Studies on Biosorption of Chromium Ions from Wastewater Using Biomass of Aspergillus niger Species

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Abstract

The biosorption capacity of immobilized biosorbents for Cr (VI) was found to depend on pH, contact time, biosorbent dose and initial concentration of Cr (VI). In this study, the maximum uptake of Cr (VI) was 93.4, 96.2 and 98.6 mg respectively at a pH 1.5 and with an increase in pH up to 11 the metal uptake decreased gradually up to 39.95, 52.35 and 66.48 mg respectively for acid treated, untreated and base treated fungal biosorbents. Increase in biosorbent dose up to 1 g of biomass and contact time up to 60 min resulted in an increase in biosorption from 20.2, 16.8 and 28.3 mg at a biosorbent dose of 0.1 g 100 ml to 93.4, 96.2 and 98.6 mg at a biosorbent dose of 1.0 g 100 ml and then further increase in adsorbent dose and contact time did not result in more Cr (VI) adsorption by per unit weight of biosorbent. The percentage metal uptake by the biosorbent was found to decrease upto 60.35, 50.64 and 82.5 percent respectively for acid treated, untreated and base treated fungal biosorbents at the 300 mg l Cr (VI) ion concentration. The resulted data was found to fit well in Langmuir model of adsorption isotherm with a high value of correlation coefficient. The biosorbed metal was eluted from the biosorbtion by using 0.1M H₂SO₄ as eluant.

Keywords: Biosorption; Aspergillus niger; Immobilization; Isotherm; Hexavalent chromium

Introduction

The main pollutant from industrial complexes is the effluent which contains heavy metals such as Cu, Ni, Zn, Pb, Cr, Hg, Cd etc. and various organic compounds such as phenols, formaldehyde etc. [1]. Wastewater usually contains about 5 ppm of chromium. To comply with the permissible limits, various techniques are used for the removal of heavy metals. The recovery of heavy metals using conventional techniques is neither economical nor eco-friendly [2]. So, there is a continuous search for an economic and eco-friendly approach of heavy metals removal. In this endeavor, biosorption, a biological method of environmental control, has emerged as an alternative to conventional waste treatment facilities as it has advantages of low operating cost, effective in dilute solutions, generates minimum secondary waste, completes with in a short time period and have no toxicity limits for heavy metals [3,4]. Biosorption is the process in which physico-chemical interaction between the charged surface groups of micro-organisms and ions in solution takes place by the process of complexation, ion exchange, microprecipitation etc [5]. Biosorption is attractive since naturally occurring biomass or spent biomass from various fermentation industries can be effectively utilized [6]. These advantages have served as potential incentives for promoting biosorption as viable cleanup technology for heavy metal pollution. Immobilization of biosorbent leads to its stability and it can be used repeatedly with ease for the process of adsorption/desorption [7]. Biotechnological exploitation of biosorption technology depends on the efficiency of regeneration of biosorbent after metal desorption. Therefore, recovery of biosorbent by mild and cheap desorbing agents is desirable for regeneration of biomass for use in multiple biosorption cycles. In the light of these observations, studies on biosorption of Cr (VI) to immobilized fungal biomass were carried out in the present study. Aspergillus niger was used for the removal of Cr (VI) from electroplating industrial effluent and highlighted the prospects of its future uses as a biosorbent material for the Cr (VI) removal.

Materials and Methods

Characterization of industrial effluent and estimation of Cr (VI)

Stock metal solutions of Cr (VI) were prepared by dissolving appropriate quantities of pure analytical grade metal salts in double distilled water. The stock solutions were diluted further with deionized distilled water to obtain working solutions of different concentrations. The effluent was collected from Hyderabad electroplating works, Hyderabad, which is an electroplating industry. The effluent collected from industry, was analyzed for different physico-chemical properties such as total dissolved solids, hydrogen ion concentration, colour, oil and grease, BOD, COD, sulphate, phosphate, chromium, copper, nickel and zinc (Table 1).

The concentration of each component was determined as per the procedure outlined in APHA [8]. Chromium analysis was carried out by spectrophotometric method by using 1,5-Di-phenyl carbazide according to APHA [8]. The hexavalent chromium was determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color was produced. The reaction was very sensitive, the absorbptivity based on chromium being about 40000 lg cm⁻¹ at 540 nm wavelength. Aspergillus niger was previously isolated from wastewater treatment plant of NIT Warangal and routinely maintained by streaking on a rose bengal agar medium and incubating at 25°C [9]. For mass culturing, liquid broth was used as a culture medium which was having the following composition (g l⁻¹): Bactodextrose, 20; Bactopeptone,
Results and Discussion

Characterization of industrial effluent

The turbid effluent with dark green colour was found to be odorless (Table 1). The amount of chromium was found to be higher than Central Pollution Control Board standards, which possess a great threat to the ecosystem. The main form of the metal present in the effluent was Cr (VI).

