Comparative Study for Biosorption of Heavy Metals from Synthetic Wastewater by Different Types of Marine Algae

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Introduction

Water pollution with metals and metalloids has become one of the major critical threats to environmental and human health [1]. Due to rapid industrialization and accelerating global development, heavy metals have greatly discharged into natural water sources, causing water degradation and ultimately increasing water pollution [2,3].

In biological systems, one of the major concepts regarding the toxicity of HMs is their ability to generate reactive oxygen species (ROS), causing oxidative stress [4,5]. They can generate ROS either via Fenton-/Haber-Weiss type reaction or by direct reaction with cellular molecules [6]. Enhanced production of ROS can oxidatively damage cellular macromolecules such as lipids, thiol proteins and nucleic acids [7], resulting in lipid peroxidation, protein modification, alternation of antioxidant defence system, stimulation of inflammatory processes, oxidative DNA damage, alternation of gene expression and apoptosis [8,9]. These modifications may eventually lead to cellular dysfunction and necrotic cell death [10]. As a result, heavy metal-induced oxidative stress has been implicated in several pathophysiological states including hepatic injury, renal dysfunction, brain damage, lung damage, cancer, cardiovascular diseases, neurological disorders, diabetes and inflammatory diseases [11-15].

Therefore, removal of HM is considered an important issue with respect to the environmental and economic considerations [16]. Several techniques have been used for metal removal from aqueous solution [17,18]. However, these conventional physicochemical methods have a number of drawbacks [3,19]. One of the emerging biological technologies for detoxification of HMs from wastewater is the biosorption process [20]. It is an economically feasible alternative technology using living or dead biomass to eliminate toxic metals from aqueous solutions [21].

A wide variety of active and inactive biomasses such as bacteria, yeast, fungi and algae have been employed as biosorbents for removal of metal ions from aqueous solutions [22,23]. Among these biological materials, marine algae are proposed as one of the most promising biosorbents; particularly when they are existed in non-living forms, due to their high biosorption capacity, low cost, availability and renewability [24]. This high metal-binding affinity in algae has mainly been attributed to the presence of polysaccharides, proteins or lipids on their cell wall surface containing different functional groups such as amine, hydroxyl, carboxyl and sulfate, which can act as binding sites for metals via electrostatic attraction, ion exchange and complexation [25,26].

The objective of the present study is to evaluate the sorption capacity of four different dried marine macroalgae, Ulva lactuca, Jania rubens, Pterocladia capillacea and Colpomenia sinosa for removal of three different metal ions Pb\textsuperscript{2+}, Cd\textsuperscript{2+} and Ni\textsuperscript{2+} from aqueous solution and to identify the major parameters affecting their biosorption.

Materials and methods

Biomass preparation

Four macroalgal species were used in this investigation; Ulva lactuca, Jania rubens, Pterocladia capillacea and Colpomenia sinosa (Figure 1). Samples of the biomass were collected from the Mediterranean Sea coast, Alexandria, Egypt, during spring season (March, 2015). The collected samples were thoroughly washed several times with D. W. to remove impurities, oven dried at 60°C for 24 h and then subsequently ground and sieved to a particle size of 0.5 to 1.0
mm. Finally, the dried biomasses were stored in polypropylene bottles at room temperature to be used as powdered biosorbents.

Chemicals

All chemicals and reagents used in this study were of analytical reagent (A.R) grade and solutions were prepared using deionized and distilled water (D. W.).

Analytical grade (AR> 99.0%) lead nitrate \( \text{Pb(NO}_3\text{)}_2 \), cadmium nitrate \( \text{Cd(NO}_3\text{)}_2.4 \text{H}_2\text{O} \) and nickel sulphate \( \text{NiSO}_4.6 \text{H}_2\text{O} \) were purchased from Sigma–Aldrich Chemical Co. (St. Louis, Missouri, USA).

Optimum pH determination

The optimum pH value for metal biosorption was determined by adjusting the heavy metal solutions to various pH values (2, 3, 4, 5, 6, 7, 8) using 0.1 M HNO\(_3\), H\(_2\)SO\(_4\) or NaOH solutions. The other parameters of metal ion concentration, biosorbent dosage and contact time were fixed at 10 mg/L, 40 g/L and 120 min, respectively.

