, non healing skin ulcers and in extreme cases it causes lung cancer (US Department of Health and Human Services 1991).

The tolerance limit for Cr(VI) discharge into inland surface water is 0.1 mg-L^{-1} whereas for potable water it is 0.05 mg-L^{-1} (EPA 1990). In order to comply with the permissible limits it is necessary to treat chromium(VI) contaminated water to reduce its carcinogenic effect. Methods realized so far include oxidation/reduction, filtration, ion exchange membrane, chemical precipitation

etc. These methods are undesirable in terms of high costs incurred and process complexities. Since the earliest times both biological and chemical adsorbents have been in use. While chemical adsorbents are quite efficient in removing Cr(VI) they are not free from drawbacks such as high material costs and inclusion of foreign chemical substances.

Use of biological adsorbents for treatment of contaminated water has been widely reported in literature. Some of this work includes leaf mould (Sharma & Foster 1994a), coconut tree sawdust carbon (Selvi *et al.* 2001), hazelnut shell carbon (Koby 2004), cow dung carbon (Das *et al.* 2000), phosphate treated sawdust (Ajmal *et al.* 1996), sawdust (Srivastava *et al.* 1989), waste tea, exhausted coffee and walnut shells (Orhan & Büyükgüngör 1993) almond shell carbon (Candela *et al.* 1995). Due to wide availability of eucalyptus and silver oak trees in the Vellore district, India these two biological adsorbents were selected to study their adsorptive capacity and compare the same.

In this work, the experimental procedures for preparation of the adsorbents and the Cr(VI) solution are

discussed first followed by the adsorption experiment. The effect of contact time, pH and adsorbent dosage are then discussed in the next section.

EXPERIMENTAL PROCEDURES

Materials

All the reagents used were of analytical grade and were obtained from Merck®. Silver oak sawdust and eucalyptus bark were collected from the nearby area in Vellore, India. Predetermined concentration of synthetic solution of Cr(VI) was prepared by dissolving potassium dichromate in double distilled deionized water. The pH adjustments were done using sulfuric acid and sodium hydroxide and other materials required for measurement purposes were 1,5-diphenylcarbohydrazide and acetone solution.

Preparation of sawdust adsorbent

Saw dust from silver oak tree was obtained from a local mill and was ground thoroughly. To avoid the release of color it was treated with 1% formaldehyde (Randall *et al.* 1976) in the ratio of 1:5 (sawdust: formaldehyde, W/V) (Orhan & Büyükgüngör 1993) and then placed in a hot air oven at 65°C for 4.5 hrs. The cake obtained was washed with double distilled deionized water and again put in the oven at 75°C for 24 hrs. Activation was done by soaking it in concentrated sulfuric acid and then by keeping it in hot air oven at 150°C for 24 hrs. To neutralize the excess sulfuric acid it was washed with distilled water and then soaked overnight in 1% sodium bicarbonate solution. It was then washed with distilled water and kept in a hot air oven at 90°C for 24 hrs. The fine black powdery substance thus obtained was thoroughly ground and sieved through 175 µm mesh to get particles of uniform size.

Preparation of eucalyptus bark adsorbent

Eucalyptus bark was collected from trees growing in and around Vellore, India. The bark was dried in open air for 4 days and then ground to a powdery form. The powder was treated with formaldehyde and sulfuric acid solution in the ratio of 3:1 to prevent the discharge of color

(Sarin & Pant 2006). Activation of the adsorbent was achieved by placing it in a hot air oven at 70°C for over 24–30 hrs. It was then sieved through a 150 µm–175 µm mesh to get particles of uniform size.

Adequate quantities of both the adsorbents were prepared to avoid the possibility of experimental differences associated with the repeatability of the preparation procedure. Although formal characterization of the adsorbents were not performed in this work, adequate care was taken to ensure preservation of physical properties of prepared adsorbents.

Preparation of Cr(VI) solution

Bore water contaminated with Cr(IV) was collected from hand pump located close to a tannery in Vellore, India. The slightly yellow colored samples were stored in airtight bottles to prevent the intrusion of foreign impurities. Preliminary lab analysis showed Cr(VI) content close to 198 ppm in the samples collected. To prevent the interference of parallel ions in the samples, a synthetic stock solution of 200 ppm was prepared by dissolving accurately weighed quantity of K₂Cr₂O₇ (AR grade) in double distilled deionized water.

