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BIOABSORPTION ABILITIES OF ALGAE INHABITING THE COAST OF KARACHI

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Abstract

Due to expansion of human population and intensification of the industrialization, heavy metal pollution has become a life threatening problems. Of the various remediation technologies, bioabsorption of heavy metals by microorganisms is one of the most successful and alternative methods. During the present studies, a great variation in bioabsorption abilities of *Padina tetrastromatica, Cystoseira indica, Ulva fasciata,* and *Codium iyengarii* inhabiting the coast of Karachi was observed. *C. iyengarii* was most efficient for Nickel and chromium removal, whereas *C. indica* and *U. fasciata* were efficient for the removal of cobalt and copper, respectively.

Key words: Heavy metal pollution, Bioremediation, Bioabsorption, Algae.

Introduction

Rapid Industrialization and urbanization has increased the disposal of heavy metals and radionuclide into the environment (Niyogi *et al*., 1998). Metal toxicity has great impact on environment and public health (Volesky & Holan, 1995). Heavy metals are now on the fore front of academic and regulatory concern. Metals discharged in water are non-degradable but can undergo chemical or microbial transformation. Conventionally Physical and Chemical methods are commonly applied to remove the toxic heavy metals from waste water (Yan & Viraraghavan, 2003) Biological methods such as bioaccumulation/bioabsorption of heavy metals provide an alternative and effective method to Physico-chemical methods (Kapoor & Viraraghavan, 1995). Microorganisms such as algae, fungi and bacteria can take up and dissolve metals successfully (Asku *et al*., 1991).

Accumulation of heavy metals in the seaweed is dependent on their concentration present in the Water (Sharp *et al*., 1988). The Karachi coastal zone is about 100 km inhabited with variety of marine algae (Shameel & Tanaka, 1992). Seaweeds obtain minerals and trace elements from the sea water and convert them into organic form (Chapman & Chapman, 1980). The metal binding abilities of marine algae have been widely investigated but the mechanisms responsible for bioabsorption of heavy metal are still poorly understood. The objective of the present work was to assess the ability of *Ulva fasciata* Delile, *Padina tetrastromatica* Hauck, *Cystoseira indica* Thivy & Doshi and *Codium iyengarii* Borgesen inhabiting the coast of Karachi for the bioabsorption of Nickel (Ni), Cobalt (Co), Copper (Cu) and Chromium (Cr) from the aqueous solutions.

Materials and Methods

Collection of samples: Buleji is one of the most frequently visited rocky ledges about 30 km away from Karachi. Fresh Biomass of *U. fasciata, P. tetrastromatica, C. indica* and *C. iyengarii*collected from Buleji either attached or as drift. The samples were washed with deionized water to remove mud debris and other epiphytes and then dried under the sun. The dried samples were then ground in powder form in an electrical blender, sieved and stored in glass bottles until further analysis. Representative specimens were mounted on herbarium sheet and also preserved in 4% formalin. Specimens are kept in the Algal Herbarium, Botany Department, University of Karachi.

Chemicals and reagents: All the high purity chemicals were purchased from Al-Beruni Scientific store, Hyderabad manufactured by Farco Chemical Supplies, Beijing, China. The stock solutions containing Ni(II), Co(II), Cu(II) or Cr (III) were prepared by respectively dissolving the Nickel acetate, Cobalt chloride, Copper acetate and Chromium acetate in the deionized water. The solutions were diluted to get 140, 160, 180 and 200 ppm concentrations. Deionized water without any added chemical served as control.

Batch Equilibrium studies: One g algal biomass was added to 250 ml Erlenmeyer flask containing 100 mL of different concentrations of a metal i.e. 0, 140, 160,180 and 200 ppm. The mixtures were shaken in shaker (O Lab Tech. Diahan Lab Tech Co. Ltd) at 150 rpm for 24 hours at 30°C after which the biomass was separated by using Whatman filter paper 40 to determine the residual total bioabsorption of the metal by he tested algae. Metal free biomass was used as control.

