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# An assessment and characterization for biosorption efficiency of natural dye waste

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ABSTRACT

The local natural dyeing house run by a women's self-help group was generating a huge amount of dye extracted pulp. We thought of using this pulp for an alternative use other than just composting it. This biomaterial was found to be excellent heavy metal adsorbents and was demonstrated to be very effective in remediation of groundwater and surface water of chrome metals in contaminated sites of tannery operations. In this article, sorption efficacy studies were carried out on selected biomaterials known for their potential usage as natural dyes. *Canna indica* flower, *Portulaca olecera* flower and stem, *Hibiscus rosa sinensis* flower and *Trapa natans* fruit skin (exocarp) were used for sorption studies. These plant parts, after the extraction of natural dye, were dried and evaluated for biosorption of heavy metal from effluent. Batch tests indicated that hexavalent chromium sorption capacity ($q_e$) followed the sequence $q_e$(*Trapa*) $>q_e$(*Hibiscus*) $>q_e$(*Portulaca*) $>q_e$(*Canna*). Due to high sorptive capacity, *Trapa* fruit skin (exocarp) was selected. The optimization studies were carried out by taking the Trapa exocarp in powdered form, and of particular mesh size. Sorption kinetic data have shown first order reversible kinetic model for all the sorbents, however the biosorption of chromium by *T. natans* biomass occurred in two stages. In the first stage, 95% sorption was reported for Chromium (VI) in 15 min followed by a slower second stage. It reached equilibrium in 1 h at which 90–98% of the Chromium (VI) was biosorbed by *T. natans*. Experimentally reported equilibrium data fitted well with both the Langmuir and Freundlich Isotherms. The FT-IR, XRD and XPS analysis showed that the main mechanism of Chromium (VI) biosorption onto *Trapa* dried powder was through the binding of Chromium ions with amide group of the biomass.

## 1. Introduction

The occurrence of toxic heavy metals such as chromium (VI) in aqueous streams is one of the most significant environmental problems. The Chromium (VI) enters the water bodies due to disorganized discharge and unhealthy clearance of wastes from industries such as electroplating, leather tanning, paints, and pigments, etc., especially in India. Chromium is a redox-active element with oxidation states from −2 to +6, but only the +3 and +6 states are ubiquitous in the aqueous phase. The two environmentally stable oxidation states, Chromium (III) and Chromium (VI), show great difference in toxicities and their mobility. Chromium (III) is relatively impenetrable in aqueous systems (above pH 5) and exhibits modest or no toxicity. In contrast, Chromium (VI) usually occurs as highly soluble as well as toxic chromate anions ($HCrO_4^-$ or $Cr_2O_7^{2-}$) (Park et al., 2006). Due to stringent environmental regulations, all the chromium related industries are now facing the issue of disposal of large quantities of wastewater containing toxic chromate ions (Sarin and Pant, 2006). Emphasis is being laid for remediation or removal of this contaminant in a big way.

Adsorption is a well-established technique for heavy metal removal. Activated carbon is the most efficient and popular adsorbent and has been used extensively for the elimination of heavy metal. But due to its high regeneration cost and losses in the application processes, it cannot be used on an industrial scale according to (Lee et al., 1998) and (Reed et al., 1996). However, biosorption is based on natural materials. Since they are available in large quantities, these materials may be waste products of industrial or agricultural operations, which have potential as sorbents for heavy metal. Recently bioremediation has gained considerable importance as an alternative technology for the treatment of heavy metal waste and also for use in conjunction with the existing methods. Several chromium removal studies were carried out using naturally available biomaterials such as Bengal gram husk (Ahalya et al., 2005), eucalyptus bark (Sarin and Pant, 2006), and sugar beet pulp (Sharma and Forster, 1994), coconut husk fibers (Huang and Wu, 1977), palm pressed fibers (Tan et al., 1993), waste tea

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(Mahvi et al., 2005) and *Ocimum basilicum* seeds (Melo and D'Souza, 2004).

Water chestnut (*Trapa natans,* Trapaceae) is an annual aquatic herb, grown in wetlands of Central and South East Europe; temperate and Tropical Asia. In India, it is extensively cultivated for edible seeds and fruits. Various studies indicate that potential productivity of water chestnut in nutrient enriched waste waters has led to its selection for phyto-remediation of various industrial effluents by different workers (Singhal et al., 2003; Verma et al., 2005). However, the use of non-living biomaterial containing metal-binding compounds would have the advantage of not requiring maintenance as well as being useful in remediating areas with high levels of contaminants. Studies shown by Lujan et al. (1994) and Gardea-Torresdey et al. (1996) that phyto-filtration using dead or inactivated biomass is very effective for the removal and recovery of heavy metal contaminants in aqueous environments.

The local natural dyeing house run by women's self-help group was generating a huge amount of dye extracted pulp. The use of this pulp for metal removal was attempted. This work was taken up mainly to use natural dye waste generated abundantly by the women members of self-help groups working with natural dyeing projects. This biomaterial was found to be excellent heavy metal adsorbents and was demonstrated to be very effective in remediation of chrome metal contaminated sites. As ground water is the source of drinking water it was imperative to purify the water by cheap and effective biomaterials.

