International Journal of Current Engineering and Technology ISSN 2277 – 4106

Available at http://inpressco.com/category/ijcet

Research Article

Removal of Chromium (VI) from Synthetic Waste water using Immobilized Algae

Praphulla Rao[a*], SaishaV[a] and Shashidhar S Bhavikatti[a]

[a]B M S College of Engineering, Bangalore, Karnataka

Abstract

Heavy metal pollution is one of the most serious environmental problems being faced by the world today. Over the past two decades, an increased interest in the phenomenon of heavy metal ion sequestering by living or inactive microbial biomass has been seen in the scientific and engineering community. In this present study, microbial species – Chlorella Pyrenoidosa was tested for its Chromium (VI) removal capacity from synthetic wastewater solution. Two different matrices for immobilization were compared, namely- calcium alginate and carrageenan. In this study effect of initial metal ion concentration, pH and contact time was studied. It was seen that the carageenaan cubes disintegrated after the 6th day of batch studies. The alginate matrix showed a more stable system for immobilization of biosorbent. The metal ion adsorption efficiency by the algae decreases with the increase in the initial metal ion concentration. Maximum metal uptake by the algae immobilized with calcium alginates beads was observed at pH 3 and concentration of 75mg/l on the 9th day of the study.

Keywords: *Heavy metal, Chromium (VI), Chlorella, Immobilization, Wastewater*

Introduction

The removal of heavy metals from aqueous solutions is an important issue faced by industries discharging waste water containing heavy etals. Thousands of tons of heavy metals are discharged from industrial processes such as electroplating, plastics manufacturing, mining and metallurgical processes. At present a number of different technologies exist for treating heavy metals bearing streams such as chemical precipitation, adsorption, solvent extraction, ion exchange, membrane separation, etc.

Biosorption of chromium from aqueous solutions is relatively a new process that has proven very promising in the removal of contaminants from aqueous effluents. Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal of and recovery of chromium ions from wastewater streams.The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical and/or biological sludge regeneration of biosorbent, no additional nutrient requirement, and the possibility of metal recovery (K. Ramakrishna et al, 2005).

One of the main interests for microalgae is focused on their use for heavy metal removal from effluents. Immobilized algal systems have been tested for their efficiency in heavy metal removal. Immobilization generally tends to increase more metal accumulation by biomass. Size of the immobilized beads is a crucial factor for use of immobilized biomass in biosorption.

More than 15 microalgal species have been already studied for their potential in heavy metal removal (L. Brinza et al, 2007).*Chlorella salina* cells immobilized in alginate were used to remove Co, Zn, and Mn heavy metals (W.G. Garnham et al, 1992). *Chlorella vulgaris* beads more efficient in heavy metal removal from sewage than free cells. The efficiency in Iron, Nickel, and Zinc removal was higher in the immobilized cells than free cells by 27, 23 and 25% respectively (M. S. Abdel Hameed, 2006).

A method was developed for mercury speciation in water using columns packed with *Chlorella vulgaris* immobilized on silica gel. This technique is appied to the analysis of spiked tap and tea processing wastewater (L. Travieso et al, 2002).

Chlorella Pyrenoidosa was immobilized on stationary support (silica gel), invoking an in exchange approach of “Donnan equilibrium concept”, to obtain biosorbents called “AlgaSORBs” of the required stability and selectivity. The performance of prepared biosorbent towards the selective separation and preconcentration of Zinc, Copper and Cadmium and Lead was studied with synthetic water samples. The inherent surge of interest in this investigation was also underlying in the search for low capacity biosorbents which could be used as packing

*Corrrresponding author: **Praphulla Rao**

material in the single column ion-chromatography (R Singh, 2012).

Objectives of the study was to analyse the potential of immobilized algae *Chlorella Pyrenoidosa* (in alginate and carrageenan) for removal of Cr (VI) from synthetic wastewater through batch studies and to optimize the operating conditions.

Materials and Methods

Microalgae *Chlorella Pyrenoidosa* was procured from National Collection of Industrial Microorganisms, Pune. Fog's media was used to culture the algae. Synthetic chromium solution was prepared by $K_2Cr_2O_7$ salt (N. Ahalya et al, 2003).

