REMOVAL OF CHROMIUM (III) FROM WASTE WATER USING *Gossypium herbaceum* AS A BIOSORBENT

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ABSTRACT

In this paper we report removal of Chromium (III) from waste water using flower of cotton plant, *Gossypium herbaceum* as a biosorbent, collected from Gwalior region. Flowers are dried at room temperature and crushed in electric grinder. The I.R. spectra of the biosorbent was recorded to determine the various organic functional groups present in order to study the mechanism of sorption experiments. The quantities of metal ion were measured by atomic absorption spectrophotometer and UV-Vis spectrophotometer. Batch experiments were performed and effect of the contact time, pH etc on the adsorption process were investigated. The isothermal studies were carried out with different doses of biosorbent in 50 ml synthetic waste water at different metal ion concentration. The initial pH of synthetic waste water was about 5 pH. The experimental results were examined using the Langmuir and Freundlich isotherms to obtain the appropriate model. The isotherm was found to be well representing the measured sorption data. The goal for this research is to develop inexpensive, highly available, effective metal ion adsorbent from nature or alternative to existing conventional adsorbents.

Key Words: Biosorption, *Gossypium herbaceum*, Heavy metal ion, Kinetics, Isotherm

INTRODUCTION

Heavy metals are common in industrial applications such as in the manufactures of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel etc. Heavy metal ions are toxic pollutants. Some of these are cumulative poisons capable of being assimilated, stored, and concentrated by organisms that are exposed to low concentration of these substances for long periods or repeatedly for short periods. Among commonly used heavy metals, Cr(III), Cu, Zn, Ni and V are comparatively less toxic than Fe and Al. Cu is mainly employed in electric goods industry and brass production. Major applications for Zn are galvanization and production of alloys. Many authors, addressed the fact that, chromium toxicity to mammals and aquatic organisms appears to be lower compared to other heavy metals, due to general low solubility of Cr(III) compounds, low mobility in the environmental compartments and limited availability to living organisms. In aquatic system, uptake is influenced by various environmental factors such as temperature, salinity, pH, and the presence of organic matter. Industrial and municipal wastewaters frequently contain metal ions. Trivalent Chromium has low acute and chronic toxicity to humans at high doses, however in lower concentration, it is considered as an essential trace nutrient. Cr (III) deficiency is characterized by impaired growth and longevity. There is also evidence that Cr (III) is involved in the glucose tolerance of the man. The inability of Cr(III) to penetrate cell membranes severely limits or precludes the possibility of carcinogenic activity. Current methods for such wastewater treatment include precipitation, coagulation/ flotation, sedimentation, flotation, filtration, membrane process, electrochemical techniques, ion exchange, biological process, and chemical reaction. In recent years, the application of low-cost sorbents has been widely studied for metal removal from water. Natural materials that are
available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents\(^5\), as they represent unused resources\(^6\), widely available and are environmentally friendly\(^7\).

This work’s goal was to study the possibility of the utilization of one kind of flower of cotton plant; *Gossypium herbaceum* for the sorption of chromium(III) from mixed solutions. The system variables studied include contact time, pH, initial ion concentration etc. Isothermal studies were achieved to find the appropriate model describing the adsorption over the studied concentration range.\(^8\)

**MATERIAL AND METHODS**

The major interest of this study was to investigate sorption of heavy metal ion using the flower of the cotton plant, *Gossypium herbaceum* present in Gwalior. Since the flower of cotton plant widely present Gwalior region therefore it has been chosen for current study.

The flower of cotton plant, *Gossypium herbaceum* was gathered from twigs into clean plastic bags. Washed with deionized water and laid flat on a clean table to dry. Dry flowers were grounded with electrical grinder. In order to study the mechanism of sorption experiments, IR spectra (of dried untreated biosorbent and acid treated biosorbent; with dilute HNO\(_3\)) were recorded on Perkin Elmer Spectrum RX 1 FT IR Spectrophotometer to examine the various organic functional groups present.

Analytical grade reagents were used in all cases. The stock solution of metal ion (1000 mg/L) was prepared, obtained from Merck. All working solutions were prepared by diluting the stock solution with deionized water.

Batch sorption experiments were performed at room temperature on a rotary flask shaker. In all sets of experiments different doses of biomass was thoroughly mixed into 50 ml Cr(III) solution. After shaking, the reaction mixtures were separated by filtration and the filtrate was analyzed with UV spectroscopy and AAS (UV-2450 and AA 6300 respectively) for metal ion content.

The removal % was calculated as:

\[
\text{Removal } \% = \left[ \frac{(C_0 - C_f)}{C_0} \right] \times 100
\]

Where: \(C_0\) and \(C_f\) are the initial and equilibrium concentration (ppm) of metal ions in solution, respectively.

**RESULTS AND DISCUSSION**

IR Characterization of biosorbent

Various parts of plants (leaves, flowers, woods etc.) are versatile natural chemical species, contain a verity of organic and inorganic compounds. Cellulose, hemicelluloses, pectins, lignins etc present in cell wall are effective sorption sites\(^9\). These biomass contain hydroxyl, carboxyl, carbonyl, amino, nitro etc functional groups and M-O, M-N, M-Si etc bond.

IR spectra of flower of cotton plant, *Gossypium herbaceum* between 400-4000 cm\(^{-1}\) was recorded using KBr as background material. The powdered biomass was washed with 0.1 M HNO\(_3\) and deionized water in order to remove impurities. IR spectra of acid treated cotton flower and untreated cotton flower are depicted in Fig. 1(a) and Fig. 1(b). From the spectra it is clear that presence of heavy metals and inorganic compound below 9000 cm\(^{-1}\) have been removed by acid treatment. The important band in the IR spectra of untreated biomass is summarized in Table 1. From the IR spectrum (Fig. 1a), it is obvious that the biosorbent contains various organic and ionizable functional groups which leaves vacant sites for metal ions attachment.

