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# Cr(VI) Removal from Industrial Wastewater using Immobilized Algae

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## ABSTRACT

Industrial effluent with heavy metals is a threat to the species in the aquatic environment. It will be the boon if the effluent are free from heavy metals before discharged to these environment. Removal of these heavy metals would make the aquatic world free of pollution. The present research work describes the absorption of heavy metals Cr (VI) from industrial wastewater by immobilization of Spirulina platensis in sodium alginate beads. Biosorption is the phenomenon followed in this work for removal of heavy metals. The effects of pH, adsorbent dose, initial concentration and bead depth on the adsorption of chromium by the biomass were studied. The optimum removal percentage of Cr (VI) was observed at pH 2 for with algae and pH 6 for without algae. For optimum conditions the removal efficiency of synthetic chromium was observed to be 78% and 95% with and without algae respectively. Removal efficiency of 82% was found for industrial effluent of triton valves using algae as biosorbent. Hence for the removal of chromium wastewater *Spirulina platensis* proved to be an efficient biosorbent.

**KEY WORDS:** WASTEWATER, BIOSORPTION, CHROMIUM, SPIRULINA PLATENSI, BEADS.

## INTRODUCTION

Environmental pollution is a very serious threat in the current circumstances. Aappreciable amounts of both inorganic and organic chemicals and its byproducts are present in industrial effluents (Werle 2014 & Sharmila A 2020). Major source for heavy metal pollutions are rapid industrialization and urbanization (Prathap Kumar 2009). Industries like electroplating, tanning etc., are major source of effluents with metals which accumulate in aquatic animals and ecosystem through food chain causing health hazards (Hazrat Ali 2014). Accumulation of heavy metals in plants and soils is due to persistent of heavy metals in nature (Raja Rajeswari T. et al.,) Chromium rank among the priority metals because of high degree of toxicity which affects public health significantly Paul B and Sonia Aslam 2017). Highly toxic carcinogen is chromium.

In humans effects like DNA mutations, nausea, nasal and skin irritation, lung carcinoma are observed. In the environment, chromium persist in two oxidation states: Cr(III) and Cr(VI). Trivalent chromium is less toxic than hexavalent Chromium. The hexavalent chromium comes under the group "A" which is having carcinogen and mutagenic properties. To meet the National Regulatory standards chromium must be removed before discharging the effluent to natural water bodies which helps in minimizing health hazard. To remove heavy metals many conventional methods are employed. Adsorption is most preferred and widely used method because of its cost, simple design and operation and insensitivity to toxic substances. For heavy metal removal biological remediation processes are very effective method. One best sustainable treatment for the treatment of industrial

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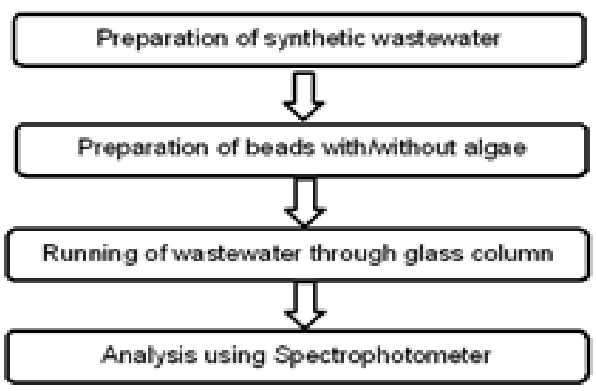
wastewater would be use of algae. Hence an attempt has been made to study the efficiency of algae in the removal of chromium.

## MATERIALS AND METHODS

The algae species Spirulina platensis of Domain -Bacteria, Phylum- Cyanobacteria and Genus- Spirulina was culture in the laboratory.

Figure 1: Flow chart of methodology




**2.1 Preparation of synthetic wastewater:** Preparation of Stock Chromium solution includes dissolving 2.484 g of potassium di chromate ($K_2Cr_2O_7$) in 1L of distilled water. Take 10mL of stock chromium solution and make it up to 1000mL to make it as standard chromium solution. Di phenyl carbozide solution is prepared by taking 1g of Di phenyl carbozide in 200mL of distilled water. 1:1 sulphuric acid is prepared by adding 100 mL of sulphuric acid in 100 mL distilled water.

