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Biosorption of heavymetal chromium (VI) by red alga *Kappaphycus alvarezii*

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ABSTRACT

Biosorption of heavy metals using seaweed has been extensively described topic. In this study *Kappaphycus alvarezii* which is available algal biomass and a valuable product with a ready market was used as a biosorbent to remediate hexavalent Chromium. *Kappaphycus alvarezii*, a red marine alga was tested for its ability to remove Cr(VI) from aqueous solution. Biosorption of Cr(VI) from aqueous solutions on *Kappaphycus alvarezii* was investigated in a well-stirred batch reactor. The biosorption mechanisms of Cr were examined by Scanning electron microscope (SEM) with (EDAX). A series of experiments were conducted in a batch system to evaluate the effect of system variables. The effect of pH, initial Cr concentration, dose of adsorbent and temperature were considered. In 37ºC, pH of 5, contact time of 120 minutes and 180g dose of adsorbent used to attain 70% of the removal level of Cr(VI). Concerning the maximum absorption efficiency *Kappaphycus alvarezii* can be used effectively as a biosorption of Cr(VI) from tannery waste water.

Introduction

Heavy metals are one of the most widespread and dangerous family of hazardous materials that can be encountered in natural and waste waters due to increasing development of industrial processes such as metal plating facilities, mining operations and tanneries (Odia *et al.,* 2016, Bailey *et al.,* 1999). Cr is among the most toxic and carcinogenic metal which is the powerful oxidizing agent. It has the potential to pass through cell membranes and reduces to reactive intermediates that attack DNA, proteins and membrane lipids causing damage to the cellular integrity and function (Vu *et al.,* 2016).

Hexavalent (Cr(VI)) and trivalent (Cr(III)) are two stable oxidation species widely existed in aquatic environments. Cr(VI) species in aquatic systems with strong oxidizing ability are highly soluble, mobile and toxic and has drawn worldwide attention. In contrast, Cr(III) species are relatively stable, less-toxic and have low solubility in water (Mu *et al.,* 2015). According to EU and WHO standards, the maximum total Cr(VI) content in drinking water is 0.05 ppm (Zelmanoy *et al.,* 2011). Conventional techniques for removing dissolved heavy metals include chemical precipitation, carbon adsorption, ion exchange, evaporation and membrane processes which depend on number of factors like waste water type and concentration, level of clean-up and economics.

In last few decades, biosorption has emerged as efficient alternative technique for the removal of heavy metals. It can be a promising alternative method of treating industrial effluents because its cost effective, high metal-binding capacity, high efficiency in dilute effluents and environmental friendliness (Pavasant *et al.,* 2006, Tbaraki *et al.,* 2014). The major advantage of this technique was reusability of biomaterial, low operating cost, removal of heavy metals from effluent irrespective of toxicity and no secondary compounds production which might be toxic (Farhan, 2015).

Various types of biosorbents such as microbes, algae, agricultural and industrial wastes were able to effectively remove Cr(VI). In general, it was not so easy to maintain a dominant microbial culture in the Cr(VI)-bearing effluents. So non-living state of biomass as yeast, microalgae, fungi and seaweed were used for removing Cr(VI). The size of seaweed biomass is large enough to facilitate its application without a cumbersome solid-liquid separation process, compared to microorganisms (Yun *et al.,* 2001). Seaweed biomass is a renewable natural resource and is available through the world. Currently, seaweed biomass is cultivated and harvested to

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manufacture hydrocolloids (agar, alginate and carrageenan) for use in the food and chemical industries. Apart from these uses, seaweed biomass is utilised to remove heavy metals from contaminated wastewater (Hashim and Chu, 2004).

Seaweeds are extremely efficient biosorbents with the ability to bind various metals from aqueous effluent because of their high surface area and high binding affinity. Numerous chemical groups may be responsible for the metal biosorption by seaweeds e.g. carboxyl, sulphonate, hydroxyl and amino group (Sari and Tuzen, 2008). The importance of these groups depends on the factors such as quantity of sites, their accessibility and affinity between site and metal. The mechanism of metal binding includes ion-exchange and complex formation, may differ according to biomass type, origin and processing to which it has been subjected (Park *et al.,* 2005, Murphy *et al.,* 2008).

