Screening of natural waste products for the removal of Cr (VI) ions from industrial effluents

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The present study was performed to explore the possibility of using biowaste materials namely paddy straw, coconut palm fibre, corn husk and pineapple crown top as biosorbents of chromium (VI) ions in aqueous solution. The batch experiments were carried out to investigate the effect of the significant process parameters such as initial pH, contact time, adsorbent dosage and the initial Cr (VI) concentration. The maximum adsorption of Cr (VI) on biowaste material was obtained at an initial pH value of 2. The removal rate of Cr (VI) increases with the increase of the adsorption time. However, it remains constant after an equilibrium time of 240 min. The removal of Cr (VI) ions increased with the increase in biosorbent concentration. The increase in initial concentration of Cr (VI) led to increase in the per cent removal of Cr (VI). In order to demonstrate the practical application of the biosorption process, biosorption of Cr (VI) was carried out in a packed bed adsorption column system using screened biowaste material. The electroplating wastewater was treated until the Cr (VI) concentrations reached the EPA standards and the concentrations of the pollutants were found to decrease after the treatment using glass column.

Keywords: Biosorption, Biosorbents, Biowaste, Wastewater, Heavy metals, Chromium (VI).

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Introduction
The discharge of heavy metals into aquatic system has become a matter of concern over the last few decades. They are extremely toxic elements, which can seriously affect plants and animals and have been involved in causing a number of afflictions. Increased knowledge about toxicological effects of heavy metals on the environment is well recognized and therefore, it is inevitable to search for different methods to reduce water pollution1. The major sources of heavy metal contaminations are the industrial waste waters. Due to their persistence in nature, it becomes essential to remove them from waste waters2.

Chromium is one such heavy metal, which being used in various industrial applications like tanning, metallurgy, electroplating, etc. It exists in two stable oxidation states, Cr (III) and Cr (VI) in nature. The trivalent form is relatively innocuous, but hexavalent form is toxic, carcinogenic and mutagenic in nature, highly mobile in soil and aquatic system and also is a strong oxidant capable of being adsorbed by the skin3.

The commonly used procedures for removing metal ions from waste waters include precipitation, lime coagulation, reduction, activated carbon adsorption, electrolytic removal, ion exchange, reverse osmosis, membrane filtration and solvent extraction4-11. Of the various treatment techniques available for chromium removal, the most commonly used ones are adsorption, reduction and precipitation, ion exchange and reverse osmosis. Among these methods, adsorption is found to be simple, cost effective and a versatile method for removing heavy metals12. In addition, adsorption can remove heavy metals to a lower level than precipitation over a wide range of pH. A number of natural and synthetic adsorbents have been studied by various researchers13-15.

An alternative method for the removal of heavy metals is biological methods of metal removal and recovery. The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase containing a dissolved species to be
sorbed (metal ions). The by-products obtained from biomaterial production are a cheap source of biosorbents. The major advantages of biosorption over conventional treatment methods include: low cost; high efficiency, minimization of sludge regeneration and the possibility of metal recovery. Developing countries suffer from water pollution; the high cost operating systems make the major problems in these countries. The cost of these biomaterials is negligible compared with ion exchange resins. Synthetic ion exchange resins are marketed for US $30-50 /kg. The search for a cheaper alternative reveals that utilizing natural processes and materials can significantly reduce the cost of wastewater treatment.

In recent years, many attempts have been made to analyze and to reduce the presence of Cr (VI) in water. Activated carbons have been found to be effective means of recovering Cr (VI) from wastewater. However, commercial activated carbons are expensive, which has led to the search for developing low cost materials with a good capacity for Cr (VI) removal. Present study reports the possibility of using biowaste materials for the removal of Cr (VI) ions from electroplating wastewater.

Materials and Methods
Sampling of electroplating effluent
Electroplating effluent was collected from Sri Ganapathi Metal Finishers, SIPCO Industrial Estate, Chennai, Tamil Nadu and the physico-chemical characteristic of raw effluent was analyzed. The effluent collected in sampling bottles containing concentrated nitric acid was stored at 4°C. The temperature and pH of the wastewater were determined on the spot using portable pH meter.