Analysis of heavy metals: The concentrations of the Ni, Co, Cu and Cr were determined with the help of Hitachi–Z5000 Atomic Absorption Spectrophotometer using air acetylene flame in the PCSIR Laboratories, Karachi. Specific quantity of metal absorbed by a species was determined by subtracting the quantity of the metal in biomass in control. The final concentration (C_f) of the metal in solution was determined by subtracting the specific quantity of the metal absorbed by the biomass from the initial concentration (C_i). The percentage of the metal ions absorbed by the species at each concentration (Q) was calculated using the following formula of Volesky (2001):

$$Q = (C_i - C_f) / C_i * 100$$

Results

All the four macroalgae *viz., P. tetrastromatica, C. indica, U. fasciata* and *C. iyengarii*showed their bioabsorption abilities when added to solution containing Ni, Co, Cu and Cr(III) at 140,160, 180, and 200 ppm (Figs. 1-4). Highest accumulation of Ni g^{-1} biomass of macroalgae was observed in *C. indica, C. iyengarii* and *U. fasciata* followed by *P. tetrastromatica* (Fig. 1). *P. tetrastromatica, U. fasciata* and *C. iyengarii* showed a gradual increase in absorption of Ni with increasing concentration in solution; the maximum accumulation was observed at 180 ppm concentration whereas at 200 ppm concentration, accumulation decreased significantly. Similarly, *C. indica* showed maximum accumulation at 160 ppm treatment that declined thereafter.

Accumulation of Co in *P. tetrastromatica* biomass increased gradually with increase in Co concentration from 140 to 200 ppm (Fig. 2). *C. indica* and *U. fasciata* dislpayed maximum Co accumulation in 140 ppm treatment that declined gradually with increase in Co concentration from 160 to 200 ppm. *C. iyengarii* did not show significant Co absorption as compared to other tested algae since the maximum accumulation was 5.5% that was observed at 160 ppm; any increase in Co concentration beyond 160 ppm resulted in gradual reduction in accumulation.

Accumulation of Cu in *P. tetrastromatica* was highest as compared to other tested algae. Maximum accumulation was observed in 160 ppm treatment that slightly reduced with increase in concentration to 180 and 200 ppm (Fig. 3). *C. indica* showed greater Cu accumulation at 180 and 200 ppm as compared to 140 and 160 ppm; the highest accumulation observed at 180 ppm. *U. fasciata* showed maximum absorption at 140 ppm and the accumulation declined gradually thereafter with increase in Cu concentration in the solution. *C. iyengarii* exhibited the lowest Cu accumulation as compared to other three algae; the accumulation of Cu was greater in 140 and 160 ppm treatments as compare to 180 and 200 ppm treatments.

P. tetrastromatica and *U. fasciata* showed greater absorption of Cr in 140 and 160 ppm treatments, whereas, the absorption reduced significantly in 180 and 200 ppm treatments (Fig. 4). *C. indica* showed more or less similar absorption at Cr all concentrations, whereas, C. *iyengarii* exhibited highest Cr accumulation at 140 ppm that was greater than the accumulation shown by all the remaining three algae. However, Cr accumulation in *C. iyengarii* biomass reduced significantly when concentration increased to 160 ppm or more.

The uptake values in different species were in the following order:

Ni: *C. iyengarii >U. fasciata> P. tetrastromatica>C. indica*
Co: *U. fasciata> C indica>P. tetrastromatica> C. iyengarii*
Cu: *C. indica> P. tetrastromatica> U. fasciata> C. iyengarii*
Cr: *C. iyengarii> C. indica> P. tetrastromatica> U. fasciata*

Discussion

Seaweeds, specially the brown algae are one of the most commonly used bioabsorbents to remove toxic metals from the aquatic environment (Lodeiro *et al*., 2010). *Sargassum filipendula* was found to be an efficient bioabsorbent for copper and nickel with maximum capacities of 1.324 and 1.070 mmol/g, respectively (Kleinubing *et al*., 2011). The polysaccharides present in the cell wall of seaweed have been identified as responsible for absorption (Salehizadeh & Shojaosadati, 2003). Variations in the affinity between the species for the same element have been attributed to the variation in nature and proportions of the chemical constituents of the cell wall among different species. The carboxyl groups of alginate and the sulfate groups of agars and carrageenans have been found responsible for ion exchange by the cell wall polysaccharides and are the main sites for capture and sequestration of the metal ions (Leonardi & Vasquez, 1999).

