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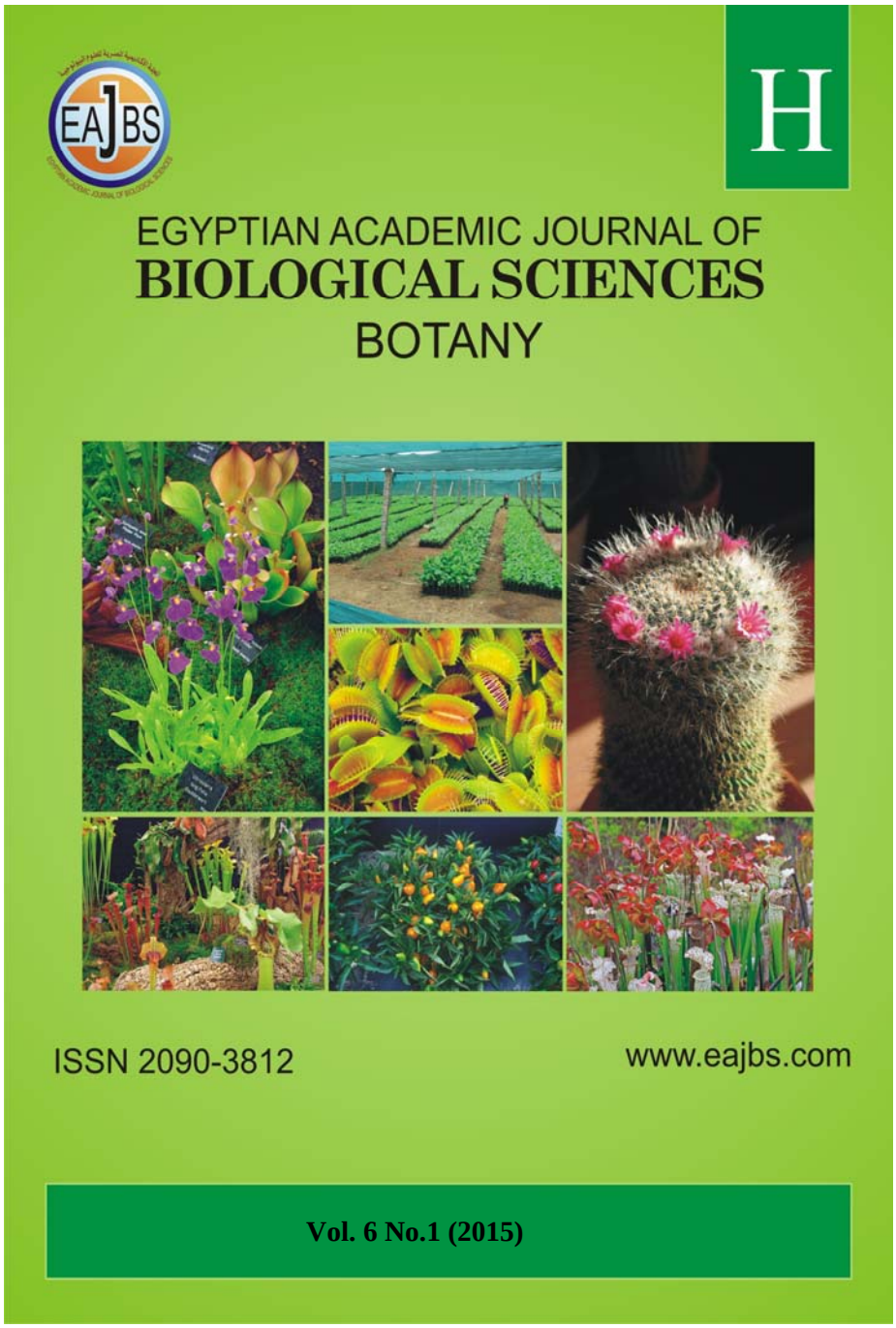

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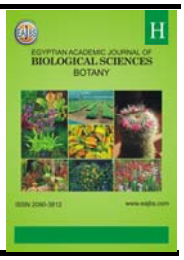