Optimum contact time determination

The optimum contact time for metal biosorption was determined by adjusting the heavy metal solutions at different time intervals (5, 15, 30, 60, 120 min). The other parameters of pH, metal ion concentration and biosorbent dosage were fixed at 6, 10 mg/L g and 40 g/L, respectively.

Optimum biomass dosage determination

The optimum biomass dosage for metal biosorption was determined by mixing the heavy metal solutions with different weights of the biomass (1, 10, 20, 30, 40 g/L). The other parameters of pH, metal ion concentration and contact time were fixed at 6, 10 mg/L and 60 min, respectively.

Optimum initial metal ion concentration determination

The optimum initial metal ion concentration for metal biosorption was determined by adjusting the heavy metal solutions at different metal concentrations (5, 10, 20, 40, 60, 80 and 100 mg/L). The other parameters of pH, biosorbent dosage and contact time were fixed at 6, 20 g/L and 60 min, respectively.

Batch biosorption procedure

Batch biosorption experiments were conducted at room temperature (25 ± 1°C) in 500 mL Erlenmeyer flasks by contacting an appropriate amount of the algal biomass with the heavy metal solution. The mixtures were agitated on a rotary shaker at 120 rpm until equilibrium was achieved. Then, the biomass was separated by filtration through Whatman filter paper (No. 40) and the filtrate was acidified and analyzed for residual metal concentration by atomic absorption spectrophotometry (AAS) (Shimaduz Atomic Absorption Spectrophotometer, AA-7000F, Japan).

FTIR spectroscopy analysis

Fourier-transform infrared (FTIR) spectroscopy was used to detect the chemical functional groups responsible for metal uptake in algal biomass [27]. Samples of fresh-dried and metal-loaded algal biomass were subsequently analyzed using FTIR spectrometer (Mattson Satellite 5000 FTIR, UK), within the wave number 500–4000 cm\(^{-1}\) under ambient conditions.

Statistical analysis

The Statistical Package for the Social Sciences (SPSS/PC) computer program was used for statistical analysis of the results. FTIR charts were performed using OriginPro for data analysis and graphing software. Comparison of variables between two groups was performed with paired samples-t-test for continuous variables. The data were expressed as mean ± standard error (S.E). Differences were considered significant at p≤0.05.

Results and Discussions

Optimization of heavy metals biosorption

Solution pH: One of the important factors affecting the biosorption of metal ions is the acidity of solution [28]. In the present study, it was observed that in almost all algal types the removal efficiency was markedly low at highly acidic conditions (pH<4). With increasing of pH value, metal adsorption increased till reached its maximum around pH 4–6 and then showed a rapid decline under highly alkaline conditions (Figures 2-4).
The poor biosorption capacity at low pH values may be due to the high concentration of the positively charged $\text{H}^+$ and $\text{H}_3\text{O}^+$ ions, which compete with metal cations for the binding sites on the algal surface [29,30]. Consequently, the algal cell wall was protonated and this restricted the approach of metal cations as a result of the repulsive force [28]. In contrast, as solution pH increased, the protons concentration decreased and the algal surface would be more negatively charged leading to electrostatic attraction of the positively charged metal ions and hence biosorption is enhanced until reached its maximum [31-33]. The decrement in the uptake capacity at higher pH values may be attributed to (i) the high concentration of $\text{OH}^-$ ions that led to precipitation of metals as hydroxides [34], and (ii) the electrostatic repulsion between the negatively charged algal surfaces and the negatively charged anionic species in solution [35,36]. Moreover, the lower uptake at higher pH values could be due to inactivating of the binding sites in alkaline conditions [37].

**Contact time:** Contact time was also evaluated as one of the most significant factors affecting the biosorption efficiency. The current study demonstrated that the adsorption rate was significantly enhanced with rise in contact time up to 60 min when equilibrium was attained, thereafter no significant changes in adsorption were observed with further increase in contact time (Figures 5-7).
The high biosorption rate at initial contact time could be related to the high concentration gradient of solute [38], as well as abundance of vacant active sites on the algal surface [39,40]. Afterward, the slow removal capacity during the later stages may be attributed to diffusion of metal ions into algal surface [41], as well as difficulty of occupation of the remaining binding sites due to forces between the solute molecules of the solid and bulk phases [42,43].

