Removal of Chromium (VI) from Synthetic Solution using dead *Spirulina* Species

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Abstract - Increasing industrialization in developing country like India leading difficulty in pollution control. One of the major causes of pollution in aquatic ecosystem is discharge of heavy metals. Wastewater containing heavy metals are treated with conventional technology like chemical precipitation, ion exchange etc. Biosorption of heavy metals from aqueous solution can be considered as an alternative technology in industrial wastewater treatment. This involves use of biomaterials like algae, fungi, bacteria, moss or waste coming from industrial operation and biological processes such as fermentation. This study was carried out to remove of Cr(VI) from aqueous solution by *Spirulina* Sp. In relating to this batch studies were conducted as function of a contact time, biosorbent dosage, pH and initial metal solution. The batch studies results showed the maximum removal efficiency of Cr(VI) as 83.6%.

Keywords – Heavy metals, Cr(VI), Biosorption, *Spirulina* Sp

I. INTRODUCTION

Water is one of the prime necessities of life and development in each and every part of the world. It is estimated that man can survive for twenty days without food, but starts struggling for life in the absence of water just after one day. In man’s body 70% is water. Blood, cells and bones contain 18%, 75% and 22% water respectively. The term water pollution, in general can be defined as any alteration in physical, chemical or biological properties of water or discharge of any sewage or industrial waste or of any liquid. Gaseous or solid substances into water as may, or is likely to, create nuisance or render such water harmful injurious to public health of safety.

Heavy metals are one of the major environmental hazards because once the metals enter the environment they cannot be destroyed. These metals then change from one form to another and persist in the environment. Chromium is a most common pollutant discharged into waste waters from industrial wastewater. Chromium has high corrosion resistance and hardness due to this it finds abundant usage. Chromium is wide application in steel and electroplating industry. Degree of health and environmental effects varies with various ionic form of Chromium. Hexavalent form is considered as more dangerous. Trivalent chromium is essential to human metabolism in micro level, and there is no proof that chromium (III) is carcinogenic. In contrast to this, exposure to hexavalent chromium is known to be a serious human health risk. Chromium in metal form has low toxicity. But hexavalent form is toxic. Exposure to the hexavalent chromium may cause skin problems like ulcerations, dermatitis, and allergic skin reactions. Inhalation may lead to perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthma bronchitis, bronchospasms and edema.

Various technologies currently exist for treating heavy metals from wastewater such as Chemical Precipitation, Solvent Extraction, Ion Exchange, Membrane Separation and Adsorption. These technologies have certain disadvantages like sludge disposal, high cost etc. Biosorption is the upcoming technology to treat the heavy metals from aqueous solution and is the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake. Algae, bacteria and fungi and yeasts have proved to be potential metal biosorbers.

The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of
the sorbent for the sorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases [5].

In the present study, batch experiments were carried out to remove hexavalent chromium from synthetic waste water using dead *Spirulina* Sp. The process parameters considered are biosorbent dosage, contact time, pH, initial metal concentration.

II. MATERIALS AND METHODS

Dead *Spirulina* Sp. powder was procured from Antenna Nutritech Foundation, Madurai. Initially the dead *Spirulina* sp. powder has been directly used for the treatment of Cr (VI) synthetic sample. It is observed that the *Spirulina* sp. powder was imparting color to the synthetic sample. Hence to remove the color pretreatment of biosorbent has been done. Biosorbent was soaked in 0.12 N HCl for an hour. Then it was washed with distilled water and dried, keeping in oven at 100ºC for 12 Hours. The biosorbent was finally crushed into powder.

The influencing parameters such as contact time, biosorbent dosage, pH and initial metal ion concentration were considered for the study. Batch experiments were carried out at room temperature in Erlenmeyer flasks of capacity 250mL. In each experiment 100 mL of metal solution of known initial concentration was shaken with a varied amount of biosorbent, contact time and pH at a speed of 150 rpm using rotary flask shaker. After reaching the equilibrium the biosorbent was separated from the metal solution by using Whatmann filter paper No.42. The metal concentration remaining in the solution was analyzed using photoelectric colorimeter for Cr(VI)[6][7].

III. RESULTS AND DISCUSSIONS

A. Effect of Contact Time

The effect of contact time on biosorption of Cr (VI) by *Spirulina* sp. was studied, under shake flask conditions at pH 7, at 150 rpm, using 50 ppm Cr (VI) as initial ion concentration and the room temperature. The contact time was varied from 30 mins to 120 mins with the regular interval of 30 mins. The constant dosage of 3.0g was maintained.