Effect of pH and biomass dose: Experiments were conducted with

| S.No. | Property       | Type/Value  |
|-------|----------------|-------------|
| 1     | Color          | Dark green  |
| 2     | Total dissolved solids | 20,250 mg/l  |
| 3     | Oil and grease | 20 mg/l     |
| 4     | BOD            | 168 mg/l    |
| 5     | COD            | 447 mg/l    |
| 6     | pH (12)        | 4.4         |
| 7     | Sulphate       | 181 mg/l    |
| 8     | Phosphates     | 0.82 mg/l   |
| 9     | Cr (VI)        | 102 mg/l    |
| 10    | Zn (II)        | 88 mg/l     |
| 11    | Cu             | 0.52 mg/l   |
| 12    | Fe             | 6.8 mg/l    |
| 13    | Ni             | 13.1 mg/l   |

Table 1: Physico-chemical properties of electroplating industrial effluent.
1 g biomass dose of biosorbent for a contact time of 60 min. The pH varied from 1.5 to 11 with the help of 0.1 M H₂SO₄ and 0.1 N NaOH. The results showed that the metal uptake was optimum at pH 1.5. Further increase in pH beyond optimal value (1.5) resulted in decrease of metal uptake. This observation agrees with the earlier reports on Cr (VI) removal by different biosorbents. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favour the adsorption of anions due to the electrostatic repulsion. The optimum pH from above experiments with contact time of 60 minutes was kept to find the optimum dose of biomass. Various doses (0.1 to 1.2 g) of biomass were tested for Cr (VI) removal from synthetic solutions of 100 mg l⁻¹ concentration. 1 g of biomass dose was sufficient for the optimum removal of Cr (VI) ions. Increase in biomass dose after optimum value did not show corresponding increase in the metal ion uptake from the solution. Interaction of biosorbent and metal ions is generally electrostatic in nature on the binding sites present on the surface of biosorbent. For a given constant biosorbent concentration, the initial metal ion adsorption increased up to the stage of saturation of all the binding sites and further increase in the dose of biosorbent did not change the metal adsorption to biomass ratio.

Rate of adsorption: Relationship between contact time and Cr (VI) removal was investigated by using immobilized biosorbent with 1 g biomass dose of each. The pH of the 100 mg l⁻¹ Cr (VI) solution was adjusted to 1.5. The maximum amount of Cr (VI) uptake was observed after 60 min. Increase in contact time from 60 to 180 min did not result in corresponding increase in uptake capacity of biosorbent. It was observed that biosorption is a rapid process as most of the adsorption (80-85%) was completed in the initial 45 min. These results indicated that the adsorption sites were bind up in the initial 60 min by the metal ions passively. After this, the increase in contact time might not help for more adsorption of metal ions with this biosorbent. As a result, 60 min was chosen as optimum contact time for further studies.

Effect of initial metal ion concentration on rate of adsorption of Cr (VI): The uptake of metal ions was observed for different initial ion concentration of Cr (VI) at optimum contact time and biosorbent dose. The results revealed that an increase in metal ion concentration resulted in gradual decrease in percent biosorption of Cr (VI) up to 100 mg l⁻¹ and after that a sharp decrease in metal uptake percentage. An increase in initial concentration of metal ions resulted in the lowering of metal ion uptake due to reduction in ratio of sorptive surface to ion concentration.

Adsorption isotherm

It was found to be linear over a wide range of concentration. Langmuir constants 'Qₘₐₓ' which is a measure of adsorption capacity expressed in mg g⁻¹ and 'b' which is a measure of energy of adsorption expressed in mg l⁻¹ were calculated from the slope and intercept of plots are shown in Table 2.

The values of ∆G (Table 2) observed to be negative, thus, indicating the spontaneous and exothermic nature of the adsorption process. The higher negative values reflect a more energetically favorable adsorption process.

Reutilization of biosorbent: The total amount of metal biosorbed and desorbed in each subsequent cycle by immobilized biosorbents were calculated as shown in Figure 1, 2 and 3. The amount of Cr (VI) adsorbed in the 5th cycle was comparable to the first cycle. Also, the amount of metal desorbed after each loading cycle corresponded well to the amount of metal biosorption, which showed that a complete elution took place. Performance of immobilized biosorbent in industrial effluent: The batch study was carried out with 100 ml industrial effluent at 28±0.15°C and 150 rpm in 250 ml Erlenmeyer flasks. Immobilized biosorbent with a biomass dose of 1 g was used for a contact period of 40 minutes and it was found that biosorption of Cr (VI) was less in industrial effluent as compared to single metal ion synthetic solutions as shown in Figure 4. This may be due to interference and binding of other metal ions to the binding sites which was not the case with single metal ion synthetic solutions as all the binding sites were available for just single metal species. Overall, the performance was good in present electroplating industrial effluent. The tendency of biosorbents for metal removal in the present effluent was found in order of base treated > untreated > acid treated.

Conclusion

The present study showed that base treated biosorbent performed better than acid treated and untreated biosorbent. The explanation

| Biosorbent   | Qₘₐₓ (mg g⁻¹) | B (mg l⁻¹) | lnKₐ | Rₑ | ∆G | Kₛ |
|--------------|---------------|-----------|------|----|----|----|
| Base treated | 24.246        | 0.3264    | 0.9882 | 0.0243 | -5.2861 | 0.0328 |
| Acid treated | 18.265        | 0.1084    | 0.9964 | 0.0788 | -9.2484 | 0.0245 |
| Untreated    | 13.482        | 0.3012    | 0.9821 | 0.0296 | -5.2873 | 0.0321 |

Table 2: Constants and correlation coefficient for immobilized Aspergillus niger.
offered is that the increase in the metal uptake may be due to unmasking of some cellular groups, which cannot participate in the sorption process without the treatment of alkali [11] also found that alkali treatment of Aspergillus niger mycelia improved their capacity to chelate various metal ions [12], in trying to explain the increase in metal uptake by A. niger after NaOH treatment, thereby suggesting that the removal of certain polysaccharides from the cell wall by alkali treatment generates more accessible spaces with in the b-glucan chitin Skelton, thus allowing more metal ions to be sequestered by this structure. Immobilization of biosorbent increases the efficiency and ease of handling the process. The effect of pH and the higher sorption capacity suggest the electrostatic attraction of metal ions onto the fungal surface. The favorable values of Langmuir constants, R factor and 3G showed that A. niger is a good option for the removal of Cr (VI) from electroplating industrial effluent.

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