Analysis of physico-chemical parameters of electroplating wastewater
The electroplating wastewater sample was analyzed promptly for determining the physicochemical characteristics using standard analytical methods. The characteristics of the wastewater such as pH, temperature, turbidity, conductivity, TDS, TSS, TS, DO, BOD, COD, sulphates, chlorides, calcium and magnesium were analysed. All analysis were performed thrice and average values were used.

Estimation of heavy metal concentration in electroplating wastewater
The concentration of heavy metals such as Copper (Cu), Nickel (Ni), Cadmium (Cd), Zinc (Zn) and Lead (Pb) in wastewater were detected using AAS. AAS was calibrated for each metal using standard solutions of known concentration before sample injection. Cr (VI) concentration in the wastewater was estimated using UV spectrophotometer at 540 nm wavelength by 1, 5-diphenyl carbazide method.

Biosorption experiments
Preparation of biosorbents
The sorbents used were the biowaste materials, viz. paddy straw, coconut palm fibre, corn husk and pine apple crown top (Plate 1). All the materials were obtained from local agricultural farm and they were washed thoroughly with deionized water, dried and then pulverized and oven dried at 60°C for 24h. After drying, the materials were kept in air tight plastic bottles. The particle size was maintained in the range of 425-600µm.

Preparation of Cr (VI) solutions
Cr solutions were prepared using K₂Cr₂O₇. Stock solution (1000 mg/l) of Cr was prepared by dissolving required quantity of K₂Cr₂O₇ in deionised distilled water. For biosorption experiments, Cr solutions having 200 mg/l were prepared and used. The pH of the solution was adjusted with 0.1 N HNO₃ and NaOH solutions.

Screening of biosorbents
For the comparative evaluation of different sorbents for Cr removal capacity, the experiments were conducted in 250 ml Erlenmeyer flasks at 28±1°C on a rotary shaker at 120 rpm. Experiments were conducted at pH 2 to 8 and initial Cr concentration of 200 mg/l was maintained. After 6 h of mixing, the samples were filtered through Whatman No. 1 filter paper, and the filtrates were analyzed using UV spectrophotometer at 540 nm wavelength by 1, 5- diphenyl carbazide method.

Batch Biosorption
The batch biosorption experiments were conducted for the screened biosorbent. The effects of various parameters on the rate of adsorption process were observed by varying contact time (5, 10, 15, 20, 25, 30, 45, 60, 120, 180, 240 and 300 minutes), adsorbent dosage (0.5 to 5.0 g/100 ml) and initial concentration of chromium ion (20 to 260 mg/l). The solution volume (V) was kept constant (100 ml).

The amount of metal ion adsorbed per gram of biomass and the sorption efficiency (%) were calculated according to the expressions:
Treatment of electroplating wastewater using glass column

The electroplating wastewater was fed through a glass column (3 cm i.d. and 10 cm long) packed with 20 g of the dried powder of biosorbent (corn husk) at a flow rate of 5.0 ml/min controlled by a peristaltic pump. After treatment, the samples collected from the exit were analyzed for physico-chemical characteristics and chromium concentrations. The wastewater was treated till the values reached to satisfy the EPA standards.21

Results and Discussion

Analysis of physico-chemical parameters of electroplating effluents

To evaluate the pollutants of the electroplating samples, various physico-chemical parameters were analyzed from the waste water samples collected from Sri Ganapathi metal finishers, Chennai. The waste water quality data obtained after carrying out the analytical studies was recorded for comparison.

The chromium concentration in the raw effluent was 204 mg/l. The other metals such as Copper (0.259 mg/l), Lead (0.010 mg/l), Nickel (0.007 mg/l), Cadmium (0.014 mg/l) and Zinc (0.521 mg/l) were also present in the effluent, respectively. The concentration of the chromium in the raw effluent was found to have higher values than the EPA standards.

