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Evaluation of the Marine Algae *Gracilaria salicornia* and *Sargassum* sp. For the Biosorption of Cr (VI) from Aqueous Solutions

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Abstract: In this study, the adsorption properties of two different marine algae (*Gracilaria salicornia* (red algae) and *Sargassum* sp. (brown algae) were investigated. Equilibrium isotherms were studied to evaluate the relative ability of the two algae to sequester Cr (VI) from aqueous solutions. The maximum biosorption capacity obtained was 45.959 mg g⁻¹ for *G. salicornia* and 33.258 mg g⁻¹ for *Sargassum* sp. at a solution pH of 4 and 50 mg L⁻¹ initial chromium concentration. A significant fraction of the total Cr (VI) uptake was achieved within 60 min. Biosorbed chromium ions concentrations increased with increasing concentrations of biosorbents and increasing pH. The biosorption of Cr (VI) on *G. salicornia* and *Sargassum* sp. could best be described by the Langmuir model ($R^2 > 0.997$ for *Sargassum* sp. and $R^2 > 0.999$ for *G. salicornia*).

Key words: Biosorption, chromium (VI), *Sargassum* sp., *G. salicornia*, equilibrium isotherms, pH

INTRODUCTION

Biosorption is an emerging and attractive technology which involves sorption of dissolved substances by a biomaterial. It is a potential technique for the removal of heavy metals from solutions and recovery of precious metals (Veglio and Beolchini, 1997). The process has gained importance due to its advantages over conventional separation techniques such as chemical precipitation, ion exchange, reverse osmosis, membrane filtration and activated carbon adsorption, which are used to remove toxic metals from waste streams. These advantages are the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time and no production of secondary compounds which might be toxic (Spinti *et al.*, 1995; Srinath *et al.*, 2002). A number of chromium compounds have great economic importance and are used extensively in chemical, metallurgical and refractory industries. The International Agency for Research on Cancer (IARC) has determined that Cr (VI) is carcinogenic to both humans and animals (International Agency for Research on Cancer, 1997). It is well recognized that the presence of heavy metals and aromatic compounds in the environment can be detrimental to a variety of living species, including man. Hexavalent chromium (chromium (VI)) has been found together with a variety of aromatic compounds including phenol, naphthalene and trichloroethylene (TCE) at high

concentrations in a number of contaminated sites. Chromium (VI) and its organic copollutants often originate from industrial sources such as leather tanning, photographic-film making, wood preservation, car manufacturing, petroleum refining and agricultural activity. Chromium (VI) and phenol containing effluents are also discharged from a wide range of industries, including dye, textile, tannery, petrochemical and many others (Patterson and Stoneham, 1985; Chirwa and Wang, 2000; Aksu and Akpinar, 2000). These industries contain Cr (III) and Cr (VI) at concentration ranging from 10 to 100 mg L⁻¹ (Park *et al.*, 2005). Among the biological materials investigated for heavy metal removal, the biomass of marine algae otherwise known as seaweeds has been reported to have high uptake capacities for a number of heavy metal ions (Bailey *et al.*, 1999; Pagnelli *et al.*, 2000). Numerous studies on metal biosorption by brown seaweeds such as *Sargassum* have been reported in the literature. However, the applicability of green seaweed biomass such as *Ulva* for metal removal has not been extensively investigated yet despite its large abundance in the world's shorelines (Morand and Birand, 1996; Valiela *et al.*, 1997). Over the past two decades, attention has been concentrated on identifying materials that can effectively remove heavy metals from aqueous environments. These materials are known as biosorbents and the passive binding of metals by living or dead biomass is referred to as biosorption (Schiewer and Wong, 2000). Seaweeds have been shown to be extremely efficient biosorbents with the ability to bind a variety of

metals (Volesky and Holan, 1995). In particular, the potential of non-viable seaweeds in the recovery of heavy metal ions from aqueous effluents has been studied by Yun *et al.* (2001) and Davis *et al.* (2003). Seaweeds possess a high metal-binding capacity (Ramelow *et al.*, 1992; Holan and Volesky, 1994). Metal ion uptake by biomass is believed to occur through interactions with cell wall (Wang *et al.*, 2001). This is due to the presence of various functional groups such as carboxyl, amino, sulphate and hydroxyl groups, which can act as binding sites for metals. The main mechanisms of binding include ionic interaction and complex formation between metal cations and ligands on the surface of the seaweeds (Yun *et al.*, 2001). In the present study, we report the biosorption of Cr (VI) by two different marine algae. *Gracilaria salicornia* (red algae) and *Sargassum* sp. (brownalgae). The effects of contact time, concentration of algal biomass and pH were studied.

MATERIALS AND METHODS

Preparation of biomass: *Gracilaria salicornia* and *Sargassum* sp. were collected from Persian Gulf coast of Iran in May 2007. After harvesting from sea, these were washed several times using deionized water to remove the sand particles and salts. They were then dried in an oven at 60°C until constant weight. Dry biomass was chopped and sieved and particles between 50-70 mesh (0.2-0.3 mm) were used for biosorption experiments.

