



Biosorption of chromium (VI) from aqueous solutions by the husk of Bengal gram (*Cicer arietinum*)

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Abbreviations: bgh: Bengal gram husk
FTIR: fourier transform infrared spectroscopy

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The discharge of heavy metals such as lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, gold, silver, copper, nickel, etc. into aquatic ecosystems has become a matter of concern over the last few decades due to pollutants' carcinogenic and mutagenic nature. These toxic materials are generated during mining operations, refining ores, sludge disposal, fly ash from incinerators, the processing of radioactive materials, metal plating, or the manufacture of electrical equipment, paints,

alloys, batteries, pesticides or preservatives.

Chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction are commonly used techniques for removing metal ions from effluents. However, these techniques are economically expensive with inherent disadvantages like incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal. This necessitates the development of efficient and environment friendly methods to minimize heavy metal content in the environment.

The process of heavy metal removal by biological materials is known as biosorption and the biological materials used are called biosorbents. Various biosorbents like bacteria, fungi, yeasts, agricultural by products, industrial wastes, etc have been used for biosorption. In this regard, considerable attention has been focused in recent years upon the field of biosorption for the removal of heavy metal ions from aqueous solutions (Volesky and Holan, 1995). This article focuses on the investigation of the potential of Bengal gram husk (bgh) (*Cicer arietinum*) for the removal of Cr (VI) ions from aqueous solutions. bgh (*Cicer arietinum*) is a milling agrowaste available in plenty in a tropical country like India. Also, the protein content in bgh is less than 5%, which is advantageous over the protein rich algal and fungal biomass, since proteinous materials are likely to putrefy under moist conditions.

Chromium is a toxic metal of widespread use and exists in several oxidation states. Among the several oxidation states, Cr (VI) is considered to be the most toxic. It is usually associated with oxygen as chromate (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions. The hexavalent form of chromium is considered to be a group "A" human carcinogen because of its mutagenic and carcinogenic properties. Chromium (VI) is a common pollutant introduced into natural waters from a variety of industrial wastewaters including those from the textile dyeing, leather tanning, electroplating and metal finishing industries. The untreated effluent from electroplating industry contains approximately 100 mg/l Cr (VI), which is much higher than the permissible limit of 0.05 - 1 mg/l (De Filippis and Pallaghy, 1994).

The bgh collected from legume seed splitting mill was washed in distilled water and boiled to remove colour. The husk thus processed was used to study the influence of several operational parameters such as dose of adsorbent, agitation speed, initial pH and contact time. The Freundlich and Langmuir models were used to fit the experimental data in order to assess the maximum adsorption capacity corresponding to biomass surface saturation and the adsorption intensity of the sorbent towards the biomass. The Cr (VI) ion concentration was determined spectrophotometrically at 540 nm after complexation with 1,5 diphenylcarbazide (Eaton et al. 1995). Infrared spectral analysis was carried out to determine the functional groups responsible for uptake of Cr (VI).

The data obtained fit both Langmuir and Freundlich models, indicating the applicability of a monolayer coverage of the Cr on the surface of adsorbent. The maximum adsorption capacity calculated from Langmuir isotherm showed that 91.64 mg of Cr(VI) was adsorbed per gram of adsorbent, which is considerably higher compared to the values obtained with other adsorbents.

Chromium exhibits different types of pH dependent equilibria in aqueous solutions. The optimum initial pH for biosorption of hexavalent chromium on to bgh (husk of *Cicer arietinum*) was observed at pH 2.0. About 99.6% of Cr ions was adsorbed from a solution of 10 mg/l at pH 2.0, whereas a 23% reduction in biosorption was determined as the pH shifted from 2.0 to 4.0. The percentage of Cr ions adsorbed at pH 2.0 decreased with increasing metal concentration. At the optimum sorption pH 2.0, the dominant species of Cr ions in solution are HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$ and $\text{Cr}_3\text{O}_{10}^{2-}$. These chromate anions interact strongly with the negatively charged ions of the bgh matrix.

The concentration of both the metal ions and the biosorbent is a significant factor to be considered for effective biosorption. It determines the sorbent/sorbate equilibrium of the system. The rate of adsorption is a function of the initial concentration of ions. Results indicate that removal efficiency increased with an increase in contact time before equilibrium is reached. Other parameters such as dose of adsorbent, pH of solution and agitation speed was kept optimum.

The time taken to attain equilibrium for 10, 20, 50 and 100 mg/l chromium solution were 180 min. As

the chromium concentration increased, the percentage of chromium biosorption progressively decreased from 99.65% in 10 mg/l to 75% in 100 mg/l solution, even though the sorption equilibrium was achieved during the same period of 180 min. This is due to the increase in the number of ions competing for the available binding sites in the biomass and also due to the lack of binding sites for the complexation of Cr ions at higher concentration levels. The equilibrium time is one of the important parameters for an economical wastewater treatment system

Bgh biomass was varied from 1 to 40 g/l and brought in contact with chromium solutions of different concentrations. For 99% removal of chromium from 10, 20 and 50 mg/l metal solutions, the bgh biomass required was 10, 20 and 40 g/l at approximate ratio of 1:1000. This shows that the rate of increase of chromium removal was not proportionate to the increase in bgh biomass suggesting the decline is due to the saturation of the sorption sites.

The effect of agitation speed on removal efficiency of Cr was studied by varying the speed of agitation from 0 (without shaking) to 180 rpm, while keeping the optimum dose of adsorbents and optimum pH as constant. The results indicate that a moderate speed of 120 rpm was optimum as it facilitates proper contact between the metal ions in solution and the biomass binding sites and thereby promoting effective transfer of sorbate ions to the sorbent sites. An un-reacted bgh sample and bgh pre-treated with 100 mg/l Cr (VI) solution were analysed using Fourier transfer infrared spectrometer, which indicate that carboxyl, hydroxyl and amide groups are involved in the biosorption of Cr (VI).

Thus the use of bgh for chromium ion removal appears to be technically feasible, economically viable and eco-friendly apart from higher efficacy.

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