Screening of biosorbents

The experiments were conducted with initial Cr (VI) concentration of 204 mg/l and biosorbents dose of 2 g/l at different pH. The results are presented in Fig. 1. At pH 2, the Cr (VI) removal was 26.8, 31.7, 45.7 and 73.6% for paddy straw (PS), pine apple crown top (PA), coconut palm fibre (CPF) and corn.

Sorption efficiency (%)=\(\frac{(C_o - C_f)}{C_o}\times100\)

where, \(Q\) = amount of metal ion biosorbed per gram of biomass, mg/g. \(C_o\) and \(C_f\) are the initial and equilibrium concentrations (mg/l), \(V\) the volume of solution (L), \(M\) the weight of biosorbents (g) and \(C\) is the solution concentration at the end of the sorption process.

Plate 1—Biowaste materials

Paddy straw

Coconut palm fibre

Pine apple crown top

Corn husk
species like HCrO$_4^-$ be due to occupation of the adsorption sites by anionic oxyanions of chromium and OH$^-$ ions in the bulk. The decrease in adsorption at high pH values may be due to the competiveness of the oxoanions of chromium and OH$^-$ ions in the bulk. These results suggest that pH affects the solubility of metals and the ionization state of the functional groups like carboxylate, phosphate and amino groups of the cell walls of the biosorbent. In general, the Cr (VI) adsorption by different biosorbents have shown similar trend and the optimum pH 2 has been reported.

**Effect of contact time on sorption**

Since other biosorbents, CPF, PA and PS showed less potentiality for adsorption of Cr (VI) ions when compared to CH, further studies were carried out using corn husk (CH) as adsorbent. The equilibrium time required for the biosorption of Cr (VI) on the corn husk with 2 g/l of the biosorbent at different time intervals was studied. Fig. 2 showed that adsorption capacity sharply increased with increase in time and attains equilibrium in 240 min. The removal rate of Cr (VI) increases with the increase of the adsorption time. However, it remains constant after an equilibrium time of 240 min, which indicates that the adsorption extends toward saturation at 240 min. Therefore, the adsorption time was set to 300 min in each experiment. The rate of adsorption is higher in the beginning due to large available surface area of the biosorbent. After the capacity of the adsorbent gets exhausted, i.e. at equilibrium, the rate of uptake is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the biosorbent particles.

**Fig. 1— Effect of pH on biosorption of Chromium (VI)**

The decrease in adsorption at high pH values may be due to the competiveness of the oxoanions of chromium and OH$^-$ ions in the bulk. The decrease in adsorption at high pH values may be due to the competiveness of the oxoanions of chromium and OH$^-$ ions in the bulk. These results suggest that pH affects the solubility of metals and the ionization state of the functional groups like carboxylate, phosphate and amino groups of the cell walls of the biosorbent. In general, the Cr (VI) adsorption by different biosorbents have shown similar trend and the optimum pH 2 has been reported.

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**Biosorption experiments**

**Effect of pH on sorption**

Aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the sorbent. Hence, metal sorption is critically linked with pH. Not only different metals show different pH optima for their sorption but may also vary from one kind of biomass to the other. In order to establish the effect of pH on the biosorption of Cr (VI) ions onto the four different biosorbents mentioned above, the batch sorption studies at different pH values were conducted in the range of 2.0 to 8.0 (Fig. 1). It was observed that the maximum adsorption of Cr (VI) ions was observed at pH 2.0 for all the biosorbents and significantly decreased by increasing the pH values up to 8.0. At lower pH, the biosorbent is positively charged due to protonation and dichromate ion exists as anion leading to an electrostatic attraction between them. A sharp decrease in adsorption above pH 4 may be due to occupation of the adsorption sites by anionic species like HCrO$_4^-$; Cr$_2$O$_7^{2-}$; CrO$_4^{2-}$, etc., which retards the approach of such ions further toward the sorbent surface. Uptake of Cr (VI) increased markedly with decreasing pH.