Variations in the absorption pattern for different metals were exhibited by different algae. *P. tetrastromatica* showed a positive correlation between the bioabsorption efficiency and the increasing concentration of cobalt in solution. An increase in biomass adsorption capacity with the increasing initial metal concentration has been previously reported for both single and mixed metal solutions and attributed to the higher mass transfer and kinetic energy, thus the probability for collision between metal ions and the bioabsorbents (Atkinson *et al*., 1998; Donmez *et al*., 1999; Lesage *et al*., 2007).

During the present studies, *C. indica* and *U. fasciata* showed negative correlation between the bioabsorption efficiency and the increasing concentration of cobalt in the solution. Similar trends were shown by *C. indica* for cobalt and *U. fasciata* for copper and cobalt. An earlier study reported that decrease in percent absorption with increase in the metal ion concentration may be due to saturation of all binding sites with metal ions and establishment of equilibrium between adsorbate and bioabsorbent (Bai & Abraham, 2001).

The third and the most commonly observed trend was an increase in bioabsorption of the metal up to certain concentration of the metal in the solution followed by decline in the bioabsorption efficiency with increase in metal ion concentration. It was exhibited by all the four tested algae for Ni, *C. iyengarii* for Co, Cr and Cu, *P. tetrastromatica* for Cu, *C. indica* for Cu, and *U. fasciata* for Cr. The decrease in bioabsorption efficiency after a certain concentration of the metal may be probably due to the saturation of the absorption sites on the adsorbent after that no more metal was removed from the solution due to unavailability of the binding sites. Malkoc (2006) also observed that higher bioabsorption yields were observed at lower metal concentration and increase in metal concentration had a negative effect on bioabsorption efficiency. Similarly, Ozturk *etal*. (2004) reported that the Cu concentration above 100 mg L^{-1} did not increase the bioabsorption significantly and percent metal removal remained almost constant or showed even a decrease indicating saturation of all the binding sites on algal surface beyond a particular concentration.

In our study the uptake of Cu was more by *C. indica* (21.8%), *P. tetrastromatica* (20.4 %) and *U. fasciata (*20.04 %) as compared to *C. iyengarii* (9.4 %). The Cu absorption capacity of *Ulva reticulata* was evaluated by Vijayaraghavan *et al*. (2004) who found relatively high absorption as compared to other bioabsorbents. The maximum absorption ability of *U. fasciata* for copper and zinc was also recorded by Prasanna *et al*., (2006). Sheng *et al*. (2004) observed up to 90% absorption of copper, cadmium, lead, nickel and zinc from dilute aqueous solutions by species of *Sargassum*, *Padina*, *Ulva* and *Gracilaria*.