The most common types of algae (Chlorophyta, Phaeophyta and Rhodophyta) showed different sorption behavior due to the different structures of the cell wall polysaccharides. Several reports have shown evidence for the use of brown, green and some of red algae in Cr(VI) biosorption. Typical algal cell walls of Phaeophyta and Rhodophyta are comprised of fibrillar skeleton and an amorphous embedding matrix. The Phaeophyta algal embedding matrix consists predominantly of alginic acid or alginate with a smaller amount of sulfated polysaccharide whereas the Rhodophyta contains a number of sulafated galactants (Wang *et al.,* 2008).

Kappaphycus alvarezii, a tropical red alga, native to Philippines, is primarily carried out for its carrageenan content (Ghosh *et al.,* 2015). In southeast coast of India, it was successfully cultivated in Gulf of Mannar and Palk Bay coast of Tamilnadu on commercial scale due its demand from phycocolloid industry. *Kappaphycus alvarezii* was reported as a potential biosorbent for remediation of Cr(VI). So, in this study *Kappaphycus alvarezii* was used as a biosorbent to reduce Cr(VI) because of its easily available nature and metal adsorbing capacity.

Materials and Methods

Seaweed collection and identification

Red seaweed *Kappaphycus alvarezii* was collected from Mandapam, Tamilnadu, India. Sample was collected in ice cold bags and taken to laboratory. Fresh seaweed was further rinsed with double distilled water to remove the impurities and mineral contamination present in seaweed due to seawater habitation. Sample was shade dried, powdered, sieved and stored at -4°C for further use.

Chemicals

$K_2Cr_2O_7$ which was used to prepare Cr(VI) solution, was purchased from Sigma Aldrich, Mumbai, India. All the chemicals were of analytical reagent grade and used without further purification. In all experiments deionized water was used.

Biosorption studies

The experiment was carried out by batch method. 250mL conical flask was taken and the stock solution of Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ in deionized water to make a final concentration of Cr(VI). Then required volume of powdered seaweed was added in that conical flask and kept in shaking condition for 24 hours at 180rpm. The reduction efficiency was calculated by the following equation.

$$\text{Biosorption}(\%) = ((Ci - Cf) / Ci) \times 100$$

Whereas, Ci=initial concentration and Cf= final concentration (Yakouta *et al.,* 2015).

Analytical method

In all experiments, 5 ml of sample was periodically withdrawn and separated in four 1 ml aliquots, which were centrifuged in eppendorf tubes for 2minutes using an eppendorf minispin centrifuge at 13,000 rpm. The supernatant of each sample was used for Cr_{tatol} analysis (Montensinos *et al.,* 2014). The total Cr was analyzed using Atomic Absorption Spectrometer (AAS) (Varian AA240).

Statistical Analysis

All the experiments were performed in triplicate and the data obtained were expressed as mean ± standard error. One-way ANOVA was used to calculate the mean difference is significant at p value, $P < 0.001$. All statistical was done using SPSS,version 16.0 software. (Balaji *et al.,* 2015)

SEM and EDAX report of Seaweed

The untreated and treated seaweed was examined using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray analysis (EDAX). SEM has been recorded by FEI quanta FEG200-High resolution. The sample was observed at 10,000X magnification with an accelerating voltage of 20kV.