**2.2 Preparation of beads with and without algae:** Beads are prepared by using sodium alginate powder. 3g of Sodium alginate powder is weighed and dissolved in 100 mL of distilled water and it is stirred thoroughly for uniform mixing of alginate with distilled water. Alginate solution is kept in refrigerator for about 30 minutes. Then the semi liquid alginate solution is drawn into syringe. Calcium chloride solution is prepared by weighing 2g of $CaCl_2$ and dissolved in 100 mL of distilled water. The alginate solution taken in syringe is dripped into $CaCl_2$ solution drop wise and it is left overnight. Thus the alginate beads are prepared which is as shown in flow chart (Figure 1). Same procedure is followed for the preparation of beads for known dosage of algae.

**2.3 Treatment of synthetic wastewater through glass column:** The synthetic chromium solution prepared with the optimum conditions are taken into beaker, with the help of peristaltic pump the solution is let to flow through the beads in the glass column. Constant rate of flow is maintained. Constant head is maintained by controlling inlet and outlet flow. The solution coming out from the glass column is collected at equal time intervals.

**2.4 Analysis using Spectrophotometer:** The collected sample is taken into Nessler's tube (50mL) and the reagents are added. To analyse the chromium solution in spectrophotometer 2.5 mL of 1:1 sulfuric acid is added and is left for 10 min for the reactions to take place and 2 mL of Di phenyl carbozide solution is added the solution turns pink in color. The spectrophotometer is calibrated with blank solution and the wavelength is set to 540nm. Once the instrument is calibrated the solution is analysed.

## RESULTS AND DISCUSSION

This deals with the results obtained for various conditions using sodium alginate beads with and without algae. It also includes the results of industrial wastewater for optimum conditions.

**3.1 Beads without algae:** Initial pH range from 2 to 7 was changed to study the effect of pH. The Cr(VI) concentration of 3mg/L, bed depth 10cm and contact time of (8, 16, 24) minutes were maintained. Figures 2-7 indicates the relation between the contact time and initial pH of the solution. Figure 2 shows the relation between pH and removal efficiency of Cr(VI). Maximum Cr(VI) removal efficiency of 64% was observed at pH 2. At pH 6, Cr(VI) removal efficiency was about 53%. At low pH value biosorbent is positively charged due to protonation. Electrostatic attraction occurs due to dichromate ions as anion.