Chlorella was subcultured in 500ml EM flasks with Fog's media in a 1:5 ratio of algal suspension to media. The cells were incubated at 32ºC and pH 7. The algal suspension was exposed to natural light for growth. The flasks were placed in orbital shaker (Remi make) for continuous shaking at 100rpm to avoid clumping. 70% air space was maintained through out to ensure sufficient CO_2 supply. (S C Agarwal et al, 2007).

Immobilization

Two different gelling agents were used namely Calcium alginate (1.5%) prepared by addition of calcium chloride to sodium alginate and Carrageenan (2.5%). In both cases, blank and algal beads were prepared.

Immobilization of algae with Calcium alginate

1.5% of the gelling agent was prepared as follows. 10.5g of sodium alginate was added to 560ml of distilled water. Calcium chloride solution was prepared by adding 33g of calcium chloride in 1.5l of distilled water. Both the solutions were autoclaved for 20 minutes at 15 psi. After the solutions cooled to room temperature, in the LAF 140ml of the culture was added to the alginate solution and mixed well. Aseptically, using a peristaltic pump, the beads were formed of approximately 3mm diameter. These beads were kept for curing in calcium chloride solution for two hours at 4ºC. After curing, the beads were washed with sterile distilled water for 3 to 4 times. Blank beads were prepared without adding the culture.

Immobilization of algae with Carrageenan

Carrageenan is the generic name for a family of gel-forming, viscosifying polysaccharides that are obtained commercially by extraction of certain species of red seaweeds (Rhodophyceae).i-carrageenan was used for immobilization of the algae, C*hlorella Pyrinoidosa*. Initially 1.5% of the gelling agent was prepared. Few drops of methylene red indicator were added as the gel in order to differentiate the beads from clear solution. The solution was autoclaved for 20 minutes at 15 psi. When the temperature of the solution was about 35-40ºC, 200ml of algae was added and mixed well which finally made the concentration of carrageenan 2.5%.The solution was poured into different petri-plates about 4mm thick and allowed to cool. The solidified gel was cut into identical cubes of approx 4.3mm to match the surface area of that of alginate beads. These cubes were transferred to sterile distilled water for curing. The beads were kept for curing overnight at 4ºC.

Batch Studies

The batch adsorption studies were carried out in 250 ml EM flask at room temperature. Experiments were conducted for different initial concentration of chromium VI (0, 25, 50, 75, 100, 125, 150mg/l) and different pH conditions (3, 5 and 7). The flasks were placed in orbital shaker with continuous shaking at 100rpm at room temperature. 200 beads were counted (Blank and Algal beads/cubes) and mixed with 100 ml solution of different concentrations in 250 ml conical flask. The 100 ml solution contains 50 ml of chromium solution and 50 ml of media. At regular intervals (once in 4 days) 3ml of sample was taken and concentration of chromium was checked using UV spectrophotometer.

Cr(VI) Analysis

Background correction was performed with blank solution and absorbance of reference solutions and samples were measured at 540 nm using 10 mm cell in a UV spectrophotometer (Systronics Pvt. Ltd.). Diphenylcarbazide Assay was used for the analysis. Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. Product obtained was in red-violet color. Concentration was determined using the calibration plot. The percentage removal of Cr (VI) was calculated (APHA et.al, 1998).

Results

The batch adsorption studies for removal of Cr (VI) were carried out using algae immobilized in Calcium Alginate beads (1:5). The blank beads of calcium alginate were

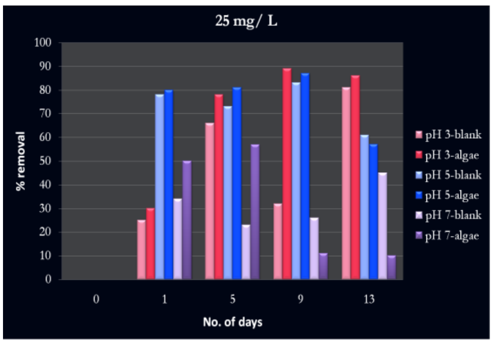

Figure 1: Percentage removal of Cr (VI) at 25mg/l initial conc. of Chromium solution with contact time