Results

In this study, the powdered seaweed was used for the biosorption of Cr(VI). The red seaweed *Kappaphycus alvarezii*

Fig.1. *Red seaweed* Kappaphycus alvarezii

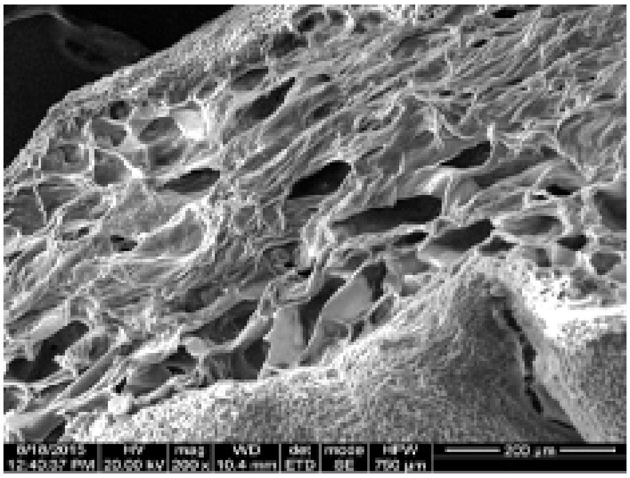

Fig. 2. *SEM image of* Kappaphycus alvarezii *cross section*

is shown in Figure 1 and the cross section of the seaweed is given in figure 2.

Effect of pH on Biosorption

In biosorption process pH of the solution is an important parameter. The effect of pH on the biosorption of Cr(VI) by *Kappaphycus alvarezii* was studied with different pH values from 3 to 11. The highest biosorption efficiency occurred at the level of pH 5. The influence of pH on the percentage biosorption of Cr(VI) is depicted in the figure 3. The biosorption decreased at both lower (acidic) and higher (alkaline) pH of the solution.

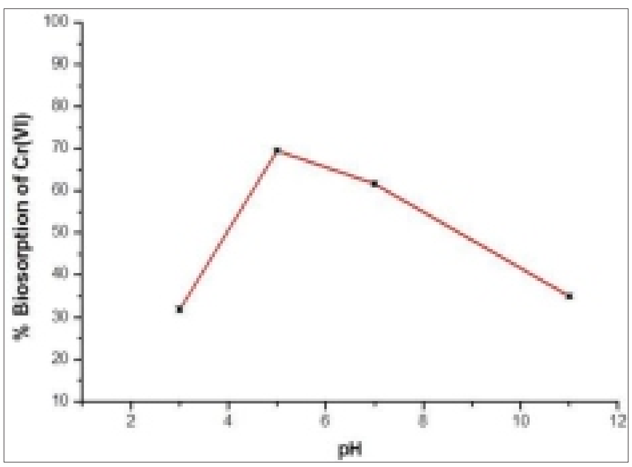

Fig. 3. *Effect of pH on Cr(VI) biosorption*

Effect of Biomass dosage on Biosorption

Batch experiment was conducted to investigate the influence of biomass dosage of *Kappaphycus alvarezii* on the biosorption of Cr(VI) ions and the trend is shown in Figure 4. The biomass was studied at different dosage range from 30mg to 180mg. The maximum biosorption of the metal occurred at the biomass dosage of 180mg. At higher dosage the biosorption

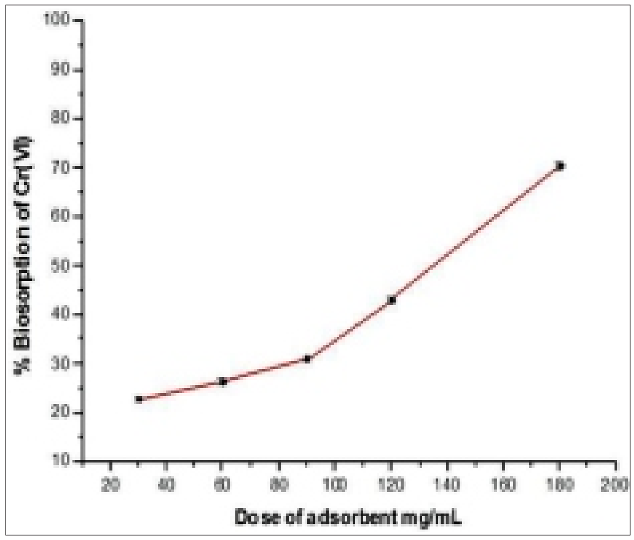

Fig. 4. *Effect of absorbent* (Kappaphycus alvarezii) *dose on Cr(VI) biosorption*

of Cr(VI) was not increased significantly.