Figure 2: Contact time (min) v/s Removal efficiency of Cr(VI) for pH 2

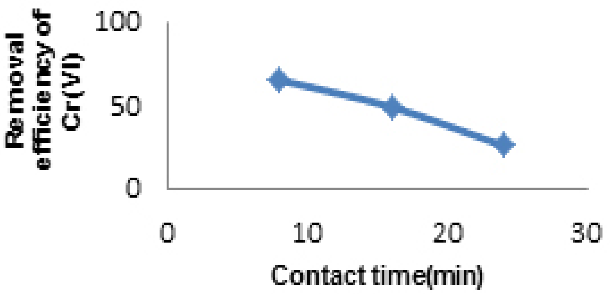



Figure 3: Contact time(min) v/s Removal efficiency of Cr(VI) for pH 3

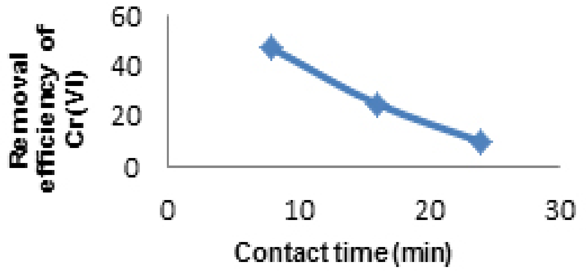


Figure 4: Contact time (min) v/s Removal efficiency of Cr(VI) for pH 4

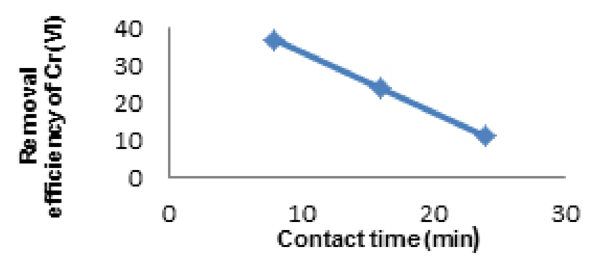



Figure 5: Contact time (min) v/s Removal efficiency of Cr(VI) for pH 5

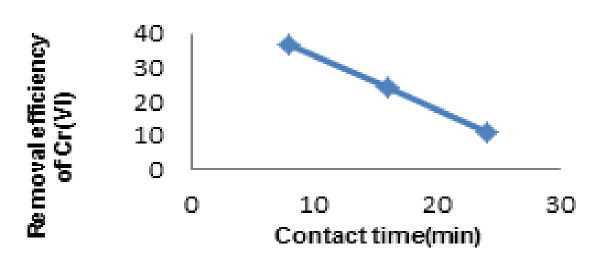



Figure 6: Contact time (min) v/s Removal efficiency of Cr(VI) for pH 7

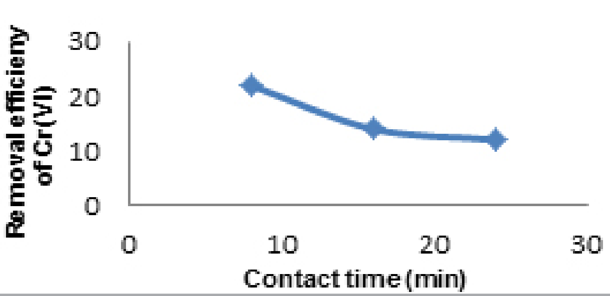
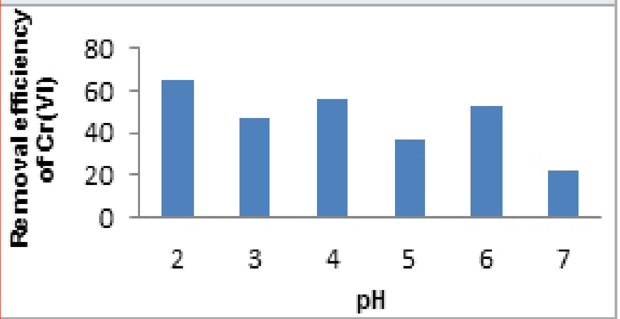



Figure 7: pH v/s Removal efficiency of Cr(VI)




**3.2 Effect of initial Cr(VI) concentration:** The effect was observed with maintaining pH of the solution to 2, contact time 8, 16 & 24 minutes and bed depth of 10cm along with varying Cr(VI) concentration and results were presented in Figures 8-11. Maximum removal of Cr(VI) was observed in Cr(VI) concentration of 1.5 mg/L of about 78%. With the varying concentration of Cr(VI) from 1mg/L to 5mg/L, adsorption increased. Two factors responsible for adsorption efficiency are positive force due to lower concentration of Cr(VI) which enhances the adsorption process and increase in binding sites for greater number of Cr(VI) absorption. Binding sites saturation was observed which led to gradual decline in removal percentage of Cr(VI).

Figure 8: Contact time (min) v/s Removal efficiency of Cr(VI) concentration of 1.5 mg/L