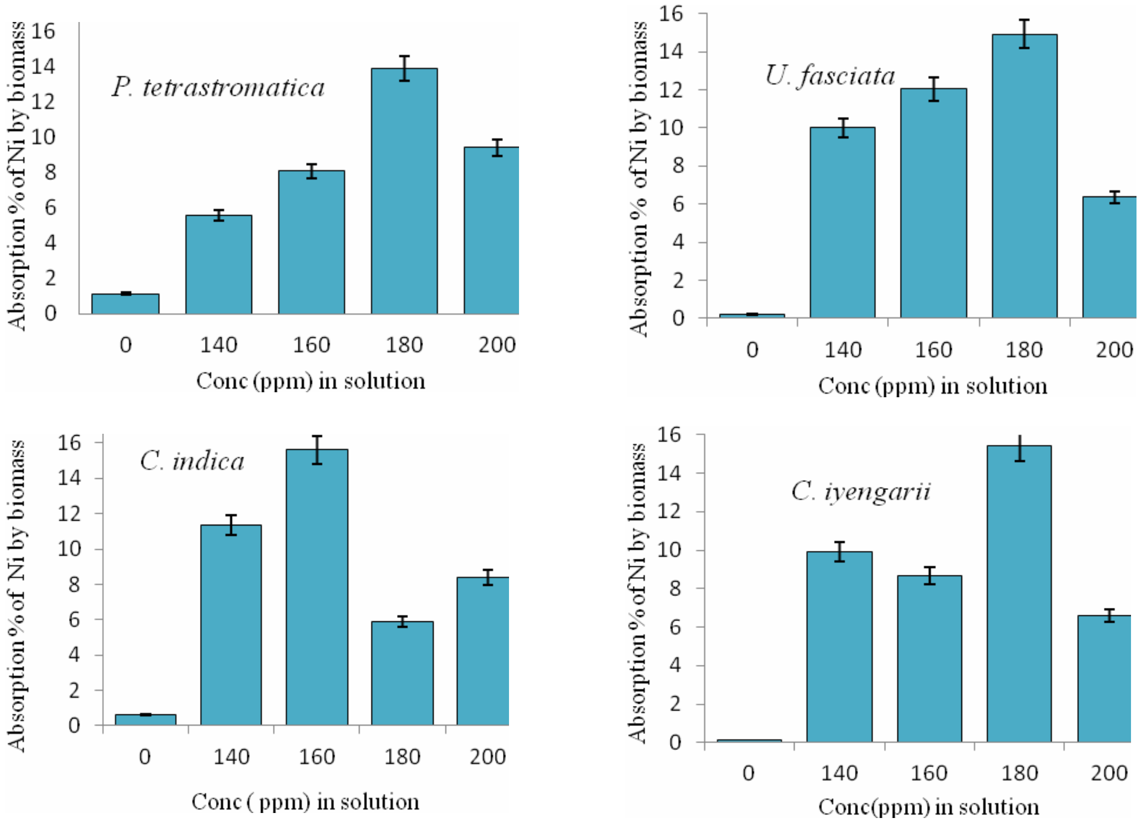

Fig. 1. Absorption of nickel by the tested algae.