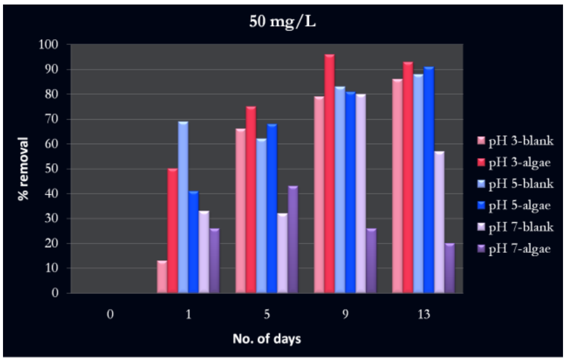

Figure 2: Percentage removal of Cr (VI) at 50mg/l initial conc. of Chromium solution with contact time

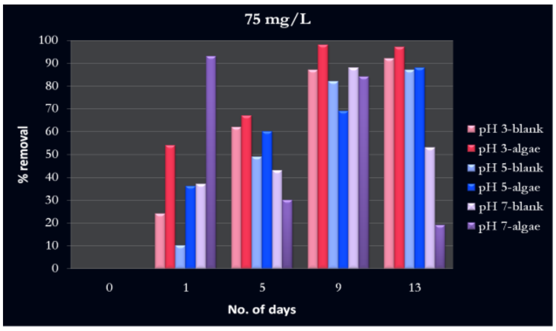

Figure 3: Percentage removal of Cr (VI) at 75mg/l initial conc. of Chromium solution with contact time

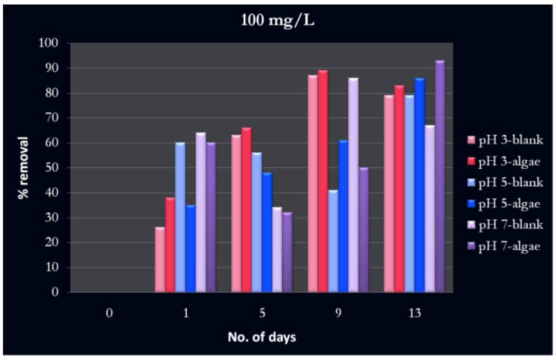

Figure 4: Percentage removal of Cr (VI) at 100mg/l initial conc. of Chromium solution with contact time

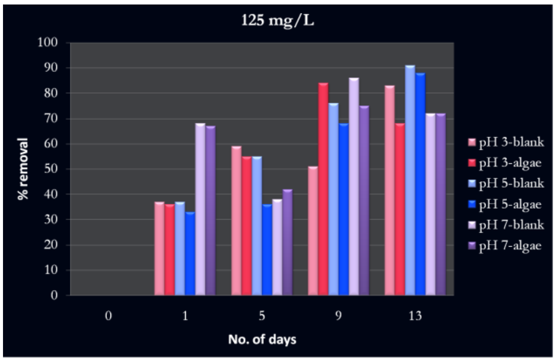

Figure 5: Percentage removal of Cr (VI) at 125mg/l initial conc. of Chromium solution with contact time

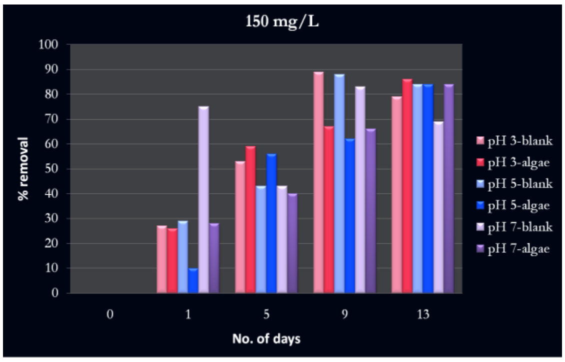

Figure 6: Percentage removal of Cr (VI) at 150mg/l initial conc. of Chromium solution with contact time

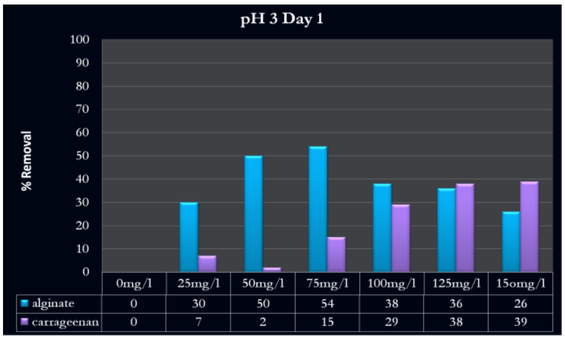

Figure 7: % removal of Cr(VI) by immobilized alginate and carrageenan at pH 3 Day 1