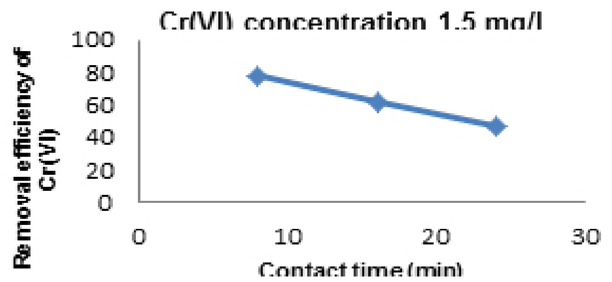



Figure 9: Contact time(min) v/s Removal efficiency of Cr(VI) concentration 5mg/L

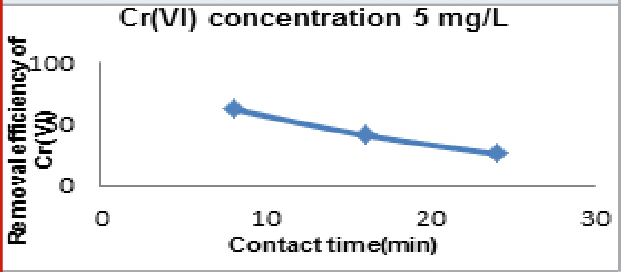



Figure 10: Contact time (min) v/s removal efficiency of Cr(VI) concentration of 3 mg/L

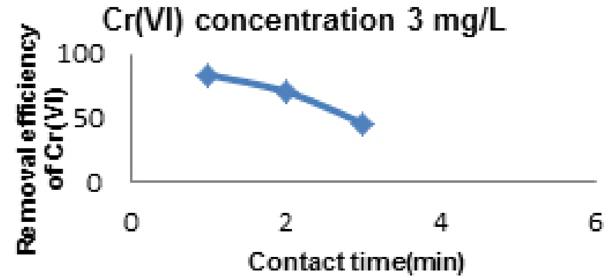
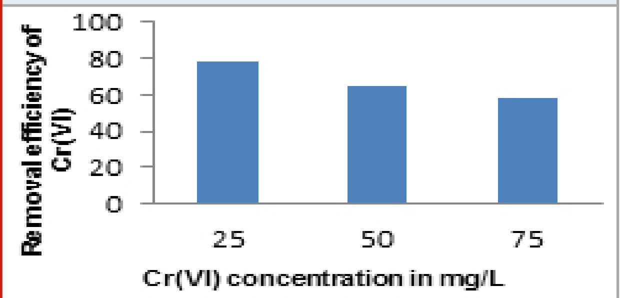



Figure 11: Concentration of Cr(VI) v/s Removal efficiency of Cr(VI)



**3.3 Effect of bed depth:** The Cr(VI) solution passed through column having varying bed depth of 5cm and 10cm. The pH was maintained to the optimum pH of 2 and 1.5mg/L concentration of Cr(VI) was maintained. Removal efficiency of Cr(VI) is shown in Figures 12-14. The study was carried for varying bed depth of 5 cm and 10 cm. It was observed that, increase in bed depth showed maximum removal efficiency of chromium (95%). This is because of more number of sites available for adsorption.

Figure 12: Contact time(min)v/s Removal efficiency of Cr(VI) for bed depth of 5 cm

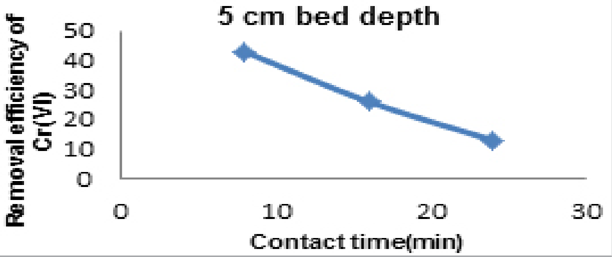



Figure 13: Contact time(min) v/s Removal efficiency of Cr(VI) for bed depth of 10cm

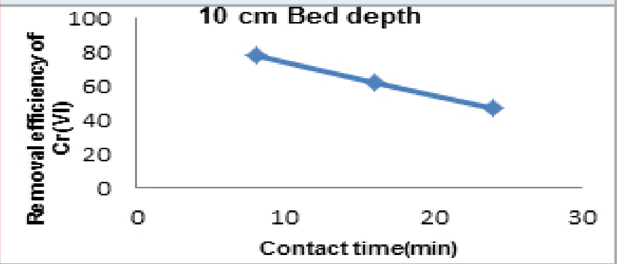



Figure 14: Bed depth in cm v/s Removal efficiency of Cr(VI)