**Table 1 : Tentative assignment of important bands in the IR spectra of flower of cotton plant *Gossypium herbaceum***

<table>
<thead>
<tr>
<th>Band position (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3427</td>
<td>-OH</td>
</tr>
<tr>
<td>2924</td>
<td>C-H str Methyl</td>
</tr>
<tr>
<td>1618</td>
<td>C=O str</td>
</tr>
<tr>
<td>1374</td>
<td>Carboxylate group</td>
</tr>
<tr>
<td>1056</td>
<td>C-OH, C-O-C str</td>
</tr>
</tbody>
</table>
Effect of contact time

At equilibrium time 2 g of adsorbent was added to 100 ml of Cr(III) solution (100 ppm) and it was shaken at 100 rpm at 30 °C. The pH was maintained at 6. After different interval of batch experiment the solution was filtrated are analyzed by AAS (AA-6300). The amount of metal sorption was calculated using equation:

\[ q = \frac{v(C_0 - C_f)}{m} \]

Where, \( C_0 \) = Initial concentration of solution, \( C_f \) = Final concentration, 
\( M \) = Mass of adsorbent, \( V \) = Volume.

The effect of contact time is shown in Fig. 2. As the figure shows, concentration becomes constant after 35 minutes where 80% uptake has been achieved.

Fig. 1 (a) : IR spectra of untreated biosorbent

Fig. 1 (b) : IR Spectra of acid treated biosorbent
Effect of pH

The pH of the system exerts profound influence on the sorption of adsorbate molecule due to its influence on the surface properties, presence of various organic functional groups of the adsorbent and ionization/dissociation of the adsorbate molecule. pH of solution was varied from 5 to 8 by adding 0.1 M HCl solution and 0.1M NaOH solutions. As Fig. 3 indicates the maximum Cr sorption was found at pH = 5. The percentage sorption increased from 50% at pH 5 to 76% at pH 6 and significantly decreases with increase of pH. From the pH trend observed in this case, we can conclude that at pH 6 *Gossypium herbaceum* showed maximum percent of biosorption.
Effect of adsorbent dose

If we take other parameters like pH 6 and contact time 35 minutes are fixed, the adsorbent dose was varied from 1 to 6 mg/mL. As the Fig. 4 shows the optimum biomass concentration noted at 3.5 mg/ml and beyond this it is constant.

This may be due to the unavailability of binding sites to the metal and also due to the blockage of binding sites with excess biomass.

Adsorption Isotherm

Several equilibrium models have been developed to describe adsorption isotherm relationships. Langmuir model originally developed for adsorption of gases onto solids is based on the assumption that adsorption occurs on localized sites with no interaction between adsorbate molecules and maximum adsorption occurs when the surface is covered by a monolayer of adsorbate. For solid–liquid systems the linear form of the isotherm can be expressed by the Eq. (1):

$$\frac{1}{q_e} = \frac{1}{bq_0}C_e + \frac{1}{q_0}$$  \hspace{1cm} (1)

Freundlich isotherm model is the empirical model for adsorption and expressed as

$$q_e = kC_e^n$$  \hspace{1cm} (2)

where $q_e$ is the amount of solute adsorbed per unit weight of adsorbent corresponding to complete coverage of available sites, $C_e$ the residual liquid phase concentration at equilibrium, $b$ the adsorption coefficient, and $k$ and $n$ are the constants related to adsorption capacity and adsorption intensity.

Effect of temperature on Chromium biosorption is presented in Fig. 5. It was found that the temperature 30°C is most suitable that of the lower or higher temperatures. Good sorption percentage of 70% was observed at 30°C. In these experiments, there was an increase in sorption percentage with increase in the temperature but there was a gradual decrease with further increase in temperature. Analysis of the data over a concentration range from 5 to 50 ppm of the metal ions, showed that the adsorption of Cr(III) onto Gossypium herbaceum was best described by the Langmuir isotherm model The plausible explanation of this type of behaviour is the shrinkage of cells in the higher and lower temperatures which reduces the surface area of contact.
By maintaining all the parameters at optimum levels the initial metal concentrations were varied (10, 15, 20, 25, 30 mg/L). The percentage sorption was decreased constantly with increase in initial metal concentration. The decline in the percentage biosorption was depicted in Fig. 6.

**Fig. 5**: Effect of temperature on the removal of Cr(III) ions by the adsorption on *Gossypium herbaceum* at pH 6, contact time 35 minutes, 10 mg/L initial metal concentration.

**Fig. 6**: Effect of initial metal ion concentration on the removal of Cr(III) ions by the adsorption on 3.5 mg/mL *Gossypium herbaceum* at 30 °C.
CONCLUSION

In summary, it has been found that flower of cotton plant, *Gossypium herbaceum* is a very effective biosorbent for Cr(III) removal. Results showed that maximum sorption of Chromium was observed at 6 pH. A maximum sorption of 75% was observed using flower of cotton plant; *Gossypium herbaceum* at the optimum dosage and temperature of 3.5 mg/ml at 30 °C respectively. 80 % metal uptake has been achieved by 35 minutes of contact time. From IR spectra, it has been inferred that biosorbent contains verities of organic functional groups (ionized and unionized) which are effective sites for Cr(III) sorption.

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REFERENCES


When we heal the earth, we heal ourselves.