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Biosorption of Cr (III) from aqueous solutions using indigenous biomaterials

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ABSTRACT: In the present study, an indigenous medicinal plant, *Tridax procumbens* (Asteraceae) was used as bioadsorbent for the removal of Cr (III) ions from synthetic wastewater and the method was also applied for real sample analysis. The biosorption of Cr (III) was a two-stage batch reactor process. In the first stage, raw biomaterial was used to the conversion of Cr (VI) into Cr (III). The amount of the biomaterial was 2.5g. The percent conversion was 100. The second stage involved the biosorption of Cr (III) onto the activated carbon of the biomaterial. The result indicated that, the biosorption of Cr (III) was 98.5 % at the optimum pH of 3.2. The experiments were carried out at the temperature of 25 ± 2^{0}C. The optimum contact time was 150 min and the adsorbent dose was 2.5g of activated carbon. The effect of concentration was also studied for the design of the treatment systems and this methodology is highly suitable for the treatment of chromium containing wastewater.

Key words: Wastewater, Biosorption, Biomaterials, Chromium (III), Medicinal plants, Tridax procumbens

INTRODUCTION

In the past years, industrial activities have grown rapidly. The increasing contamination of urban and industrial wastewaters with toxic metal ions is a serious environmental problem (Santhy and Selvapathy, 2004). Metals have a high degree of toxicity, which can be deleterious for both the human beings and the environment. Inorganic micro pollutants are of considerable concern because they are non-biodegradable, highly toxic and have a carcinogenic effect (Cimino, *et al.*, 2000).

Chromium is a toxic metal of widespread use in many industries such as plating facilities, mining operations and tanneries (Fiol et al., 2003). Cr (III) and Cr (VI) are the species usually encounter in the environment. The hexavalent form is of particular concern because of its greater toxicity. In general, Cr (VI) exists in the aqueous solution as oxyanions such as $Cr_2O_7^{2-}$, $HCr_2O_7^-$, $HCrO_4^-$ and CrO_4^{2-} (Lee, *et al.*, 2005). The tolerance limit for Cr (VI) to discharge into inland surface waters 0.1ppm and in potable water is 0.05 ppm (EPA, 1990). Hence, the removal of Cr (VI) from industrial effluents is important. A conventional method for removing metals from industrial effluents includes chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion – exchange and adsorption. Most of these methods suffer with high capital and regeneration costs of the materials (Huang and Wu, 1975).Therefore, there is currently a need for new, innovative and cost effective methods for the removal of toxic substances from wastewaters. Biosorption is an effective and versatile method and can be easily adopted in low cost to remove heavy metals from large amount of industrial wastewaters.Recent studies have showed that heavy metals can be removed using plant materials such an palm pressed fibers and coconut husk (Tan, *et al.*, 1993),

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water fern *Azolla filiculoidis* (Zhao and Duncan, 1997), peat moss (Gosset et al., 1986), duck weed *Wolffia globosa* (Upatham, *et al.*, 2002), lignocellulosic substrate extracted from wheat bran (Dupont, *et al.*, 2003), *Rhizopus migricans* (Bai and Abraham, 2001), cork and yohimbe bark wastes (Villaescusa, *et al.*, 2000 and Lee, *et al.*, 2005) and leaves of indigenous biomaterials, *Tridax procumbens* (Singanan, *et al.*, 2006). Apart from the plant based material chemical modification of various adsorbents, phenol-formaldehyde cationic matrices (Swamiappan and Krishnamoorthy,1984), polyethylonamide modified wood (Freeland, *et al.*, 1974), sulphur containing modified silica gels (Verwilghen, *et al.*, 2004) and commercial activated charcoals also employed (Qadeer and Khalid, 2005).

In this aspect, biosorption is a versatile and simple method. Biosorption is a simple process used for the removal of contaminants from industrial effluents. This process is particularly suitable for the treatment of wastewater streams containing heavy metals. The most convenient means of determining metal uptake abilities is through a batch reaction process.In the present research work, *Tridax procumbens (Asteraceae)* a novel medicinal plant material was used as low-cost sorbent for the conversion of Cr (VI) into Cr (III) and subsequent removal of Cr (III).