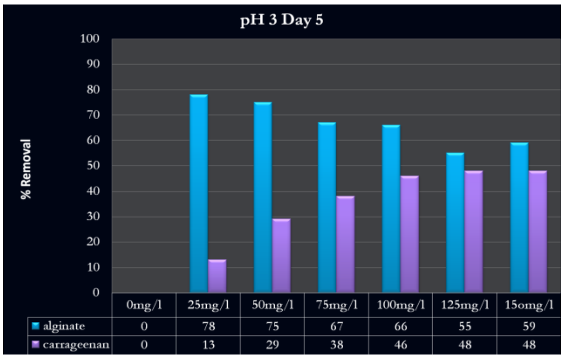

Figure 8: % removal of Cr(VI) by immobilized alginate and carrageenan at pH 3 Day 5

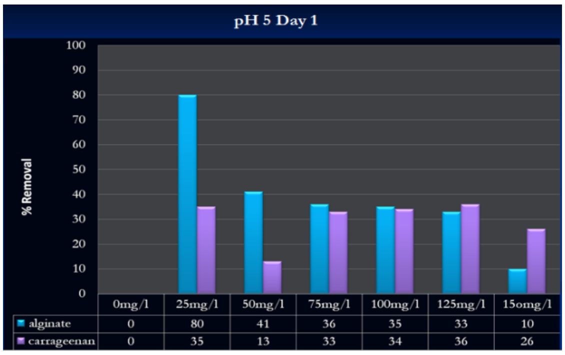

Figure 9: % removal of Cr (VI) by immobilized alginate and carrageenan at pH 5 Day 1

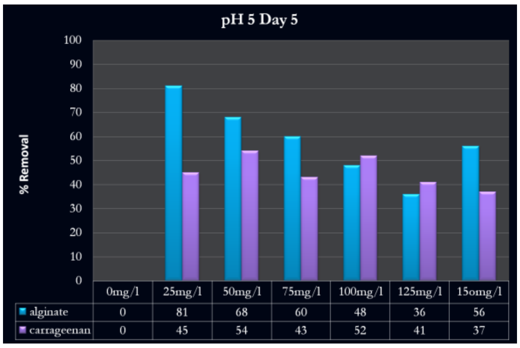

Figure 10: % removal of Cr (VI) by immobilized alginate and carrageenan at pH 5 Day 5

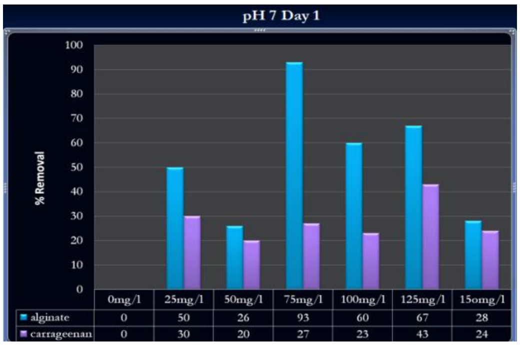

Figure 11: % removal of Cr (VI) by immobilized alginate and carrageenan at pH 7 Day 1

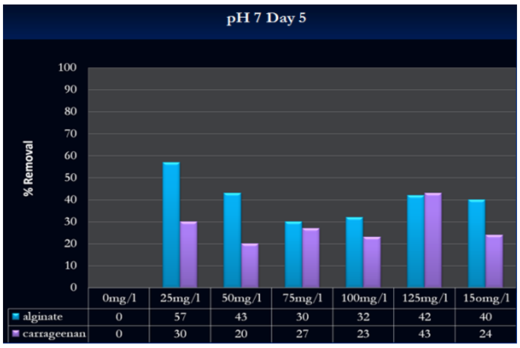

Figure 12: % removal of Cr (VI) by immobilized alginate and carrageenan at pH 7 Day 5

prepared without adding algal sample. The percentage removal of Cr(VI) by blank alginate beads and algae immobilized alginate beads for at different initial metal ion concentration (25-150mg/l) at regular intervals (4days) and 3 different pH (3, 5 and 7) was measured. The results are shown in figure 1 to 6. Figure 7 to 12 represent the metal removal efficiency by the immobilized algal alginate beads and immobilized algal Carageenan cubes