Bioremediation of Hexavalent Chromium by Some Marine Algae

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ABSTRACT

The discharge of chromium (VI) into aquatic ecosystems has become a matter of concern in all the tannery areas over the last few decades.In this study, biomass of *Padina pavonia* (Linnaeus) Gaillon, *Sargassum hornschuchii* C. Agardh, *Cystoseira sp.* C. Agardh, *Ulva lactuca* L. and *Gelidium crinale* (Turner) Gaillon were tested for bioremediation of chromium (VI). The results clarified that the amount of metal removed by algae from solution is obviously affected by biomass concentration and the metal removal increased with increasing the biomass of the tested algae. It is also observed that there is consistent increase in the chromium (VI) removal by all tested algae with time in approximately all used concentrations, especially from 4 to 8 hours. Meanwhile, the relative metal removal percentages decreased by increasing the initial metal concentrations and higher removal for metal was observed at lower concentrations. Accordingly, a bioremediation process based on algae biomass is sustainable keeping in account the cost effectiveness and associated environmental benefits.

INTRODUCTION

Environmental pollution is a very serious menace in the present circumstances. Rapid industrialization and urbanization are the main reason for water pollution as they are continuously discharging waste into rivers and other water bodies. Many industries like electroplating, tanning, paper, textile etc. are key component of discharging effluents causing heavy metal pollution (Jyoti and Awasthi, 2014). These heavy metals accumulate in the food chain of aquatic and terrestrial ecosystem posing health hazards (Ahluwalia and Goyal, 2007).

Out of all the heavy metals, Chromium is found to be highly toxic and carcinogenic. In humans, it poses health problems like DNA damage, nausea, vomiting, nasal irritation and ulceration, skin irritation, eardrum perforation and lung carcinoma (Dayan and Paine, 2000).It persists in environment in two oxidation states Cr (III) and Cr (VI) (Shanker, *et al.* 2005). Hexavalent Chromium is more toxic than trivalent chromium and often present in wastewater as chromate and dichromate(Barnhart, 1997).

The discharge of chromium (VI) into aquatic ecosystems has become a matter of concern in all the tannery areas over the last few decades. This pollutant is introduced into the aquatic systems significantly from the chrome tanning effluents of leather processing units. In this process about 60–70 % of chromium reacts with the hides and about 30-40 % of chromium remains in the solid and liquid wastes (especially as spent tanning solutions).(Shukla, *et al.* 2012).Therefore, prior treatment of Cr (VI) is essential before discharge in natural water bodies.

A number of physico-chemical methods achieve Cr (VI) reduction and detoxification (Eary & Rai, 2001; Cabatingan, *et al.* 2001; Xu *et al.* 2004 and Sarin & Pant, 2006), however, these methods appear unsuitable owing to excessive sludge production, the use of expensive chemicals, regeneration of the adsorption matrix etc. (Singhvi and Chhabra, 2013).Accordingly, a new effective and inexpensive technology is needed to overcome the limitation of conventional methods and providing heavy metals concentrations to at least environmentally acceptable standards. Hence, the present study exploited the potentiality of some marine algal species to bio-remediate chromium (VI) in aqueous solution.

MATERIALS AND METHODS

Algal materials

In this study, biomass of five algal species were tested for bioremediation of chromium (VI). Namely, these species are: *Padina pavonia* (Linnaeus) Gaillon, *Sargassum hornschuchii* C. Agardh, *Cystoseira sp.* C. Agardh, *Ulva lactuca* L. and *Gelidium crinale* (Turner) Gaillon. All specimens were collected during May 2015 from Abo-Qir bay, Alexandria, Egypt, except *Cystoseira sp.* which was collected from the seashore of Marsa-Matrouh city, Egypt. Algal specimens were washed with sea water, tap water, and then distilled water several time, to remove extraneous and salt, then dried in an oven at 50ºC until complete dryness. The dried algae biomass was chopped, sieved and kept under dry conditions until used.