Chromium analysis technique

The standard colorimetric method (APHA 1985) using diphenylcarbazide was adopted for determining the concentration of Cr(VI) in sampled solutions. Samples were not acid digested and hence only the Cr(VI) concentration and not the total chromium concentration were determined through this method. As the colorimetric method is useful for the determination of Cr(VI) in the range from 100 to 1,000 µg/L (APHA 1985), test samples and the standards prepared were appropriately diluted to comply within the measurement limits of the method. A UV-Visible Spectrophotometer (Hitachi U-2800) was used at 540 ± 0.3 nm to obtain accurate measurements of Cr(VI) concentration in the sample solutions using deionized water as reference. Calibration curve was drawn between percentage absorbance and Cr(VI) concentrations in the prepared standard solutions.

Adsorption experiment

To study the performance of the two adsorbents, 100 ml of prepared stock solution (200 ppm) was subjected to different experimental conditions such as pH, contact time and adsorbent dosage. The batch solutions were placed in a temperature controlled shaker set at 180 rpm and $30 \pm 2^\circ\text{C}$. The experiments were designed to first determine the optimal adsorbent dosage at the pH and contact time described in literature. After fixing the dosage, the pH was optimized followed by determination of batch time required for maximum chromium removal. After subjecting the batches to the prescribed conditions for each of the adsorbents, the solutions were filtered and three samples were drawn to reduce uncertainty in the measured values. The percentage absorbances for the treated samples determined from the spectrophotometer were plotted in the calibration curve to obtain the final Cr(VI) concentration. To account for slight losses of Cr that may have occurred during analytical operation both the test samples and the standard solutions were subjected to the same procedure.

RESULTS AND DISCUSSION

Effect of adsorbent dosage on Cr(VI) removal

The effects of varying dosages were studied for both the adsorbents (Figure 1). For eucalyptus bark the studied dosages were 0.15, 0.20, 0.25, 0.30, 0.35 grams/100 ml of

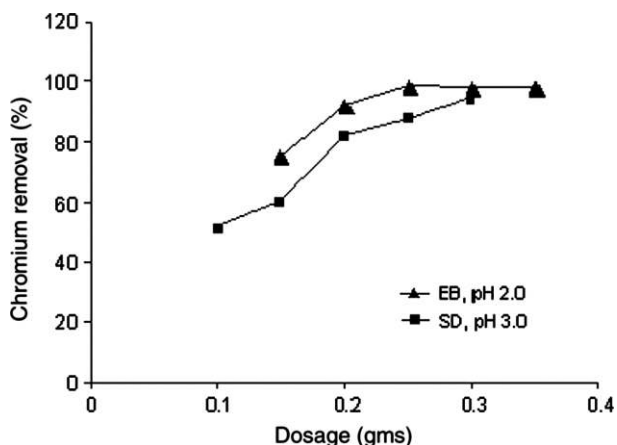


Figure 1 | Effect of adsorbent dosage on the rate of chromium removal. For EB optimum dosage was 0.25 g/100 ml and for SD it was 0.30 g/100 ml of stock solution.

Cr(VI) stock solution. The pH of the solution was set at 2 (Sarin & Pant 2006) and the contact time was 4 hrs. With increase in dosage from 0.15 to 0.25 grams the rate of Cr(VI) adsorption increased from 75.3% to 98.2% presumably due to an increase in surface area and active sites. On further increasing the dosage from 0.25 to 0.35 grams the efficiency dropped to 95.5% probably due to clustering and blockage of the active sites.

For sawdust contact time was set to 4 hrs and pH set to 3.0 (Garg et al. 1994). The dosage was varied from 0.1 to 0.3 g/100 ml of Cr(VI) solution in the interval of 0.05 grams. It was found that with the increase in the dosage the efficiency increased from 52.32% to 94.57%, beyond which the efficiency drops probably due to the non availability of active sites. Calculated optimum dosage for both the adsorbents were found to resonate well with the Freundlich equation given by

$$\log X/m = \log k + 1/n \log C$$

In this work the term adsorption was only referred to the Cr(VI) removal from the solution and does not distinguish between physical and chemical adsorption.