**Algal dosage**: Another important variable during metal uptake is the biomass concentration that can significantly affect the sorption process [44]. In the present study, it was observed that the removal percentage of metal ions increased with subsequent increasing in the algal dosage up to 20 g/L, where the biosorption capacity reached its maximum value and the equilibrium between the sorbent and sorbate was attained; afterwards the removal capacity was almost constant (Figures 8-10).

The increase in removal uptake at initial biosorbent doses could be attributed to the greater surface area of biosorbent, which in turn increased the availability of active sites for metal ions [20]. However, at higher biosorbent concentrations (>20 g/L), the removal uptake was maintained constant due to the partial aggregation of biosorbent particles that reduces the effective surface area for biosorption [45], and lead to protection of the active sites from being occupied by metal ions [46].

**Metal ion concentration**: The initial metal ion concentration strongly influences the metal uptake process, as it provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases [47]. The current study showed that the adsorption capacity for the different metal ions increased as the initial concentration increased until reached its maximum at concentration of 40 mg/L for Pb²⁺ and Cd²⁺ and 20 mg/L for Ni²⁺. After that, with increasing the metal concentration, the adsorption capacity remained unchanged (Figures 11-13).
The enhanced biosorption at initial stages could be attributed to the greater driving force of metal ions into the algal surface and abundance of vacant binding sites on the biosorbent surface [48]. Thereafter, with increasing metal concentration, the removal rate was almost constant due to saturation of all available sorption sites on algal surface and attainment of equilibrium between the sorbent and sorbate, thereby thus preventing further adsorption of metal ions [49,50]. Accordingly, high biosorption yields were observed at lower metal ion concentrations [47].

**FTIR spectroscopy**

FTIR analysis was performed as a quantitative analysis to determine the main functional groups present in different algal powders that are involved in biosorption of heavy metal ions [51].

In the present study, compared to the fresh-dried algal biomass, significant changes in the wave number of the bands after loading of Pb^{2+}, Cd^{2+} or Ni^{2+} indicated that the functional groups (hydroxyl, amine, phosphate, C−O and C=O) could be involved in biosorption of the three metal ions onto the surface of different algal powders (Figures 14-17).

**Figure 11:** Effect of initial concentration on removal efficiency of Pb^{2+} by different algal powders.

**Figure 12:** Effect of initial concentration on removal efficiency of Cd^{2+} by different algal powders.

**Figure 13:** Effect of initial concentration on removal efficiency of Ni^{2+} by different algal powders.

**Figure 14:** FTIR spectrum of unloaded and metal-loaded *U. lactuca* biomass.

**Figure 15:** FTIR spectrum of unloaded and metal-loaded *J. rubens* biomass.
bands, suggested that these bands were not involved in the sorption lipid or other carbohydrate content of the four genera of algae [54].

Figure 16: FTIR spectrum of unloaded and metal-loaded P. capillacea biomass.

Figure 17: FTIR spectrum of unloaded and metal-loaded C. sinosa biomass.

As these considerable changes observed in the spectra may be resulted from metal ion–biomass interactions [52,53]. On the other hand, no shifts were observed in the alkene and aliphatic chains –CH bands, suggested that these bands were not involved in the sorption process. These variations in the adsorption efficiency of the four different marine macroalgae may be due to differences in the protein, lipid or other carbohydrate content of the four genera of algae [54].

Conclusion

This study clearly demonstrated the biosorption performance of four different marine macroalgae for removal of Pb(II), Cd(II) and Ni(II) ions from aqueous solution and also identified the operating parameters affecting their biosorption efficiency. According to the obtained results, the red marine alga J. rubens was selected as the most effective and alternative biomass for removing of metal ions from aqueous solution due to its considerable high biosorption capacity, availability and cost-effectiveness. Moreover, the results indicated the higher uptake capacity of J. rubens alga for Pb(II) and Cd(II) than Ni(II) ions, which revealed its weaker binding to the biomass sites. Consequently, J. rubens alga can be considered as a promising, effective and safe biosorbent for detoxification of heavy metals and purification of wastewater.

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