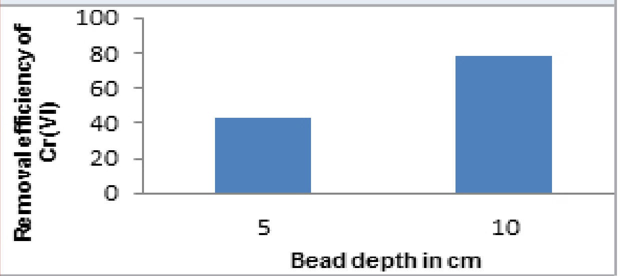



Figure 15: Contact time(min) v/s Removal efficiency of Cr(VI) for pH 2

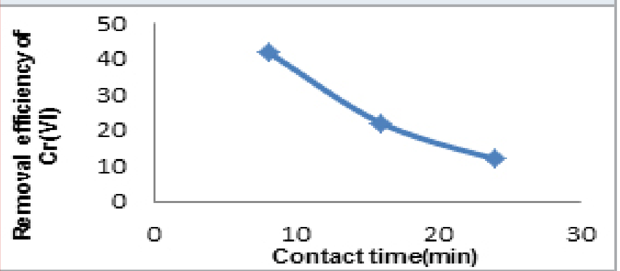



Figure 16: Contact time(min) v/s Removal efficiency Cr(VI) for pH 3

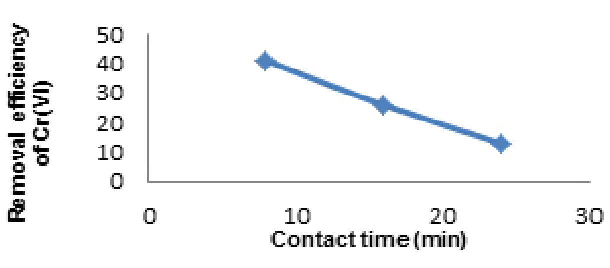



Figure 17: Contact time(min) v/s Removal efficiency of Cr(VI) for pH 6

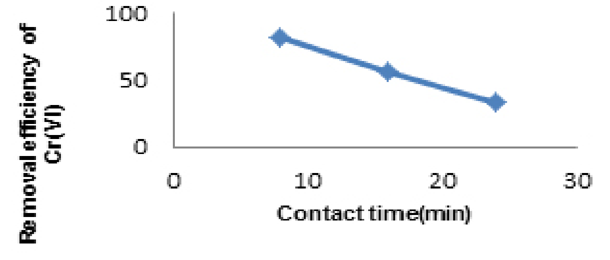



Figure 18: Contact time(min) v/s Removal efficiency of Cr(VI) for pH 7

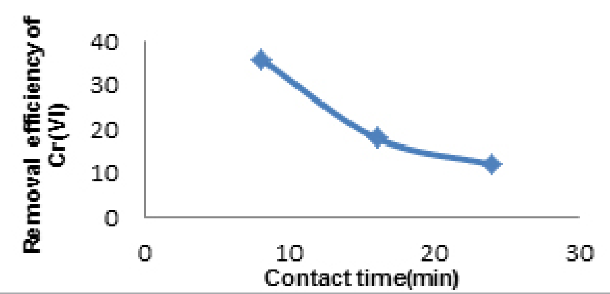
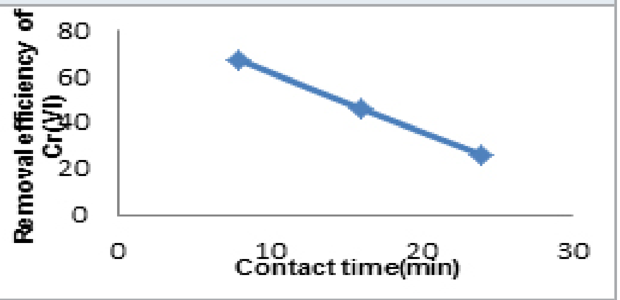



Figure 19: Contact time(min) v/s Removal efficiency of Cr(VI) for pH 9




### 3.4 Beads with algae

**3.4.1 Effect of pH:** The pH of 2, 3, 6, 7 & 9 was preferred to know the effect of biosorption of Cr(VI). 3mg/L of Cr(VI), biosorbent dosage of 20mL, contact time was varied from 8, 16, 24 minutes and bed depth of 10 cm was maintained. The maximum removal efficiency of different pH is as shown in Figures 15-20. The Figure 19 showed increases in metals ions adsorption with increase in pH from 2 to 6. Cell wall protonation affects biosorption while preparation of algae at acidic pH. With increase in pH this effect becomes minimum. At pH 6 maximum adsorption was obtained. Initially interaction will be with phosphate and carboxylate groups of the cell wall component.