Effect of temperature on Biosorption

Effect of temperature on Cr(VI) biosorption is presented in Figure 5. It was observed that the room temperature (32°C) is favourable than that of the higher temperatures. The experiment was conducted with different temperature (32°C,60°C,80°C,120°C). Good sorption percentage around 62% was observed at 32°C.

Effect of initial metal concentration on Biosorption

Biosorption experiments were conducted by taking different initial metal concentrations like v*iz.,* 10ppm, 30ppm, 50ppm and 100ppm. Metal solutions were prepared as mentioned earlier. With the increase in metal concentration percentage of absorption was decreased (Fig. 6).

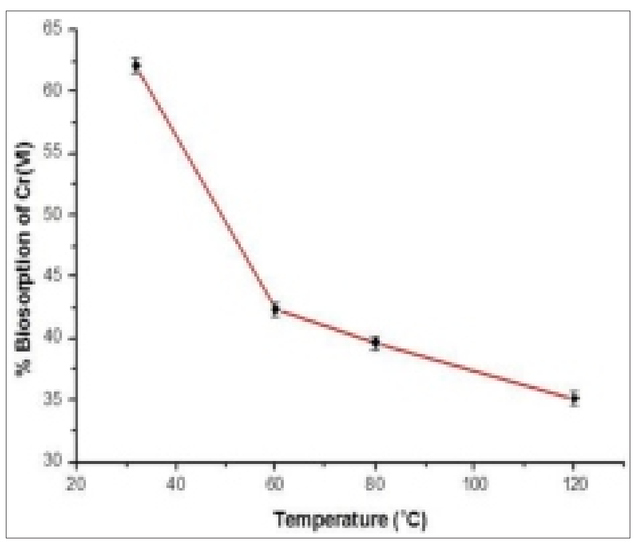

Fig. 5. *Effect of temperature on Cr(VI) biosorption*

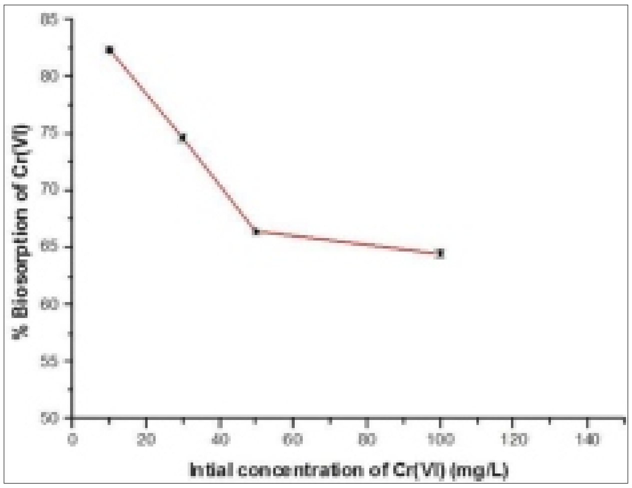

Fig. 6. *Effect of initial concentration on Cr(VI) biosorption*

Effect of contact time on Biosorption

The adsorption experiments of Cr(VI) were carried out for different contact times (0 to120minutes) with a fixed adsorbent dose of 180 mg/ml, initial concentration 100ppm at pH 5 and the temperature was 32C. The results obtained were plotted in Figure 7. The biosorption percentage of metal was increased with increase in contact time. The maximum sorption took place at 120 min and again after 120min there was no effective changes in biosorption process.