Effect of pH on Cr(VI) removal

Study of the effect of pH on chromium sorption was done for both the adsorbents (Figure 2). The pH was varied from

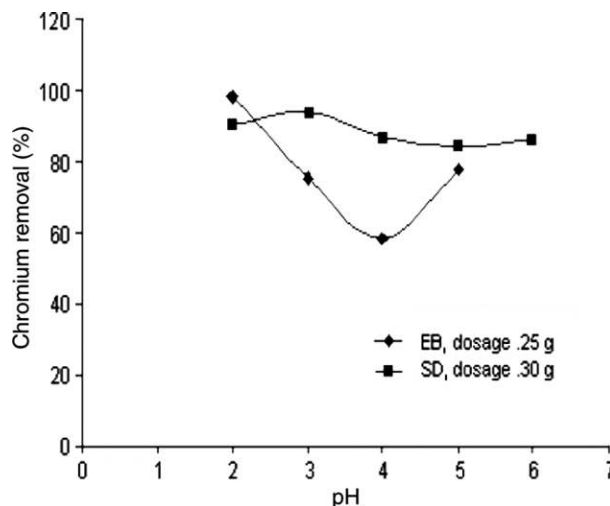
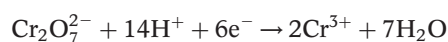


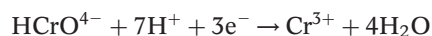
Figure 2 | Effect of pH on Cr(VI) removal from stock solution. Adsorbent dosage for EB was 0.25 g/100 ml and for SD it was 0.30 g/100 ml. Contact time was set to 4 hrs.

2.0 to 5.0 and the contact time was fixed to 4 hours. For both the adsorbents the dosage was set to the optimal value as determined above. Eucalyptus bark showed Cr(VI) removal of 98.7% at pH 2.0 whereas sawdust adsorbed 94.5% of chromium at pH 3.0. In all the cases studied the adsorbents were found to be more efficient at lower pH values. This may be because of the reduction of hexavalent chromium to trivalent form (Sharma & Foster 1994b).

At very low pH the following reaction takes place



whereas at moderate pH the reaction takes the form



Due to high availability of H^+ ions at lower pH on the surface of adsorbent the reduction of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) is easier. At a pH greater than 6.0 the adsorption becomes insignificant due to hindrance between CrO_4^{2-} and OH^- in which adsorption of OH^- predominates. As the formation of Cr(III) is favorable at lower pH value, it is highly probable that sorption occurs after the reduction of Cr(VI) to Cr(III). Eucalyptus bark showed maximum chromium removal at a pH 2.0 and sawdust at pH 3.0. These optimum pH values were used for further studies.

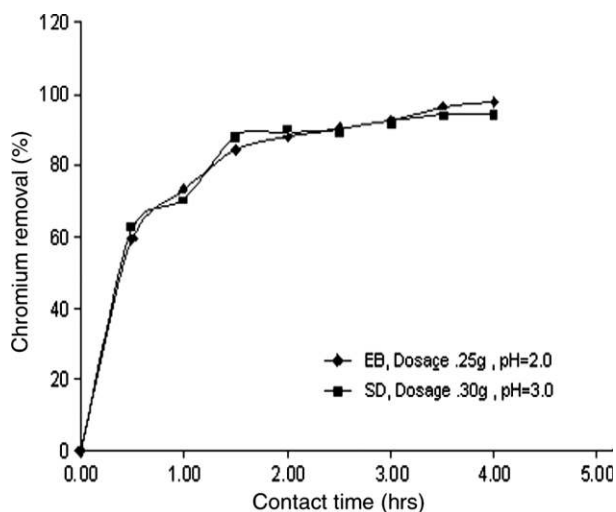


Figure 3 | Effect of contact time on chromium removal using both EB and SD. Graph shows maximum removal within first 2 hrs and after 4 hrs the equilibrium was established.

Effect of contact time on chromium(VI) removal

Influence of contact time on chromium adsorption was studied (Figure 3) by maintaining optimum dosage and pH found above. The readings were taken after every 30 minutes till the equilibrium was established. To confirm the equilibrium state a sample was withdrawn after 12 hours and checked against any further change in chromium concentration.

Eucalyptus bark showed a high rate of chromium removal in the first 2 hrs, whereas for sawdust it was within first 2.5 hrs. After the equilibrium was established eucalyptus bark showed a Cr(VI) removal of 98.6% whereas sawdust showed 94.24% removal.

CONCLUSION

Hexavalent chromium has been a serious environmental problem; contamination in the ground water supply from nearby tanneries has irrevocable effects on the health of the local population. A detailed comparative study was carried out to find out a suitable biological adsorbent in terms of its adsorptive capacity. Based on the investigation, it can be concluded that eucalyptus bark exhibited a superior absorptive capacity as compared to sawdust. Eucalyptus bark removed 98% of Cr(VI) from a 200 ppm stock solution as compared to 94% removal by sawdust. The adsorbent dosage for eucalyptus bark was 0.05 gm less than required for sawdust for a 100 ml stock solution. However the removal doesn't fall within the international standards laid down by the World Health Organization. Further treatment, for example repetitive batch processing, would be essential to make it suitable for its safe use.

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