Figure 20: pH v/s Removal efficiency of Cr(VI)

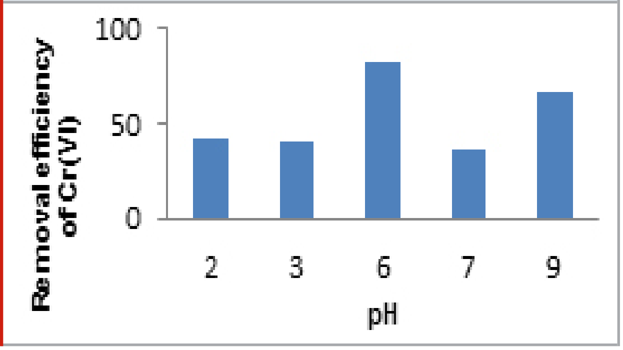



Figure 21: Contact time(min) v/s removal efficiency of Cr(VI) 1.5 mg/L

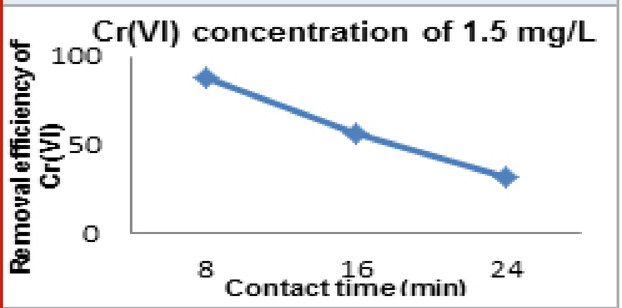



Figure 1: Conceptual Model of Cultural Tourism for Chinese Tourists

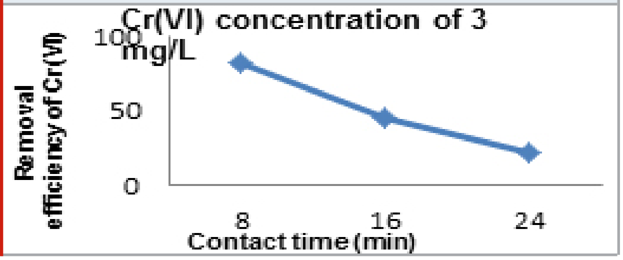
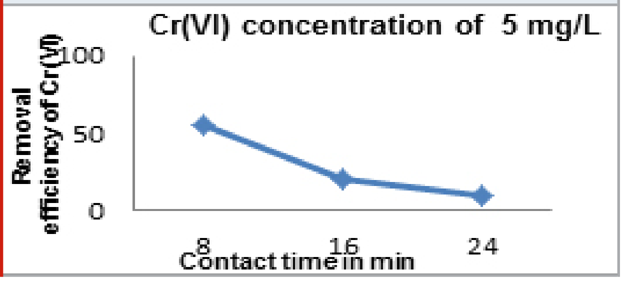



Figure 23: Contact time(min) v/s Removal efficiency of Cr(VI) concentration 5 mg/L




**3.4.2 Effects of Concentration of Cr(VI):** At the start Cr(VI) concentration varied from 1.5 mg/L to 5 mg/L with pH of the solution to 2 ,contact time 8, 16, 24 minutes, spirulina dosage of 20mg/L, and bed depth of 10cm. The results were presented in Figures 21-23.