Our earlier study on utilization of dye extracted plant material for phyto-remediation (Vankar et al., 2010) and (Vankar et al., 2011) prompted us to study a comparative evaluation of *Canna indica* flower, *Portulaca olecera* flower and stem, *Hibiscus rosa sinensis* flower and *Trapa natans* fruit skin (exocarp) for removal of Chromium (VI) from simulated wastewater. Since the self-help group was using these 4 plant materials we thought of comparing the efficacy of metal removal by these materials. Based on their efficacy, *Trapa* fruit skin was found to show best results and was thus selected for further study. The effect of pH, contact time and adsorption equilibriums were investigated in the present study.

## 2. Material and methods

All the chemicals used were of analytical grade. The deionized-distilled water was used throughout the experiment. Final concentration of Chromium (VI) was determined by UV–VIS spectrophotometer of Thermo-Heλios α model at a wavelength of 540 nm using the complex engagement of 1,5-diphenylcarbazide (S.D. Fine–Chem Ltd.) in acidic medium. All experiments were done in triplicate.

### 2.1. Biosorbent preparation

The sorbents used were *Canna* flower, *Portulaca* stem and flowers, *Hibiscus* flower and *Trapa* fruit skin (exocarp). These plants were used by the self-help group women for exploring their potential as natural dyes. The pulp of these materials left after color extraction were oven dried at 80 °C overnight and then crushed with pestle-mortal. These dried powders were then sieved in 10 mm mesh size sieve and kept in air tight vessels. All the materials were used as such and no further treatment was given to the materials.

### 2.2. Preparation of stock solution

An aqueous solution (10 mg $L^{-1}$) of Chromium (VI) ions was prepared using $K_2Cr_2O_7$ salt. The pH was adjusted using 5 N $H_2SO_4$ and 1 N NaOH. Fresh dilutions were used for each study. The prepared solutions were simulated as contaminated ground water.

### 2.3. Biosorbent screening

For comparative assessment of different sorbents for Chromium (VI) removal capacity, the experiments were conducted in 100 ml beakers at 28 °C. Experiments were conducted at pH 4, 6 and 9 and initial Chromium (VI) concentration of 10 mg $L^{-1}$ was maintained. Samples were filtered through Whatman No.42 filter paper after certain time intervals. Filtrates were analyzed for residual chromium concentration with UV–Vis spectrophotometer.

### 2.4. X-ray photoelectron spectroscopy (XPS) analysis

XPS was employed to determine the oxidation state of the chromium bound on the biomaterial. The Chromium-laden biomaterials were obtained through contact with 200 mg $L^{-1}$ of Chromium (VI) solutions at pH 4, 6 and 9 for 6 h. Prior to mounting for XPS, the biomaterials were washed with deionized-distilled water several times, and then freeze-dried in a vacuum. It must be noted that thermal drying of samples can cause change in oxidation state of chromium species so it freeze drying was adopted. The resulting biomaterials were analyzed on spectrometer. $CrCl_3.6H_2O$ (Sigma) and $K_2Cr_2O_7$ (Kanto) were used as Chromium (III) and Chromium (VI) reference compounds, respectively. XPS spectra were collected on Perkin-Elmer model 1287. The XPS was performed with a spectrometer with Al Kα X-ray source (energy 1486.6 eV) with 100 W and pass energy 100 meV for general scan and 40 eV for core level spectra of each element. The calibration of binding energy of the spectra was performed with C 1S core level peak at binding energy ~284.6 eV. To deconvolute various oxidation states of Chromium core level XPS spectrums peakfit software was used.

## 3. Results and discussion

### 3.1. Screening of biosorbents

Initially experiments were conducted with 10 mg $L^{-1}$ Chromium (VI) concentration and 2 g $L^{-1}$biosorbent dose at different pH i.e. 4,6 and 9 on ambient temperature. In aqueous phase pH governs the speciation of metals and also the dissociation from the functional sites on the sorbent. Hence, metal sorption is linked with pH. A low pH makes the biomaterial surface more positive. The more positive the surface charge of the biomaterial, the faster the rate of Chromium (VI) removal from the aqueous phase, since the binding of anionic Chromium (VI) ion species with the positively-charged groups is enhanced. A low pH also accelerates the redox reactions of chromium, since the protons take part in these reactions. Meanwhile, if there are a small number of electron-donor groups in the biomaterial or protons in the aqueous phase, the chromium bound onto the biomaterial surface may remain in the hexavalent state (Park et al., 2008).

At pH 4, the Chromium (VI) removal was 2.97%, 5.92%, 54.87%, 96.57% with *Canna, Portulaca, Hibiscus* and *Trapa,* respectively after contact time of 4 h; which at pH 6 was found to be 3.61%, 6.42%, 59.92% and 95.75%. Notably this biosorption decreased by 25–30% at pH 9 as shown in Fig. 1.

The preliminary results indicated Chromium (VI) removal capacity of *T. natans* in pH range of 4–9 to be much higher than other biosorbents. The sequence of Chromium (VI) removal was *Trapa*>*Hibiscus*>*Portulaca* > *Canna.* Though percentage removal of Chromium (VI) decreased with increase in pH.

### 3.2. Sorption kinetics

Adsorption for Chromium (VI) concentration of 10 mg $L^{-1}$by 2 g $L^{-1}$ dose of *Trapa*, *Hibiscus, Portulaca* and *Canna* biosorbents as a function of time was analyzed at pH 5.0–5.5 (Fig. 2).