Reagents and Biosorption methodology

Metal stock solution (1,000 ppm) was prepared by potassium dichromate salt of Merck AR grade and distilled water. In 250 ml Erlenmeyer flasks, aqueous chromium (VI) solution with initial concentrations (200, 300 and 400 ppm) was prepared and 100 ml of each solution was taken and the pH was maintained between 5.5 and 6.2 to which the weighed amount (05, 1.0 and 2.0 gm) of dried algal biomass was poured. The batch was then kept on a shaker (moderate shaking speed) at room temperature, samples were withdrawn from it at different time intervals for determination of chromium (VI) by atomic absorption spectrophotometer (at central laboratory, Faculty of Science, Alexandria University). Percentage reduction in chromium (VI) concentration was calculated.

RESULTS AND DISCUSSION

In recent years, there has been an increasing research interest in microorganisms that are able to transform the highly toxic and water-soluble chromium (VI) to the less toxic and insoluble chromium (III) or remove chromium (VI) by adsorption (Shukla, *et al.* 2012). Algae have high metal binding capacities, since polysaccharides, proteins or lipids on the surface of their cell walls have some functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals. Meanwhile, the presence of functional groups with binding abilities do not always

guarantee biosorption due to steric or conformational hindering or other barriers (Macfie & Welbourn, 2000; Gupta & Rastogi, 2008; Dayana *et al.*, 2013; Koutahzadeh *et al.*, 2013 and Pakshirajan, *et al.* 2013).

The biosorption experiments were carried out in batches with standard chromium concentration (200, 300 and 400 ppm) and pH of 5.5–6.2. The percentage of removal of the chromium (VI) concentration by the tested algal species at different time periods are shown in Figures 1,2 and 3. With some exceptions, according to the results, it is observed that there is consistent increase in the chromium (VI) removal by all tested algae with time in approximately all used concentrations, especially from 4 to 8 hours.Initially Cr binding was rapidly (after 4 hours), but also reaches maximum values after 12 hours, this rapid biosorption at the beginning of the experiment was approvedby some previous works (e. g. Singh *et al.*, 2013 and Rao *et al.* 2013).

As appear in Figures 1, 2 and 3 there are fluctuations in the removal capacity at different metal concentrations. In many cases, the relative metal removal percentages decreased by increasing the initial metal concentrations and higher removal for metal was observed at lower concentrations. This may be due to the saturation of the sorption sites on the biosorbent as the concentration of the metal increased (Aksu & Tezer, 2005 and Gill *et al.*, 2014).