**3.4.3 Effect of bed depth:** In this study, the Cr(VI) solution was passed through the column having varying bed depth of 5cm and 10cm. The optimum pH of 2, initial Cr(VI) concentration of was maintained to 1.5mg/L, spirulina dosage of 20mg/L and contact time 8, 16 & 24 minutes were maintained. The efficiency of Cr(VI) after removal is as shown in Figures 24-26.

Figure 24: Contact time(min) v/s Removal of Cr(VI) for bed depth of 5 cm

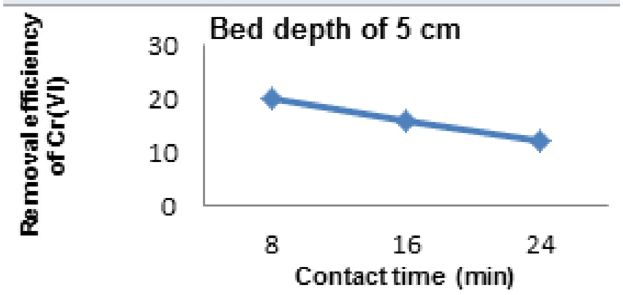



Figure 25: Contact time(min) v/s Removal efficiency of Cr(VI) for bed depth of 10 cm

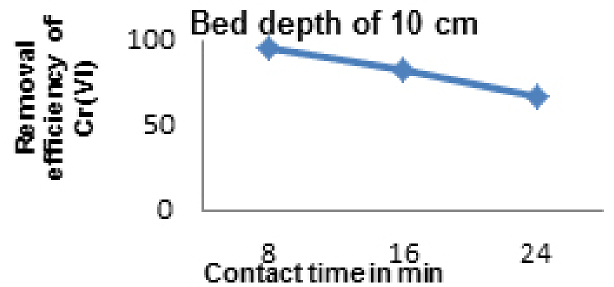
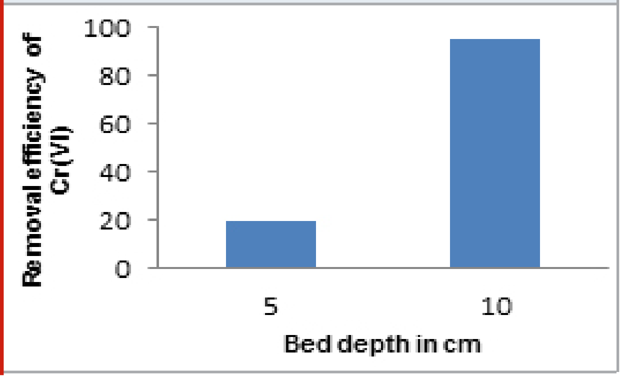



Figure 26: Bed depth in cm v/s Removal efficiency of Cr(VI)




**3.4.4 Effect of biosorbent dosage:** Spirulina platensis dosage was varied in 20mL, 40mL and 60mL to 3 w/v sodium alginate solution. It was observed that beyond

20mg/L the beads formed were not perfect and solution did not mixed well. The sodium alginate solution becomes very viscous and beads formation through the syringe becomes difficult. Biosorption of metal ions increased with dosage of 60 mL biosorbent to sodium alginate solution. The increase is probably attributed to the surface area available for the sorption of metals.

**3.5Characterization of algal beads using SEM:** To study the surface morphologies of the biosorbent Scanning Electron Microscopy (SEM) is preferred. SEM images of alginate beads exposed to chromium ions for different magnification are presented in Figure 27- 30. SEM images indicates that unexposed beads are uniform and smooth surface and exposed beads showed relatively dynamic and rough surface. Images clearly shows the ability of Spirulina platensis biomass to adsorb and remove chromium ions from the solution. Biomass wall with fragile, irregular surface with bright spots observed after accumulation of Cr(VI).

**3.6 Chromium removal for Industrial wastewater:** The Industrial effluent of Triton valves having initial Cr(VI) concentration of 3.7 mg/L was passed through the column having bed depth of 10cm, optimum pH of 6, Spirulina dosage of 20mg/L and contact time 8,16 & 24 minutes were maintained. The result showed maximum removal efficiency of 82%. This proved that the algae is one of the effective method for the chromium removal from industrial wastewater.