At pH 2 and 8 corresponding uptake yield values were found to be 73.6% and 8.2% for CH, 45.7 and 5.6% for CPF, 31.7 and 2.6% for PA, 26.8 and 1.1% for PS. So, the maximum uptake of Cr (VI) at pH 2.0 was recorded in corn husk (CH) and thereafter decreased with further increase in pH. Equilibrium is dependent on pH, with HCrO$_4^-$ and CrO$_4^{2-}$ existing primarily in acidic media and CrO$_4^{2-}$ being the lone species of Cr(VI) above pH 7.0. At higher pH range, the fraction of Cr$_2$O$_7^{2-}$ species rapidly decreases with increasing pH above 5. In the removal of Cr (VI) process, the anion is not a simple monovalent anion but rather a series of chromate anions depending upon the pH and concentration of the solution. The total chromate species represented are Cr (VI). In the neutral solutions at low concentrations, Cr (VI) will be present in the form of HCrO$_4^-$ and CrO$_4^{2-}$. At acidic pH, HCrO$_4^-$ is the predominant Cr (VI) species in aqueous phase. The decrease in adsorption at high pH values may be due to the competiveness of the oxoanion of chromium and OH$^-$ ions in the bulk. The decrease in adsorption at high pH values may be due to the competiveness of the oxoanion of chromium and OH$^-$ ions in the bulk. These results suggest that pH affects the solubility of metals and the ionization state of the functional groups like carboxylate, phosphate and amino groups of the cell walls of the biosorbent. In general, the Cr (VI) adsorption by different biosorbents have shown similar trend and the optimum pH 2 has been reported.

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Effect of biomass dosage on Cr (VI) sorption by Corn Husk

The effect of biosorbent dosage on the removal of chromium (VI) by corn husk is shown in Fig. 3. Amount of sorbent was varied from 0.5 to 5 g/l and equilibrated for 240 min at an initial Cr (VI) ion concentration of 200 mg/l. The results indicated that the percent removal of chromium (VI) increased with the increase in the amount of adsorbent and removal efficiency for corn husk with the maximum dosage (5g/l) was 79.9%. The highest uptake yield was obtained at biosorbent concentration of 2.5g/l for corn husk. The removal of metal ions increased with the increase in biosorbent concentration and attained equilibrium after 2.5 g/l of adsorbent dosage. This was due to availability of more biosorbent as well as greater availability of surface area. It is apparent that by increasing the adsorbent dose the adsorption efficiency increases but adsorption density, the amount adsorbed per unit mass, decreases. The decrease in adsorption density with increase in the adsorbent dose is mainly due to unsaturation of adsorption sites through the adsorption reaction.

Effect of initial metal concentration on sorption by corn husk

The effect of initial metal ion concentration is shown in Fig. 4. In case of low Cr (VI) concentrations, the ratio of the initial number of moles of metal ions to the available surface area is smaller and subsequently the fractional adsorption process becomes independent of initial concentrations. However, at higher concentrations, the available sites of adsorption become fewer and hence the percentage removal of metal ions depends upon the initial concentration. The results showed that the increase in initial concentration of Cr (VI) led to increase in the adsorption capacity [q (mg/g)] of Cr (VI). The amount of Cr (VI) ions absorbed per unit mass of the biosorbent increased with increase in the initial metal ion concentrations up to 200 mg/l and remained nearly constant after equilibrium time. When initial chromium concentrations increased from 20 to 200 mg/l, the metal uptake increased from 1.21 to 7.59 mg/g. When chromium concentrations were above 200 mg/l, metal uptake attained equilibrium and the curves flattened. This was due to the saturation of the sorption sites on adsorbents. The initial concentration provides a significant driving force to overcome all mass transfer resistance of metal ion between the aqueous and solid phases. Hence, a higher initial concentration of Cr (VI) increased the rate of biosorption.
Column experiments using electroplating wastewater