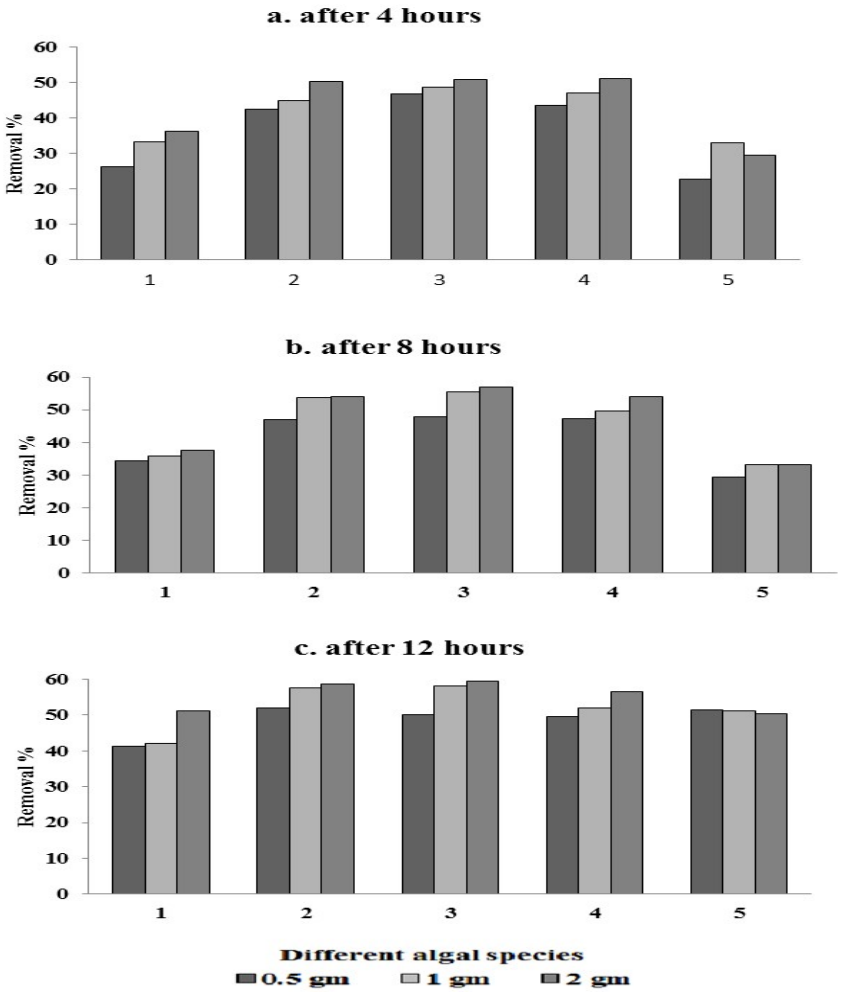

Fig. 1: Removal percentages of hexavalent chromium by different algal species at 200 ppm initial concentration. 1-*Padina pavonia*, 2-*Sargassum hornschuchii*, 3-*Cystoseira sp.*4-*Ulva lactuca* 5-*Gelidium crinale*.

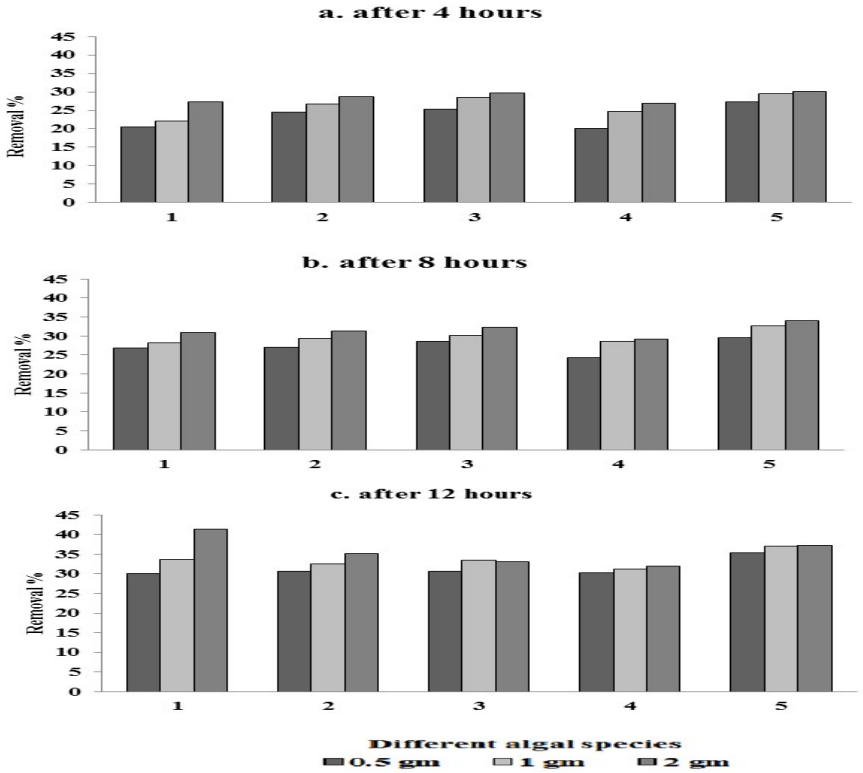

Fig. 2: Removal percentages of hexavalent chromium by different algal species at 300ppm initial concentration. 1-*Padina pavonia*, 2-*Sargassum hornschuchii*, 3-*Cystoseira sp.*4-*Ulva lactuca* 5-*Gelidium crinale*.

