An evaluation of chromium and zinc biosorption by a sea weed (*Sargassum sp.)* under optimized conditions

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Abstract: Biosorption is a promising alternative method to treat industrial effluents, mainly because of its low cost and high metal binding capacity. In this work, Zinc and Chromium biosorption process by *Sargassum sp.* seaweed biomass was studied. The work considered the determination parameters of Zinc and Chromium sorption such as pH, temperature, agitation speed and biomass size. The optimum conditions were: pH3, temperature (303k) room temperature, biomass size 0.5mm and agitation speed 150rpm. The maximum uptake of Chromium and Zinc is 65% and 53% respectively. The kinetic study revealed that the adsorption of Chromium and zinc by *Sargassum sp*. fitted the Langmuir isotherm.

Keywords: Biosorption, chromium, zinc, heavy metal, *Sargassum* sp.

Introduction

Heavy metal pollution of waste water is a common environmental hazard, since the toxic metal ions dissolved can ultimately reach the top of the food chain and thus become a risk factor for human health. This metals are present in the waste water of several industries such as metal cleaning and plating baths, refineries, paper and pulp, tanning industries etc (Periasamy & Namasivayam, 1996; Ghazy *et al.*,2008).The excessive intake of metal by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation and possible necrotic changes in the liver and kidney (Kalavathy *et al.*, 2005). For more than a decade, researchers have been looking for cheaper and more effective methods to remediate heavy metal contaminated waters and reduce the growing public health risk. Biosorption is proven to be quite effective at removing metals ions from contaminated solution in a low-cost and environment-friendly manner (Volesky, 1990) The major advantages of biosorption over conventional treatment methods include low cost, high efficiency of metal removal from dilute solution, minimization of chemical and/or biological sludge, no additional nutrient requirement, regeneration of biosorbent and the possibility of metal recovery (Kratochvil & Volesky, 1998). Marine macro-algae are harvested or cultivated in many parts of the world and are therefore readily available in large quantities for the development of highly effective biosorbent materials. Chromium, Zinc, like the majority of heavy metals, is toxic but it has been widely used in metallurgical and tanning industries. Chromium deficiency in humans results in symptoms comparable to those associated with diabetes (Aksu *et al.*, 1999). The objective of the present work was to evaluate chromium and zinc biosorption by *Sargassum sp.*, and also to evaluate the influence of different parameters on zinc and chromium uptake such as pH, temperature, agitation and size of the biomass was investigated and the maximum biosorption capacity of the biomass, based on dry weight was determined from the equilibrium data measured under optimized conditions of pH and modeled according to Langmuir model. The main reason for the extended use of Langmuir model was that they incorporate easily interpretable constants (Davis *et al.*, 2007). The Langmuir sorption isotherm has traditionally been used to quantify and contrast the performance of different biosorbents. In its formulation, binding to the surface was primarily by physical forces and implicit in its deviation was the assumption that all sites possess equal affinity for the sorbate. Its use was extended to empirically describe the equilibrium relationships between the bulk liquid and solid phases (Azizian, 2006).

Materials and Methods

Preparation of biomass

The biomass used in the present study was the brown seaweed *Sargassum sp.*, collected from the southern coast of India. After harvesting from sea, the samples were washed with distilled water to remove particulate materials and salts from the surface. They were then dried in an oven at 60°c for 24hrs and then used as biosorbent for further studies (Da costa & De franca, 1997).

Synthetic effluent and metal ions analysis

Analytical grade $ZnSO4.7H_2O$ and $K_2Cr_2O_7$ were dissolved in distilled water in order to obtain a solution containing zinc and