SEM and EDAX report of seaweed

The untreated and Cr(VI) treated seaweed biomass samples were analyzed using SEM and EDAX. The SEM image in Figure 8 showed that the untreated biomass sample had an irregular and porous surface, which provided a large surface area. In Figure 9, the SEM image showed Cr(VI) treated biomass sample with considerable differences in surface morphology. The EDAX (Figure 10) was taken after treatment of Cr(VI). The peaks at C, O, Na, Mg, S, Cl, and K were naturally

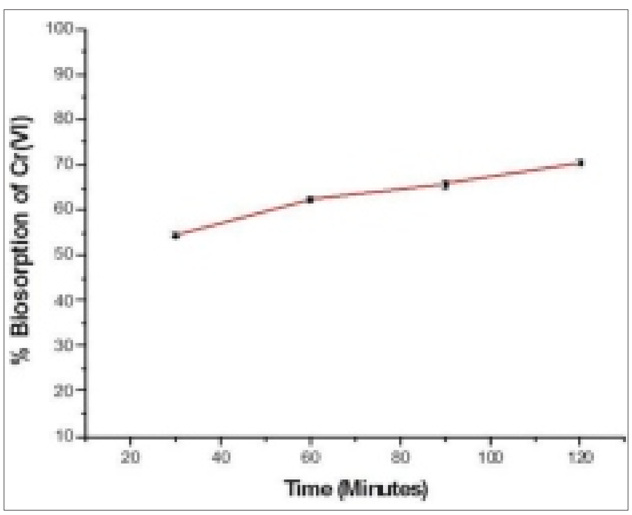

Fig. 7. *Effect of time on Cr(VI) biosorption*

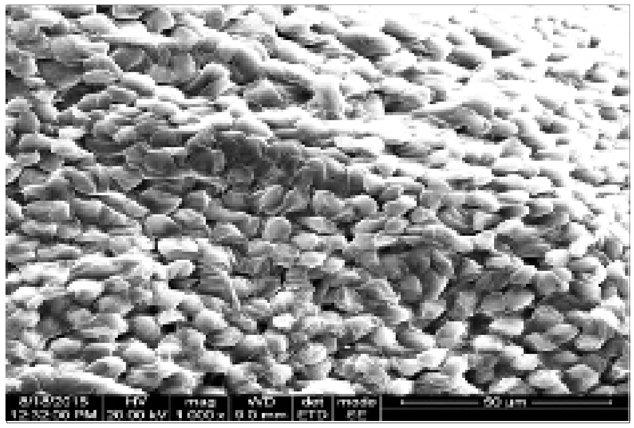

Fig. 8. *SEM image of Cr(VI)-untreated seaweed*

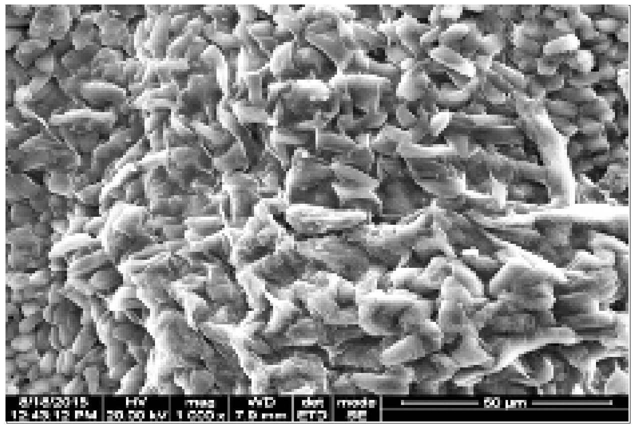

Fig. 9. *SEM image of Cr(VI)-treated seaweed*

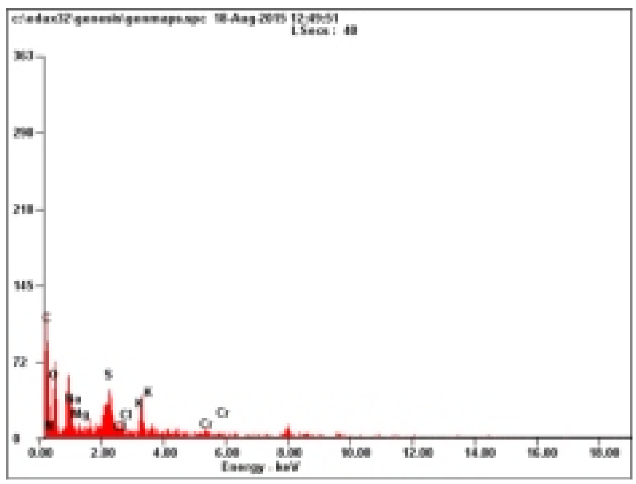

Fig.10. *EDAX of Chromium treated seaweed*

present in seaweed and Signal at Cr indicated the adsorption capacity of seaweed.