MATERIALS & METHODS

Chromium solutions (1000 ppm) were prepared by dissolving appropriate amounts of sodium dichromate ($Na_2Cr_2O_7$) in double distilled water. NaOH and HCl solutions were used for pH adjustment of the metal solution. These reagents were analytical grade and were purchased from BDH, Mumbai, India LTD. The stock solutions were diluted appropriately to obtain the working solutions of different concentration ranges 25, 50 and 100 ppm respectively. The leaves of *Tridax procumbens (Asteraceae)* were collected from the agricultural fields of southern Tamilnadu, India during the months of November – December in 2006. The fresh leaves were rinsed three times with double distilled water, dried in an air oven at 110^0C for 72 h. The dried leaves were powdered and stored in airtight polythene containers for further use. This powdered material was used as raw bioadsorbent for Cr (VI) conversion into Cr (III).

The Raw bioadsorbent powder was used for the experiments. Activated carbon of the biomaterial was prepared by treating with the concentrated sulphuric acid (Sp.gr.1.84) in a weight ratio of 1:1.8 (biomaterial: acid). The resulting black product was kept in an air – free oven maintained at $160^0 \pm 5^0$C for 6 hours followed by washing with distilled water until free of excess acid and dried at $105^0 \pm 5^0$C.The activated carbon obtained from biomaterial was ground and the portion retained between 90 and 125 µm sieves was used for metal adsorption experiments (Stephen Inbaraj and Sulochana, 2003).

About 100 mL of 100 ppm Cr (VI) solution was shaken at 250 rpm with the bioadsorbent dose of 3.0g at room temperature for a period of 240 min. The initial pH of the solution was maintained as 3.2. The color reduction was followed every 20min interval with the help of UV-Visible spectrophotometer. The formation of Cr (III) indicates the increasing density of green color. The absorption intensity of green color was measured at 440 nm. After the equilibrium time, the whole solution was filtered through Whatman 541 filter paper. The concentration of Cr (III) was found to be 100 ppm.

Biosorption studies were performed by the batch technique. Biosorption of Cr (III) on activated carbon of the plant material was carried out room temperature (25 ± 2^0C) by shaking 250 mg of adsorbent with 50 mL of 100 ppm experimental solution, until the equilibrium reached. The initial pH of the solution was adjusted to 3.2 by adding 0.1 mol/L of HCl (or) 0.01 mol/ Lof NaOH. The concentration of Cr (III) in bulk solution was determined every 20 min by taking 5 mL of the solution. The effect of pH was observed by studying the adsorption of Cr (III) over a broad pH range of 2.0 – 8.0. The sorption studies was also carried out at different temperature, i.e., 25, 35, 45, 55 and 65 ^{0}C to determine the effect of temperature and to evaluate the sorption thermodynamic parameters. Adsorption of Cr (III) was also studied at different doses of adsorbent. The amount of Cr (III) was estimated by using phenyl carbazide method using UV-visible spectroscopy. The absorption of the species was measured at 540 nm.The percent removal of selected heavy metals on the adsorbents calculated from % removal = $\{(C_o - C_f) / C_o\} \times 100$

Where C_o is the initial concentration of metal ions and C_f is the final concentration metal ions in ppm.

RESULTS & DISCUSSIONS

In the present study, finely powdered raw bioadsorbent was used for testing the efficiency of conversion of Cr (VI) into Cr (III) ions from the experimental solution. The amount of adsorbent dose was 3.0 g. The pH of the experimental solution was maintained at 3.2 and the experiment was carried out at room temperature. The results of the study indicate that 100 percent conversion of Cr (VI) into Cr (III) was possible (Fig. 1).

After optimization of the bioadsorbent dose as 2.5 g per 50 mL test solution and the pH at 3.2, the effect of contact time for the efficient removal of Cr (III) ions was studied. When the time of agitation increases, the percent removal also increases. In these studies, 98.5 percent removal was achieved at 150 min. Further, no significant changes were observed in the removal of Cr (III) ions from the solution after 24 hours of equilibration (Fig. 2).