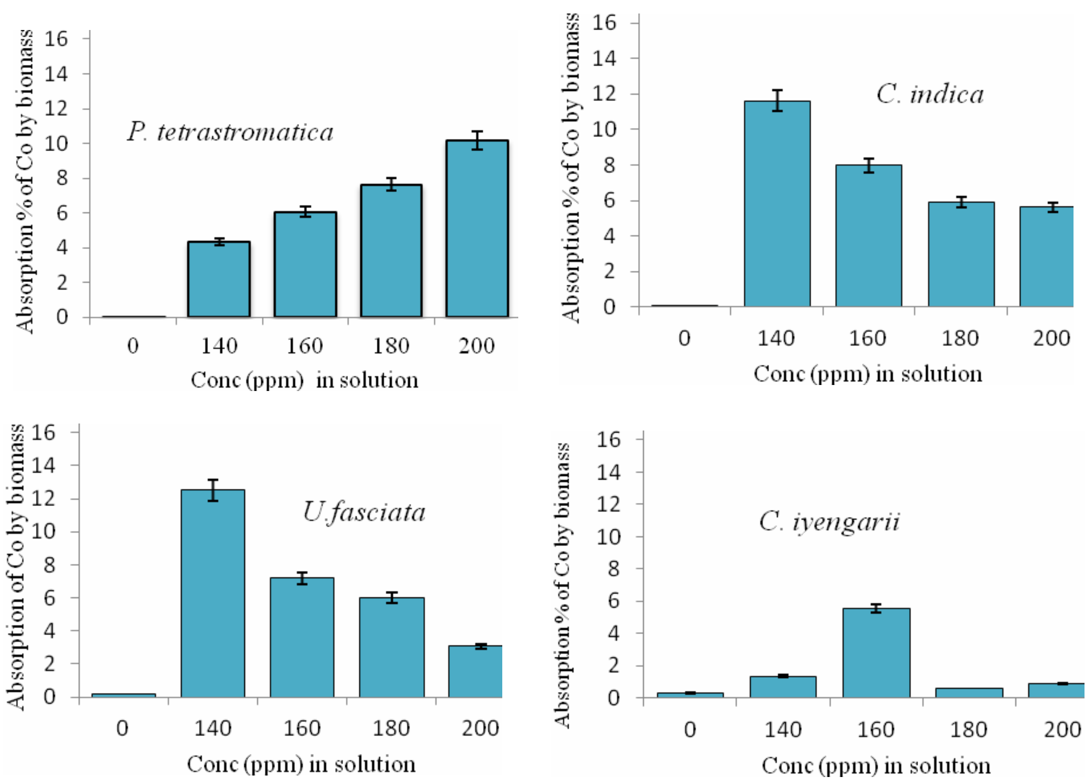

Fig. 2. Absorption of cobalt by the tested algae.

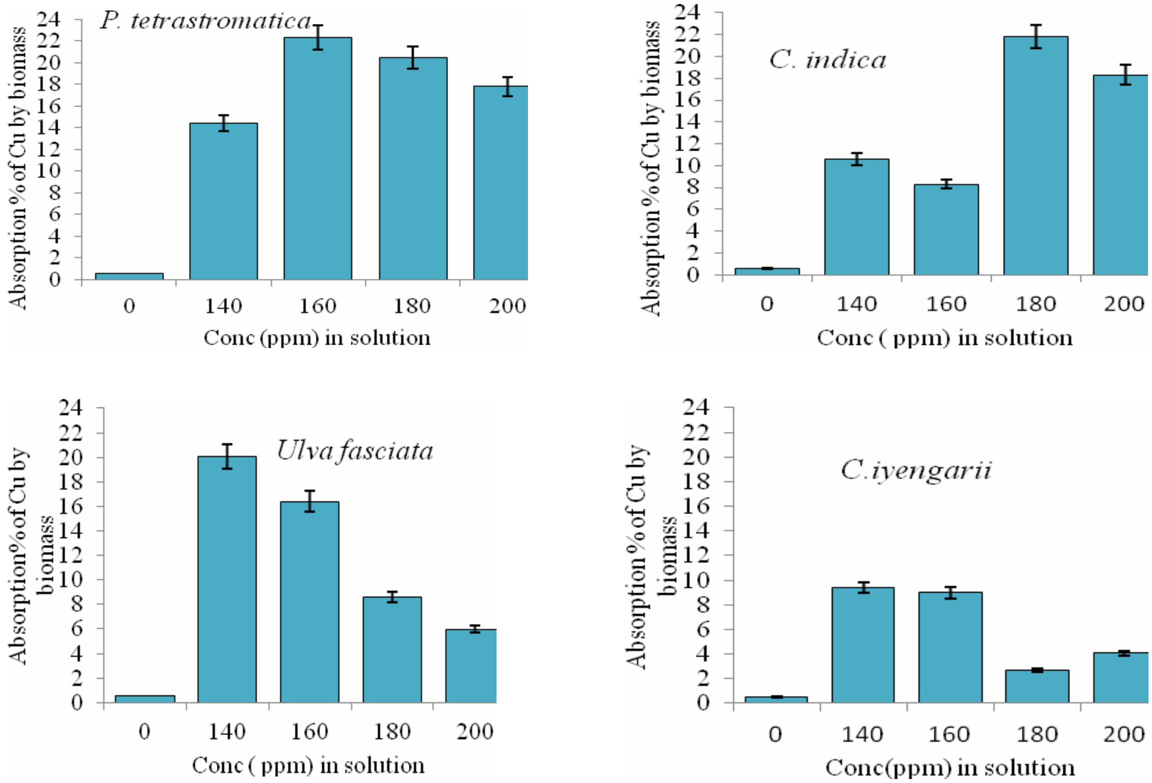

Fig. 3. Absorption of copper by the tested algae.