Chromium (VI) solutions: Stock Chromium solution (500 mg L⁻¹) was prepared by dissolving 0.1414 g of K₂Cr₂O₇ (Merck, Darmstadt, Germany) in 100 mL of deionized water. Chromium solutions of different concentrations were prepared by adequate dilution of the stock solution with deionized water. The stock solution was standardized by titrimetry.

Batch biosorption studies: All batch biosorption experiments were performed by adding 250 mg of dried biomass to 250 mL of Chromium solution in 250 mL Erlenmeyer flasks with constant Chromium concentration at 50 mg L⁻¹. The flasks were agitated at 150 rpm for 240 min. The experiments were conducted at 25±1°C. For studying the influence of pH on the biosorption of Cr (VI), experiments were conducted at various initial metal solution pH values of 3-6. Algal mass quantity was varied from 0.5 to 4.5 g L⁻¹ to know the optimum concentration. For equilibrium time, the initial pH was set at 4±0.2 and 1.0 g L⁻¹ biomass was added into metal solution. Metal-free and biosorbent-free blanks were used as controls. The residual Chromium ion concentration in the solution was analyzed using atomic adsorption

spectroscopy (braic). All biosorption experiments were carried out in triplicates to check the reproducibility of results.

RESULTS AND DISCUSSION

Effect of initial solution pH: Marine algae contain high content of ionizable groups (carboxyl groups from mannuronic and guluronic acids) on the cell wall polysaccharides, which suggests that the biosorption process could be affected by changes in the solution pH (Davis *et al.*, 2000; Matheickal and Yu, 1999). The effect of pH on Chromium (VI) adsorption by the marine algae was therefore studied first. The uptake of Chromium (VI) showed a sharp increase with an increase in pH from 3.0 to 6.0 in the case of *Sargassum* sp. and in the case of *G. salicornia* (Fig. 1). Crist *et al.* (1992) reported that the zero-point for alga cell was at pH 3.0, above which the algal cells could develop a net negative charge. Nasserri *et al.* (2002) reported the removal of chromium using *A. oryzae*, where maximum removal was observed at pH 5 also Variation of biosorbed chromium (VI) ion concentration with time was shown (Fig. 2). A significant

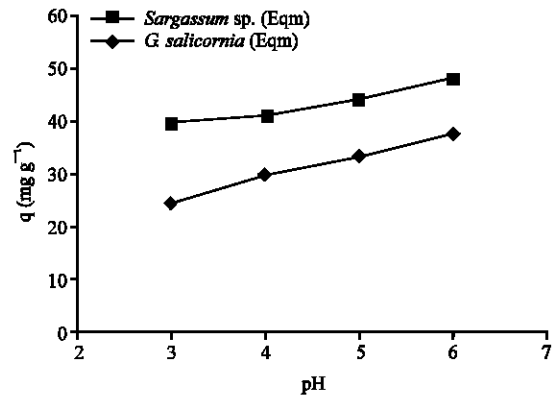


Fig. 1: The effect of initial pH on the uptake of chromium (VI)

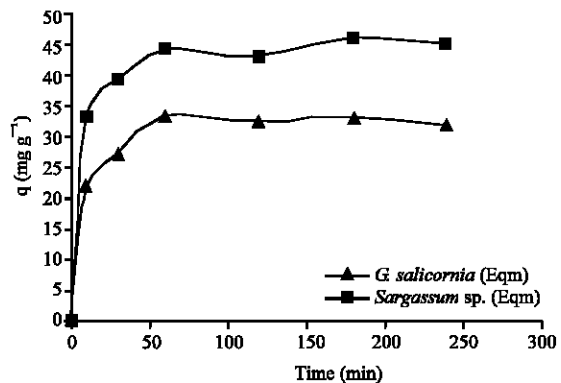


Fig. 2: Variation of biosorbed chromium (VI) ion concentration with time

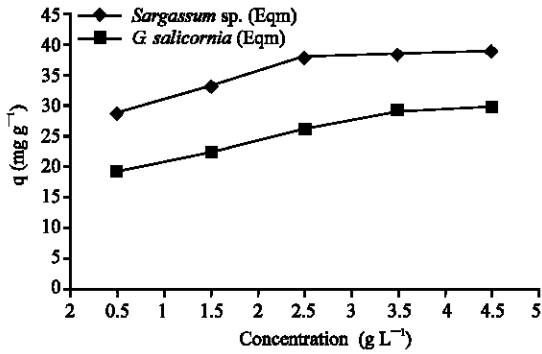


Fig. 3: Variation of biosorbed chromium (VI) ion concentration for different biosorbent concentrations

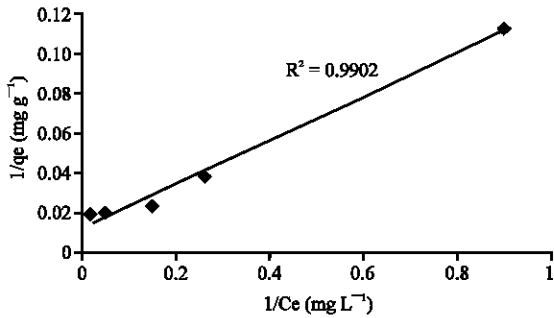


Fig. 4: Langmuir isotherm for chromium (VI) uptake by *Sargassum* sp.