Fig. 1.Chromium removal by Sargassum sp. at different pH conditions

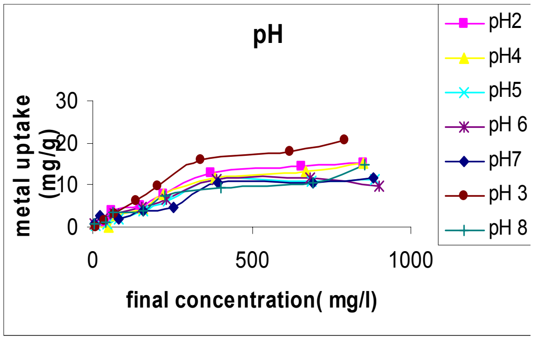


Fig. 2. Zinc removal by Sargassum sp.at different pH conditions

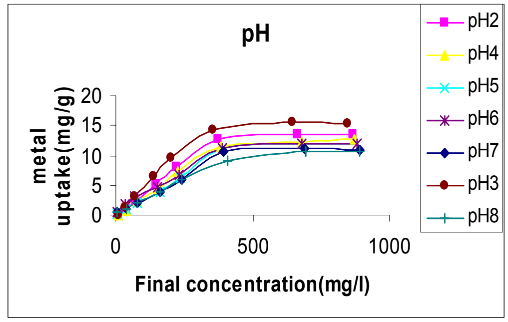


Fig 3.Effect of algal size on the removal of chromium ions

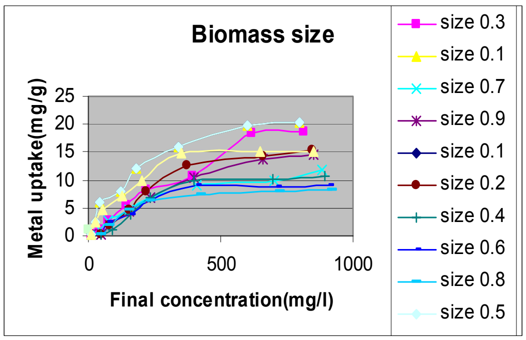


Fig 4.Effect of algal size on the removal of zinc ions

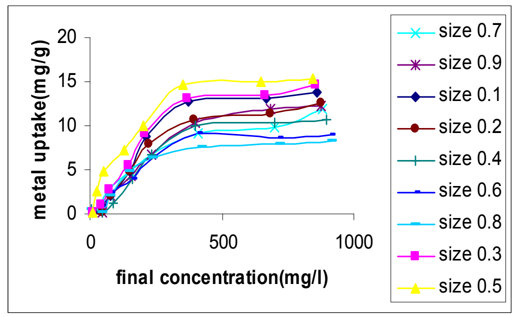


Fig 5. Adsorption capacity of chromium at different temperature

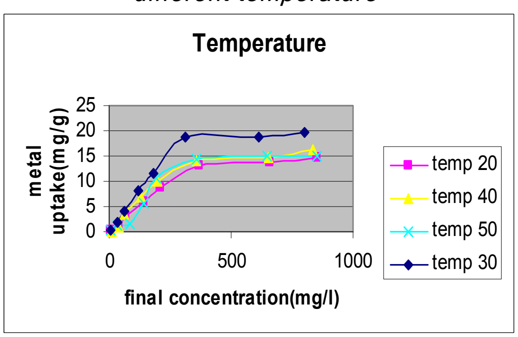
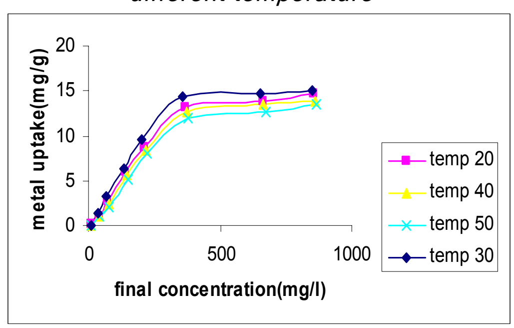


Fig 6. Adsorption capacity of zinc at different temperature



chromium. This solution was used for metal biosorption experiments. Concentrations of standard and process solutions were evaluated by Atomic Absorption Spectrometry (AAS6VARIO; Analytik jena, Germany).

Batch Experiments

Batch biosorption experiments were performed by adding 0.1- 1.0mg of dried biomass to 100ml of metal solution in 250ml Erlenmeyer flasks. The flasks were agitated at 150rpm. The experiments were conducted at room temperature. For studying the influence of pH on the biosorption, experiments were conducted at various initial metal solution pH values of 3-8. Metal free and biosorbent free blanks were used as control. The residual ion concentration in the solution was analyzed using atomic absorption spectrometry.

Equilibrium study of metal ion adsorption by seaweed biomass

The empirical form of the Langmuir adsorption isotherm equation is given as:

$$q_e = \frac{bC_e q_{max}}{1 + bC_e}$$

And the linear form is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max} b}$$

Where q_e is the removal capacity of metal mg/g. C_e is the equilibrium concentration of metal ions in solution mg/L,q_{max} is the maximum adsorption capacity (unit:mg/g or mmol/g),and b is the affinity constant (unit:L/mg or L/mmol).