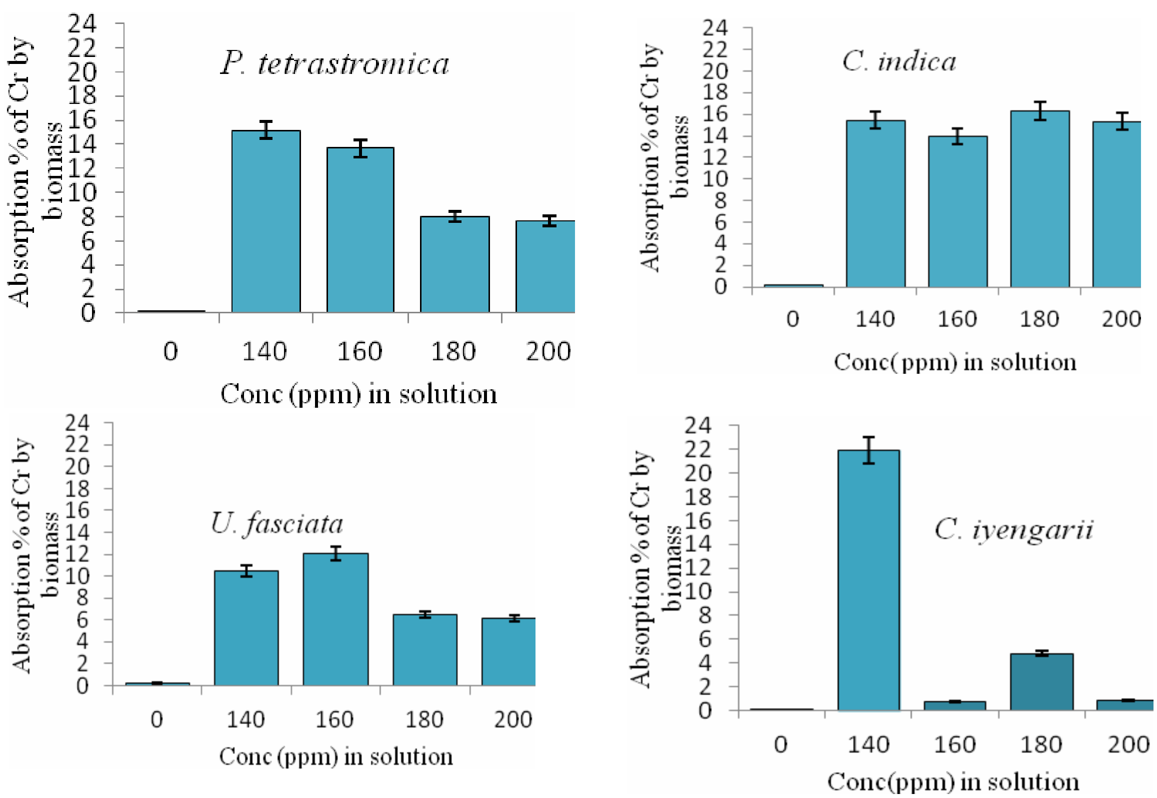

Fig. 4. Absorption of chromium by the tested algae.

The variation in absorption of different metals by a particular species would suggest that there exists a variation in number of binding sited available for different species; that's why the same species showed a positive or a negative correlation with the increasing concentration of the metal, or an increase in bioabsorption up to a particular concentration and a decline thereafter. Matheickal & Yu (1999) reported that the algal biomasses contain high amount of carboxyl groups from mannuronic and guluronic acids on the cell wall polysaccharides, which suggests that the bioabsorption process could be affected by changes in the concentration of solution.

The results of the present study clearly show the bioabsorption abilities of four tested algae. These can be utilized for the management of the unwanted heavy metals from the aquatic environment. The species may be selected on the basis of the polluting metal and its concentration in the polluted water.

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