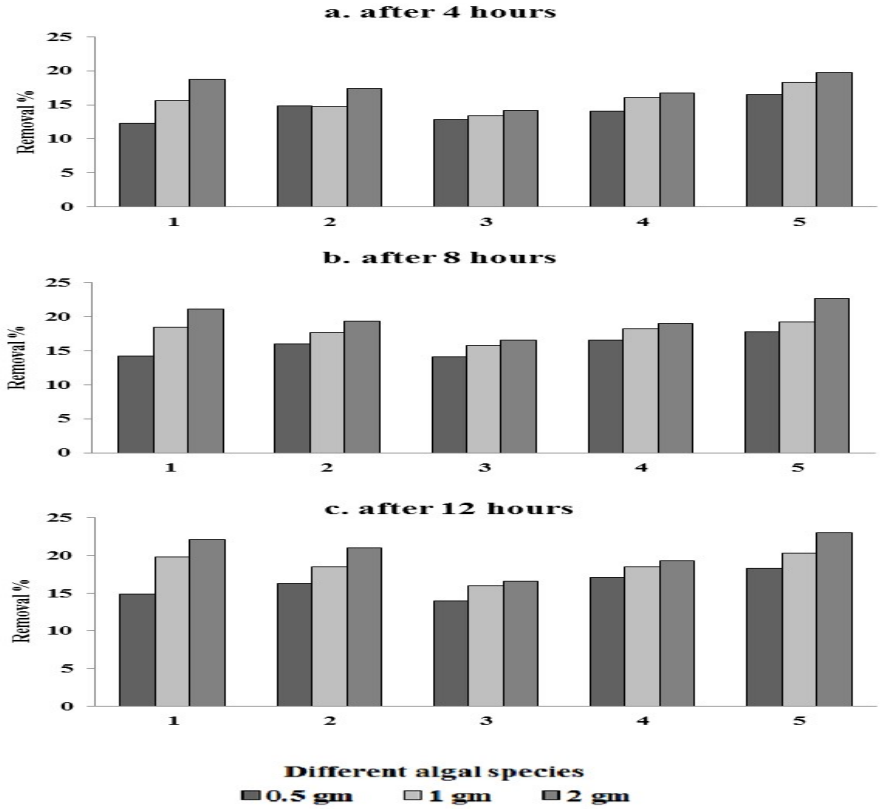

Fig. 3: Removal percentages of hexavalent chromium by different algal species at 400 ppm initial concentration. 1-*Padina pavonia*, 2-*Sargassum hornschuchii*, 3-*Cystoseira sp.*4-*Ulva lactuca* 5-*Gelidium crinale*.

The concentration of the metal ions is associated with the number of active sites on biosorbent, when the number of active sites is plenty; the biosorption capacity will be increased until the active sites in the biosorbent are equal to or lesser than the metal ions in the solutions. It was also noticed that, at low metal concentration (200 ppm) *Sargassum hornschuchii*, *Cystoseira sp.* and *Ulva lactuca* showed higher metal removal than *Padina pavonia* and *Gelidium crinale*. Meanwhile, at high metal concentration (400 ppm) the latter two species showed the reverse trend, especially after 4 and 8 hours.

The amount of metal removed by algae from solution is obviously affected by biomass concentration and differed by different algal species. It was clear that the metal removal increased with increasing the biomass of the tested algae. At 200 ppm *Cystoseira sp.* showed the maximum (59.3%) removal percentage (figure 1c), while *Padina pavonia* showed the maximum (41.5%) removal percentage (figure 2c) at 300 ppm and *Gelidium crinale* showed the maximum (23.1%) removal percentage (figure 3c) at 400 ppm. It is noteworthy to mention that these maximum removals were achieved using 2 grams from the algal biomass and after 12 hours. This result can be attributed to the increase in surface area of the biosorbent, which in turn increases the binding sites (Özer *et al.* 2006). In this respect our results were in complete agreement with several previous works (e. g. Mohan *et al.* 2002 and Royer *et al.* 2009 a & b).

In conclusion, algae biomass represents a renewable substrate which is cultivable on the mass scale while fixing atmospheric carbon-dioxide. Thus, a bioremediation process based on algae biomass is sustainable keeping in account the cost effectiveness and associated environmental benefits (Brune *et al.* 2009). At the same time, much work is needed to evaluate other bioremediation candidates and to assess the best conditions for significant bioremediation.

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