- Efficient in removal of Cr (VI) at lower concentrations (25, 50, 75, 100 mg/l). At 150mg/l of initial concentration of Cr (VI) solution, the blank beads showed slightly greater efficiency than the immobilized algal beads. It is inferred that as the initial concentration of metal ion increases efficiency of metal uptake by the algal beads decreases. This could be due to the detrimental effect of high concentration of Cr (VI) on algae.
- Maximum metal uptake was observed on 9th day for all the cases. At pH 3, % removal of Cr (VI) from Algae immobilized in alginate beads for initial metal ion concentration 25, 50, 75, and 100 mg/L was 89, 96, 98 and 89% and that from blank beads was 33, 79, 87and 88% respectively. At pH 5, % removal of Cr (VI) from Algae immobilized alginate beads for initial metal ion concentration 25, 50, 75, and 100 mg/L was 87, 80, 69 and 61% and from blank beads showed 83, 82, 82 and 41% respectively. At pH 7, % removal of Cr (VI) from Algae immobilized alginate beads for initial metal ion concentration 25, 50, 75, and 100 mg/L was 11, 26, 84 and 50% and the blank beads showed 27, 80, 88 and 86% respectively.
- When compared with the metal uptake efficiency of the immobilized alginate beads and carrageenan cubes, it was found that alginate beads had better metal uptake capacity. It was observed that the carrageenan cubes were not stable and disintegrated after 6 days of the experimental set-up. Hence, the absorbance readings could not be taken after the 6th day.

Conclusions

According to the study, it is observed there is consistent decrease in the chromium (VI) concentration uptake for both blank and algal beads at all the three pH values, i.e. 3, 5 and 7. Certain increase in the concentration of Chromium (VI) seen after day 9 may be attributed to the leaching out or desorption process which may occur in the algal cells due to saturation with the heavy metal. Immobilization of the algae in calcium alginate showed a better and more stable system of Chromium (VI) removal from the synthetic solution than carrageenan. The carrageenan cubes in the synthetic solution were seen to disintegrate after the 6th day of experimental set-up. The maximum removal of Chromium (VI) by *Chlorella pyrenoidosa* immobilized in the alginate matrix was seen at pH 3 with the initial metal concentration of 75 mg/l.

References

Abdel Hameed M S, (2006), Continuous removal and recovery of metals by alginate beads, free and alginate immobilized *chlorella vulgaris*, Africal Journal of Biotechnology, Vol.5, pp.1819-23.

Ahalya N, Ramachandra T V, Kammadi R D, (2003), Biosoption of heavy metals, Res. J. Chem. Environ. Vol.7, pp.71-78.

APHA, AWWA, WEF, (1998), Standard methods for the examination of water and wastewaters, 20th American Public Health association, American Water Works association, Water Environmental Federation.

Brinza L, Dring M J, Gavrilescu M, (2007), Marine Micro and Macro- algal species as biosorbents for heavymetals, Environment Engineering Management Journal, Vol.6, pp.237-51.

Garnham W.G., Codd G.A., and Gadd M.G., (1992), Accumulation of Cobalt, Zinc an Manganese by esturine green *Chlorella salina* immobilized in alginate microbeads, Environmental Science Technology, Vol.26, pp.1764-70.

K Ramakrishna, Ligy Philip, (2005), Bioremediation of Cr(VI) in contaminated soils, Journal of Hazardous Materials, Vol. B121, pp.109-107.

R Singh, (2012), Selective separation of lead ions from wastewater by immobilized chlorella based biosorbents, International Journal of Chemical and Environmental engineering, Vol.3, No.2, pp.119-126.

S C Agarwal and Manisha, (2007), Growth, survival and reproduction of *Chlorella vulgaris* with respect to culture age and different chemical factors, Folia Microbiol. Vol.52, No.4, pp.399-406.

Travieso L, A pellon, F. Benitez, E. Sanchez, R. Borja, N.O. Farrill and P.Weiland, (2002), Bio-alga reactor: preliminary studies for heavy metal removal, Biochem. Bioeng. Journal Vol.12, pp.87-91.