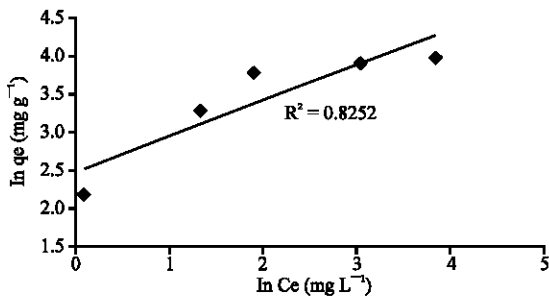


Fig. 5: Freundlich isotherm for chromium (VI) uptake by *Sargassum* sp.

fraction of the total Cr (VI) uptake was achieved within 60 min. The maximum biosorption capacity obtained was 45.959 mg g⁻¹ for *G. salicornia* and 33.258 mg g⁻¹ for *Sargassum* sp. at a solution pH of 4 and 50 mg L⁻¹ initial chromium concentration.

Effect of algae concentration: The effect of *G. salicornia* or *Sargassum* sp. concentration on the removal of Chromium was studied using algal mass in the range of

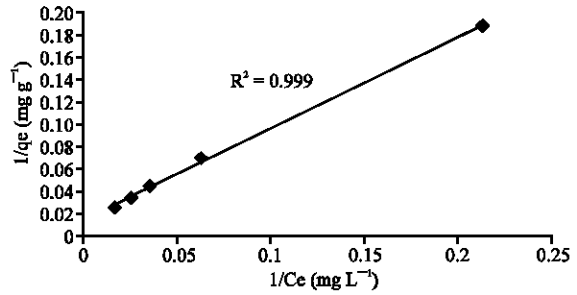


Fig. 6: Langmuir isotherm for chromium (VI) uptake by *G. salicornia*

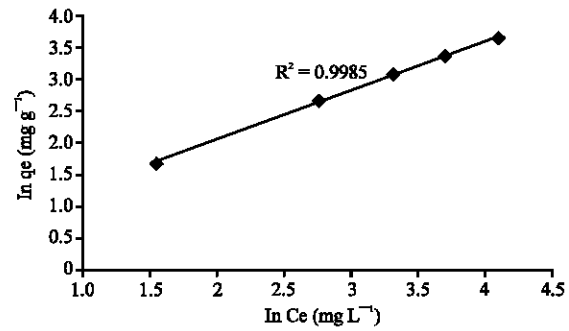


Fig. 7: Freundlich isotherm for chromium (VI) uptake by *G. salicornia*

0.5-4.5 g L⁻¹. Results showed an increased uptake of Cr (VI) with the increase of algae quantity. The maximum uptake was attained at about 4.5 g L⁻¹ (Fig. 3). Karthikeyan *et al.* (2007) reported that an increased uptake of Cu (II) with the increase of alga quantity was shown.

Adsorption isotherms: Adsorption isotherms were obtained at an optimal pH of 4 as shown in Fig. (4-7) The solution phase concentration of Cr (VI) was varied from 10 to 100 mg L⁻¹. The biosorption of Cr (VI) on *G. salicornia* and *Sargassum* sp. could best be described by the Langmuir model ($R^2 > 0.997$ for *Sargassum* sp. and $R^2 > 0.999$ for *G. salicornia*), however, the biosorption of Cr (VI) on *G. salicornia* could best be described by the Freundlich model ($R^2 > 0.9985$). Mungasavalli *et al.* (2007) reported that Isotherm analysis of the biosorption pattern for chromium on *Aspergillus niger* pretreated biomass followed the Freundlich isotherm in the entire temperature range studied.

CONCLUSION

The results obtained showed that *Sargassum* sp. and *G. salicornia* could be used as efficient biosorbent

material for the treatment of Cr (VI) ions. The uptake of Chromium (VI) showed a sharp increase with an increase in pH from 3.0 to 6.0 in the case of *Sargassum* sp. and in the case of *G. salicornia*. the strong pH dependence of Cr (VI) biosorption observed in this study could be attributed to more pronounced electrostatic attraction taking place between the biosorbents and the metal ions at higher pH. increased uptake of Cr (VI) with the increase of algae quantity could be due to the formation of biosorbent aggregates at higher biomass concentration, which in turn could reduce the effective surface area available for the biosorption. the biosorbents showed a different adsorption capacity, which might presumably be due to the presence of the different number of cell surface binding sites.

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