Discussion

Kappaphycus alvarezii is easily available seaweed and in the present study it was used as a biosorbent for remediation of Cr(VI). Wild and farmed crops of red seaweed

Kappaphycus alvarezii (Doty) Doty is primary source of commercially valuable anionic hydrocolloids called carrageenans (Barros *et al.,* 2006). The worldwide demand for carrageenan has recently increased, encouraging the commercial production and cultivation of *Kappaphycus alvarezii* outside the region of origin (Dawes, 1992). Kang, *et al.* (2011) studied the potential effect of *Kappaphycus alvarezii* biosorbent for Cr ions removal biosorption studies using seaweed in the investigation carried out so far, the powdered seaweed was used for the biosorption of Cr(VI). The parameters affecting the biosorption of Cr(VI) using the red seaweed was studied in detail. The effect of these parameters was discussed below.

Effect of pH on Biosorption

The percentage of biosorption increased from 31% at pH 3 to 69% at pH 5 and further increasing pH significantly decreases the biosorption percentage around 34%. In this study at pH 5 seaweed showed maximum percent of biosorption. This result may be correlated with the findings of Desta, (2013) using agricultural waste to remove textile metal. The pH of the solution had significant impact on heavymetals uptake. It determines the surface charge of the sorbent and its degree of ionization.

Effect of Biomass dosage on Biosorption

The dose of biomass found to be 180 mg/ml or maximum biosorption of Cr(VI) ions. Further increase in biomass does not affect the biosorption percentage greatly. This may be due to the unavailability of binding sites to the metal and also due to the blockage of binding sites with excess biomass. The amount of adsorbent (biomass) available in solution determines the number of active binding sites available for metal ions (Akpomie and Dawodu, 2015).

Effect of temperature on Biosorption

In this experiment, there was a decrease in sorption percentage with increasing the temperature and the maximum biosorption percentage around 62% was observed at 32°C. Temperature changes affect a number of factors which are important in heavy metal ion biosorption (Singh and Chopra, 2014).

Effect of initial metal concentration on Biosorption

In this study, the maximum initial metal concentration (100ppm) was maintained to check all other parameters, but the biosorbent was more effective on decreased initial concentration. Azouaou *et al.* (2013), explained the percentage of removal decreases with increasing metal ion because of all the biosorbents has a limited number of active sites, which become saturated at certain concentration and adsorption of metals by any adsorbent is highly dependent on the initial concentration of metal ion.

Effect of contact time on Biosorption

The biosorption percentage of metal increased with increasing the contact time. The equilibrium time was 120 min for reach maximum sorption (70%) level of Cr(VI). The increased contact time changed the metal sorption percentage of biomass was increased. While increasing the contact time above 120min was not appreciable increase in the biosorption. It may be due to the unavailable of binding sites in biosorbent, because of the occupation of Cr(VI) ions. Gill *et al.* (2014) stated that the reason for increased adsorption with the time may be due to the availability of large number of vacant in binding sites and afterwards it may show the repulsive between the metal ions present on the solid and liquid phases.

SEM and EDAX report of seaweed

The SEM image showed the Cr(VI) treated biomass sample with considerable differences in surface morphology. The result is exactly correlated with that of Kang *et al.* (2011). The mound-like structure indicates that Cr(VI) replaced metals on the cell wall and the strong signal at Cr in EDAX indicated the adsorption occurred in seaweed. The present investigation reveals that the red seaweed *Kappaphycus alvarezii* is very efficient on Cr(VI) adsorption. It may be developed as an efficient biosorbent for treating effluent.

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