From the figure 1, it showed that biosorption of hexavalent chromium at 60 minutes was 73.32 % whereas maximum removal efficiency of 78.28% was seen at the contact time of 120 minutes with 10.86 mg/l Cr(VI) concentration. Further continuation of biosorption process to 150 minutes resulted in reduction of removal efficiency to 58%. This is because the type of biosorbent and available adsorption sites affect the rate of adsorption of Cr(VI). At the beginning of biosorption, the concentration gradient between the film and the adsorption site is large, hence removal rate is more. Further decrease in removal efficiency is caused by desorption [8].

B. Effect of Biosorbent dosage

It was found that from the trial studies that biosorbent dosage less than 1g is not sufficient for the Cr(VI) removal. So dosage was increased to more than 1g. The Biosorbent dosage of 1, 1.5, 2, 2.5, 3, 3.5 and 4g were added to 100 mL Cr(VI) solution with 50mg/L concentration for the same contact time at a native pH of 6-7.
Figure 2. Effect of Spirulina dosage on Removal of Cr(VI)

From the figure 2, it was observed that removal capacity increases with increase in biosorbent dosage. 3.5g biosorbent dosage gave the maximum Cr removal efficiency of about 82% which considered as the optimum dosage. Further increase in dosage decreased the Cr(VI) removal efficiency to 77.16%.

C. Effect of pH

It is well known that the pH of a system is an important parameter in the adsorption of Cr (VI). In this study, effect of pH on the biosorption of Cr(VI) using Spirulina as an biosorbent was studied by changing the initial pH range from 2 to 10. The Cr(VI) concentration of 50mg/l, biosorbent dosage of 3.5g and contact time of 120 minutes were maintained constant.

Figure 3. Effect of pH on Removal Efficiency of Cr(VI)

The relation between the initial pH of the solution and removal efficiency was shown in figure 3. Maximum Cr(VI) removal efficiency of 88.8% was seen at pH 2 for a dosage of 3.5 g. At pH 6, Cr(VI) removal efficiency was reduced to 62%. Also by varying the dosage in the range of 2.5g, 3.0g and 4.0 g pH variation studies was made and the results are shown in Fig 4.

Higher extent of Biosorption was observed at the pH 2 and pH 6. pH 6 is the native pH which shows maximum removal of Cr (VI). At lower pH,(pH 2), dominant form of Cr(VI) is HCrO$_4^-$ while the surface of Spirulina was charged positively, the stable forms of chromium such as H$_2$CrO$_4$ and CrO$_3^{2-}$ exist as polynuclear species at high chromium concentration and hence the low pH value of 2 results in a higher removal of Cr(VI) [8].

D. Effect of Initial metal concentration

In this study, the biosorption experiments were performed to study the effect of initial Cr(VI) concentration by varying it from 25 to 250 mg/L while maintaining the Spirulina amount 3.5g/L and obtained results were presented in figure 4.
Removal efficiency decreased from 80.60% to 12.17% for concentration range of 25mg/L to 250mg/L. Maximum efficiency is observed as 80.6 % and 79.88% for 25 and 50 mg/L respectively. Adsorbents had a limited number of active sites, which would have become saturated above a certain concentration.

E. Adsorption Isotherm study of Cr(VI)

The adsorption isotherm is evaluated for hexavalent chromium Cr(VI). The adsorption isotherm is evaluated for following data with initial pH 6. The isotherm data is linearized using Langmuir equation and is plotted between 1/q versus 1/C_e which is shown in the figure 5. The $R^2$ value obtained is 0.9666 which indicates a good agreement between the experimental values and isotherm parameters and also confirms the monolayer adsorption of Cr (VI).

IV. CONCLUSION

From the study it can be concluded micro algae spirulina Sp. has the potential to remove the Cr(VI) from wastewater. Batch studies conducted using dead spirulina Sp. as biosorbent to treat Cr(VI) showed the optimum parameters as contact time as 120 min, biosorbent dosage as 3.5g, pH as 6 and initial metal concentration as 50 mg/L. The Cr(VI) removal efficiency at this optimized condition was 83.6 %. Adsorption isotherm studies were conducted and the correlation coefficient $R^2$ is determined for Langmuir isotherms for Cr(VI) which confirms monolayer adsorption of Cr(VI) by spirulina sp.

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