It is important to fix the amount of the activated carbon of the bioadsorbent to design the optimum treatment systems and for a quick response of the analysis. To achieve this aim, five batch experiments were conducted with the adsorbent dose as 0.5 – 3.0 g per 50 mL of test solution. When the addition of the adsorbent dose increased, the percent removal of Cr (III) also increased. It attains a maximum (98.5%) at 2.5 g of the activated carbon of the bioadsorbent. From the results, it is clearly observed that, 4.0 g of the bioadsorbent was sufficient for the effective removal of Cr (III) in aqueous solutions. A further increase in the quantity of adsorbent up to 3.0 g led to a complete removal of lead ions from the solution (100% adsorption) and hence the quantity of Cr (III) ions adsorbed remained constant (Fig. 3).

The effect of pH on the adsorption of Cr (III)) ions on activated carbon of bioadsorbent were studied using the initial concentration of the experimental solution as 100 ppm. The adsorbent dose was optimized and fixed as 2.5 g. The maximum adsorption of Cr (III) on the surface of the bioadsorbent was 98.5 percent (Fig. 4). The desired pH value for this achievement was 3.2. It is a well-known fact that upon increasing the temperature, the rate of adsorption also increases (Stephen Inbaraj and Sulochana, 2003). This fact was clearly shown in the (Fig. 5).

In the present study, we have selected 25 ppm, 50 ppm and 100 ppm as initial concentration for the comparative study for the removal of Cr (III). At 2.5 g of the activated carbon of the bioadsorbent, the effect of the concentration of Cr (III) on the removal of Cr (III) from solution was tested. The removal of Cr (III) was completed within 150 minutes in dilute solutions of 25 and 50 ppm. However, at higher concentrations (100 ppm), the removal was completed only after 210 min. only. This observation clearly indicates that the removal of Cr (III) purely depends on the amounts of adsorbents and contact time.

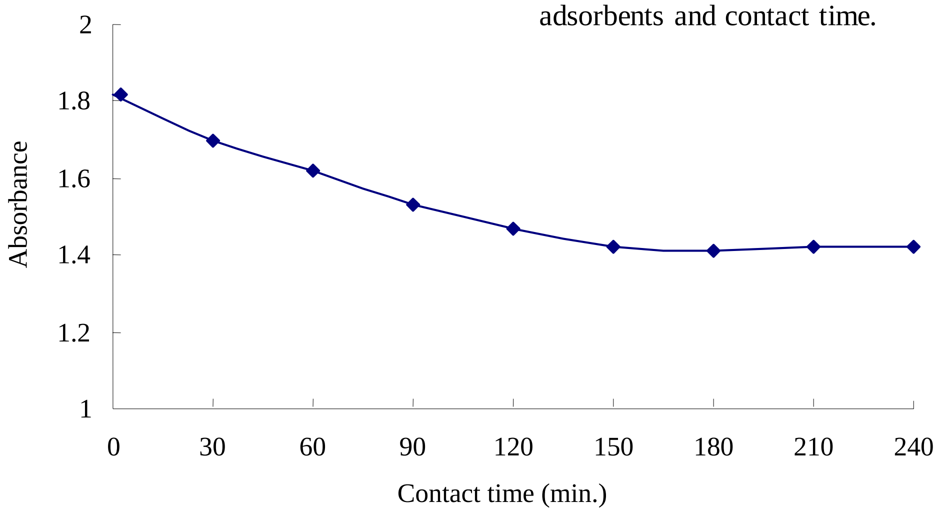

Fig. 1. Conversion of Cr (VI) into Cr (III)