Fig 7. Adsorption capacity of chromium at different agitation speed

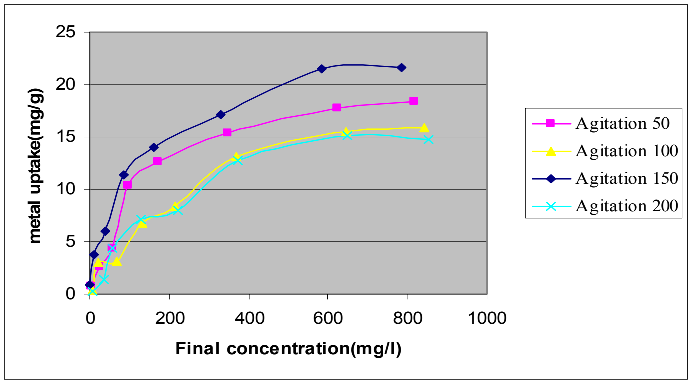


Fig 8. Adsorption capacity of zinc at different agitation speed

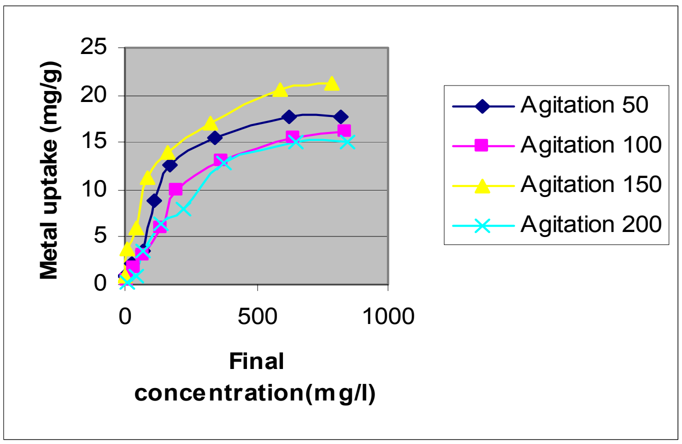
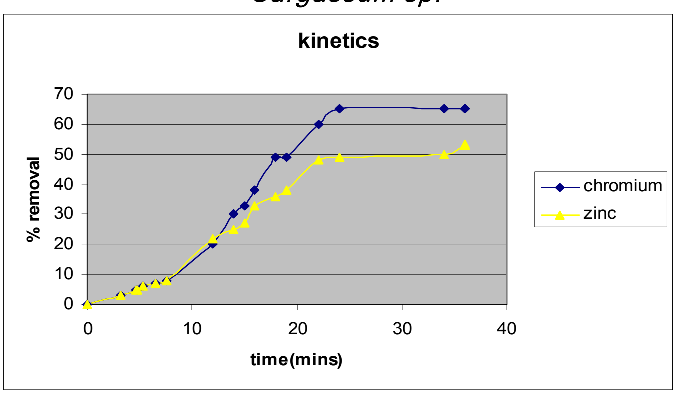


Fig 9. Kinetics of chromium and zinc biosorption by Sargassum sp.



The Freundlich isotherm holds most of the assumptions suggested in Langmuir isotherms, except that it assumes that sorption takes place on a heterogeneous surface and the binding sites are not equivalent and/or independent (Aksu *et al.*, 1999. The empirical Freundlich adsorption isotherm equation (Volesky, 1990) is given as:

$$q_e = kC_e^{1/n}$$

This equation can be linearized by taking natural log (ln) and given the following form:

$$\ln q_e = \ln k + \frac{1}{n} C_e$$

Where q_e is the removal capacity of metal mg/g, k is the adsorbent capacity and l/n is the adsorption intensity.

Result and Discussion

Effect of initial solution pH

Marine algae contain high content of ionizable groups (carboxyl 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 (Matheickal & Yu; 1999 Davis *et al.*, 2000). It was observed that the uptake of chromium and zinc was higher at pH3 (Fig.1 & 2). The maximum uptake of chromium and zinc at pH3 is 20.64 mg/g and 15.40 mg/g respectively.

Effect of algae size

The effect of *Sargassum sp.* (biomass) on the removal of chromium and zinc was studied in the size range of 0.1 - 1 mg. Fig.3 & 4 showed the maximum uptake was attained at the size of 0.5mg of algal biomass and the maximum uptake of chromium and zinc is 20.24 mg/g and 15.43 mg/g respectively.

Effect of temperature

The uptake of chromium and zinc ions by *Sargassum sp.* was evaluated varying the temperature from 20-50°c. Fig. 5 & 6 shows that chromium and zinc uptake was increases at room temperature and the maximum uptake was 19.83mg/g and 16.38mg/g respectively.

Effect of agitation

The maximum uptake was attained at 150rpm and the uptake of chromium and zinc was 21.60mg/g and 21.32mg/g respectively (Fig.7 & 8).

Equilibrium study of metal ion adsorption

The purpose of these experiments was to determine the contact time required to reach the equilibrium. Fig.9 shows the kinetic tests of sorption for chromium and zinc at different concentrations. The metallic ion fraction removed from solution was calculated by the following expression:

$$fj = \frac{(Cj^0 - Cj(t))}{(Cj^0 - Cj^*)}$$

Chromium removal is faster than zinc removal (Fig.9). Contact time for equilibrium is a function of several factors: biomass type (number and types of metal-binding sites), size and forms of biomass, state of biomass (active or inactive, free or immobilized), etc. The results of kinetic biosorption tests showed that approximately 53% of zinc and 65% of chromium had been removed. Based on Langmuir isotherm models, biomass of *Sargassum sp*. can be classified as a good biosorbent. A Langmuir isotherm allows to calculate the maximum metal uptake values and an affinity parameter indicative of the binding energy between the adsorbed solute molecules and the adsorbent (Ho *et al*., 2008). The Langmuir adsorption model described well the biosorption equilibrium of chromium and zinc ions *Sargassum sp*. Langmuir isotherm parameters were used to determine the affinity of one metal for the biosorbent in the presence of the other metal.

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