In order to demonstrate the practical application of the biosorption process, column experiment using corn husk was conducted with wastewater and the efficiency of the process was determined. The results showed that about 20g of biosorbent was sufficient to treat a wastewater volume of 2.0 litres containing Cr (VI) ions. The wastewater was treated till the chromium (VI) concentration reached the values established by EPA (0.5mg/l). Fig. 5 represents the performance of breakthrough curve at bed height of 10 cm. The higher uptake of chromium (VI) was observed at the beginning of the fixed bed column, but the concentration of chromium (VI) in the effluent rapidly increased after breakthrough time ($t_b$). The breakthrough time ($t_b$) for the column was 6 hrs. Chromium uptake ($q$) was found to be 28.49 mg/g. After treatment, the samples collected from the exit were analyzed for physico-chemical characteristics and chromium concentrations. The concentrations of the pollutants after treatment using column process were depicted in Table 1. The pH of electroplating effluent slightly increased after treatment, the colour of the effluent was changed from yellow to colourless. There was no significant difference in the other parameters such as temperature, turbidity, conductivity, DO, BOD and COD. The concentration of sulphates and chlorides were found to decrease after biosorption, as the anions competed for the adsorption sites with Cr (VI) species. There was no significant reduction in case of cations like calcium and magnesium because they did not compete with the Cr (VI) ions on the adsorption sites.

Table 1— Physico-chemical characteristics of the electroplating effluent before and after treatment

<table>
<thead>
<tr>
<th>S. No</th>
<th>Parameters</th>
<th>Before treatment</th>
<th>After treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>2.66 ± 0.1</td>
<td>2.85 ±0.1</td>
</tr>
<tr>
<td>2</td>
<td>Colour</td>
<td>Yellow</td>
<td>Colourless</td>
</tr>
<tr>
<td>3</td>
<td>Temperature (°C)</td>
<td>28 ± 2.0</td>
<td>29.2 ± 2.0</td>
</tr>
<tr>
<td>4</td>
<td>Turbidity (NTU)</td>
<td>0.01 ± 0.001</td>
<td>0.02 ±0.002</td>
</tr>
<tr>
<td>5</td>
<td>Conductivity (dSm⁻¹)</td>
<td>0.042 ± 0.01</td>
<td>0.41 ±0.02</td>
</tr>
<tr>
<td>6</td>
<td>DO (mg/l)</td>
<td>18.6 ± 0.3</td>
<td>8.5 ± 0.1</td>
</tr>
<tr>
<td>7</td>
<td>COD (mg/l)</td>
<td>331 ± 3.2</td>
<td>330.2 ± 2.7</td>
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<tr>
<td>8</td>
<td>BOD (mg/l)</td>
<td>17.5 ± 2.5</td>
<td>15.2 ± 2.1</td>
</tr>
<tr>
<td>9</td>
<td>Sulphates (mg/l)</td>
<td>99.5 ± 3.4</td>
<td>19.5 ± 2.6</td>
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<tr>
<td>10</td>
<td>Chlorides (mg/l)</td>
<td>86.1 ± 0.8</td>
<td>63.8 ± 0.5</td>
</tr>
<tr>
<td>11</td>
<td>Calcium (mg/l)</td>
<td>376.7 ± 5.0</td>
<td>362.1 ± 4.7</td>
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<tr>
<td>12</td>
<td>Magnesium(mg/l)</td>
<td>149.3 ± 2.3</td>
<td>143.2 ± 1.7</td>
</tr>
<tr>
<td>13</td>
<td>Chromium (VI) (mg/l)</td>
<td>204 ± 0.5</td>
<td>0.5 ± 0.0</td>
</tr>
</tbody>
</table>

DO=Dissolved Oxygen; BOD=Oxygen Biochemical Demand; COD= Chemical Oxygen Demand

Conclusion

The removal of Cr (VI) from electroplating wastewater by using biowaste material was investigated. For the comparative evaluation of different sorbents for Cr (VI) removal capacity, the biowaste materials viz. paddy straw, coconut palm fibre, corn husk and pine apple crown top were used. Corn husk was proved to be the potent biosorbent for the removal of Cr (VI) from electroplating wastewater. The biosorption performance of corn husk was influenced by different factors, viz. pH, biomass dosage, initial metal concentration and contact time. The maximum efficiency was observed at pH 2. Above pH 2, there was reduction in metal uptake capacity. The electroplating waste water was treated until the Cr (VI) concentrations reached the EPA standards. Corn husk wastes being suitable sorbent can be used for the removal of chromium (VI) from wastewaters through a cost-effective and environment friendly process.

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