Figure 27: SEM image of Sodium alginate beads before treatment (1mm)

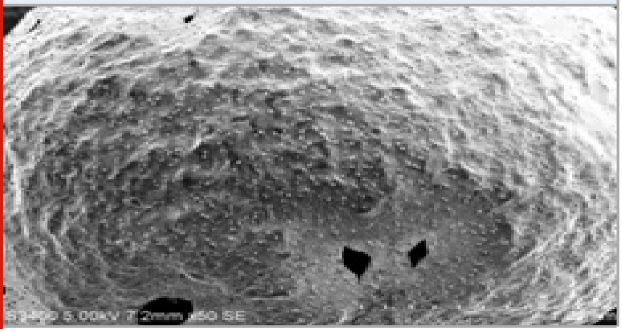


Figure 28: SEM images of Sodium alginate beads before and after treatment (500µm)

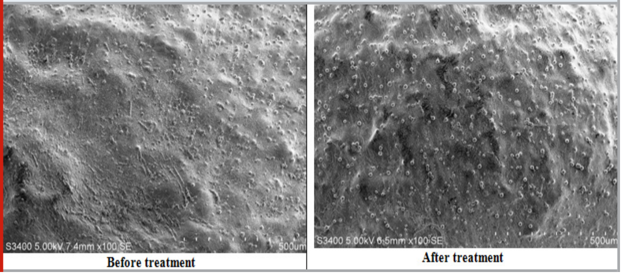



Figure 29: Sodium alginate beads images using SEM before and after treatment (100µm)

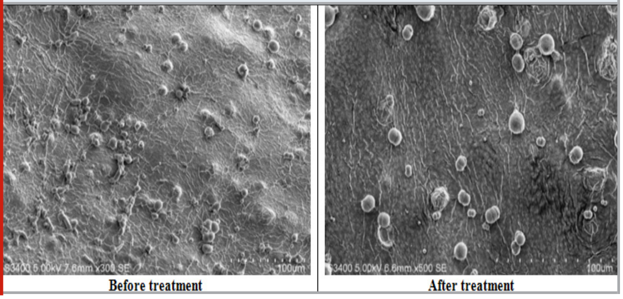
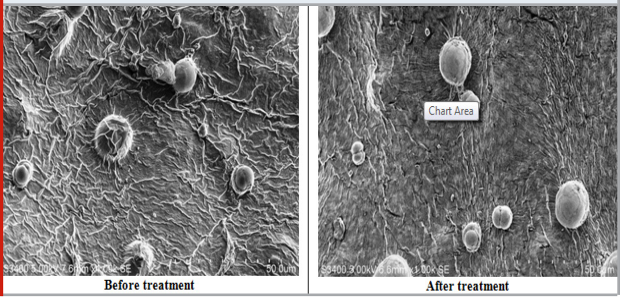



Figure 30: Sodium alginate beads images using SEM before and after treatment (50µm)




## CONCLUSION

The study shows that the Spirulina platensis as a algal biosorbent can be used as an alternative technique for removal of Cr(VI) from industrial wastewater. Based on the study, following conclusions were drawn.

- The optimum condition obtained for the maximum removal efficiency of Cr(VI) for synthetic wastewater without using algae was found to be pH 2, bed depth of 10 cm with 1.5 mg/L concentration of Cr(VI)
- The efficiency of Cr(VI) removal for synthetic wastewater without using algae for optimum condition was found to be 78%
- The optimum condition obtained for the maximum removal efficiency of Cr(VI) for synthetic wastewater with algae was found to be pH 6, bed depth of 10 cm for Cr(VI) concentration of 1.5 mg/L
- For optimum condition 95% Cr(VI) removal was observed without using algae
- After passing through beads, the fragile and irregular surface with appearance of bright spots in Scanning Electron Microscopy (SEM) images showed biosorption of chromium was effective through immobilized Spirulina Plantensis
- Maximum removal efficiency of 82% was observed for Industrial effluent for optimum condition with algae.
- Immobilized Spirulina platensis can be used as eco-friendly technique for Cr(VI) removal from industrial wastewater

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