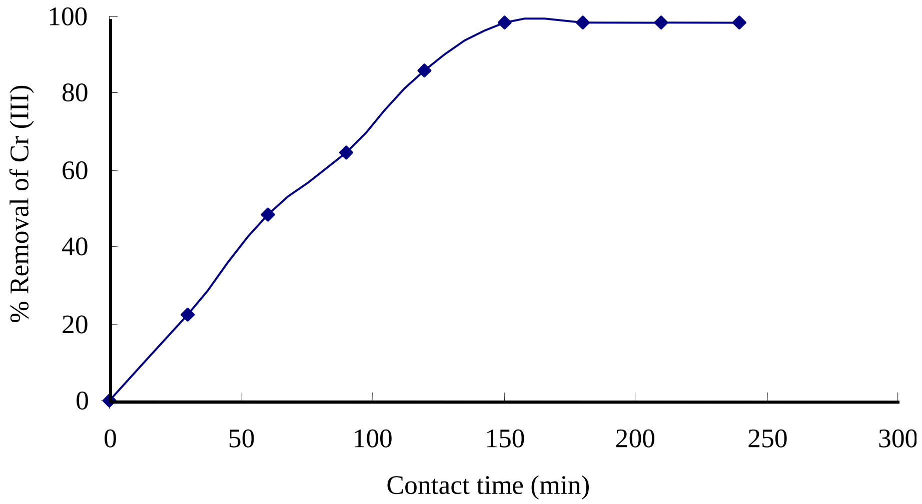

Fig. 2. Effect of contact time on Cr (III) removal

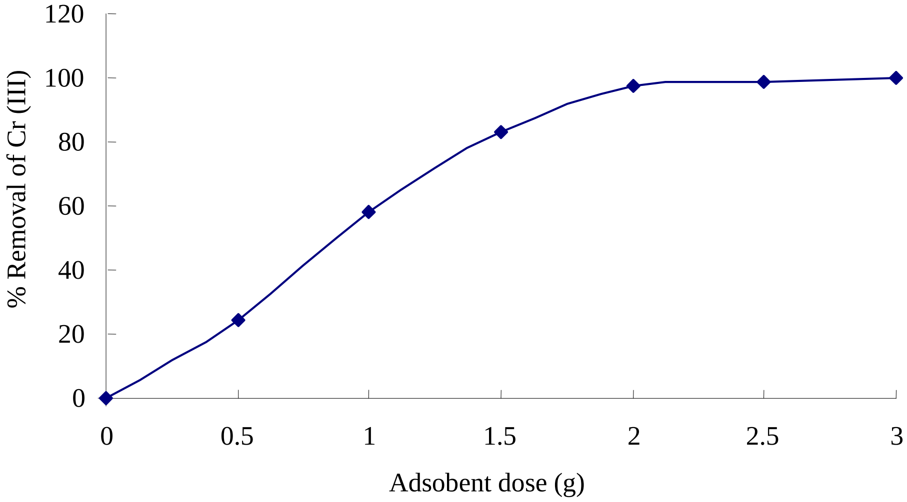

Fig. 3. Effect of adsorbent dose on Cr (III) removal

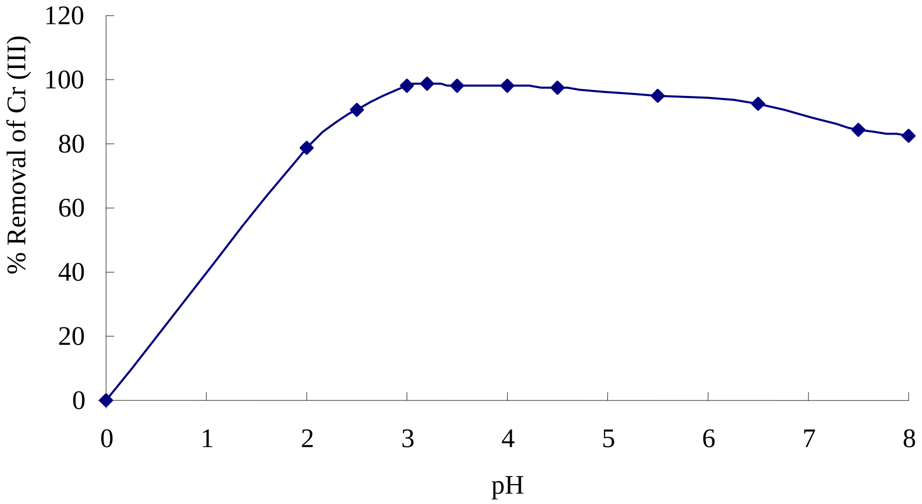

Fig. 4. Effect of pH Cr (III) removal

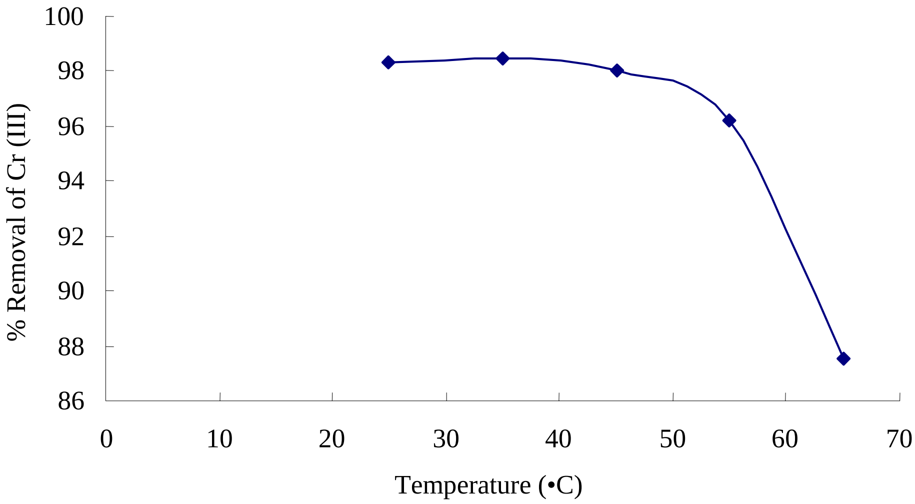

Fig. 5. Effect of temperature Cr (III) removal

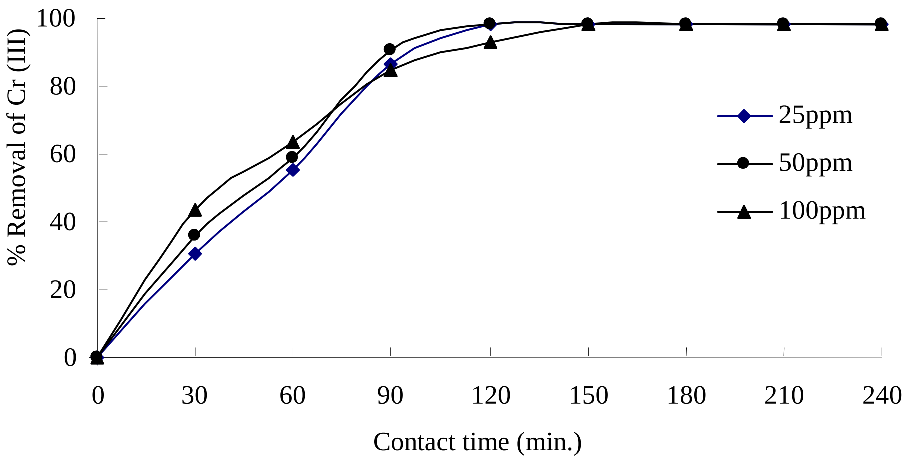

Fig. 6. Effect of concentration of Cr (III) ions

CONCLUSION

The removal of Cr (III)) in synthetic wastewater by using biosorption technology was studied in batch experimental systems. Based on the results, the following conclusions can be drawn. The raw bioadsorbent was very effective in conversion of Cr (VI) into Cr (III). Activated carbon is an efficient biomaterial for removal of Cr (III) from industrial wastewater. The percent removal of Cr (III) was 98.5 with an effective dose of 2.5 g of bioadsorbent. This process can be effectively used in Cr (III) and other heavy metals removal in industrial wastewater. The raw bioadsorbent is not suitable for the direct industrial wastewater treatment operation. Hence, preliminary treatment of the industrial wastewater is essential before application of activated carbon of the bioadsorbent.

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