Short communication

Biosorption of Lead (II) and Copper (II) Metal Ions on *Cladophora glomerata* (L.) Kütz. (Chlorophyta) Algae: Effect of Algal Surface Modification

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Abstract

Heavy metals are present in some industrial effluents, being responsible for environmental pollution. Biosorption of heavy metals can be an effective method for the removal of heavy metal ions from wastewaters. In this study Pb(II) and Cu(II) biosorption by *Cladophora glomerata* algae was investigated in batch system from a binary mixture. The effects of some important parameters such as pH, initial concentration of heavy metals and modification of algae surface by heat/acid treatment on biosorption capacity was studied. The maximum biosorption capacity of *Cladophora glomerata* was 15.0mg/g at pH 5.0 for Cu(II) and 22.5 mg/g at pH 4.0 for Pb(II) metal ions. The biosorption capacity of Pb(II) and Cu(II) ions on the acid/heat-treated biomass was increased as 1.38 and 1.45 times than untreated form, respectively. The biosorption of Pb (II) and Cu (II) heavy metal ions on *Cladophora glomerata* appears to be an efficient and low cost alternative to be considered in industrial wastewater treatment.

Keywords: Biosorption, *Cladophora glomerata*, heavy metal pollution, modification

1. Introduction

Many industrial processes produce large amounts of wastewater, which are leading to detrimental effects on human life and environment. The major pollutants in wastewater are heavy metals such as lead, zinc, copper, cadmium, mercury, chromium and arsenic. These metals accumulate in living tissues/organs and can cause accumulative poisoning and serious health problems such as cancer and brain damage. There are numerous methods currently employed to removal of these metals from aqueous environment. Some of these methods are chemical precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, membrane separation, electrochemical treatment and evaporation. Biosorption as a wastewater bioremediation process has been found to be an economically feasible alternative for metal removal. This method offers the advantages of low operating cost, minimizing secondary pollution and high efficiency in wastes.[1–5]

Algae have been found to be potential suitable biosorbents because of their cheap availability, relatively high surface area and high uptake capacity.[2–4] Algae are able to eliminate different forms of heavy metals by chelating, making complexes, catalyzing or adsorption. Harris and Ramelow[6] studied the biosorption of copper using dead *Chlorella vullgaris* and found that 90% of Cu sorption took place within five minutes. Dönmez and Aksu[7] studied with *Dunaliella sp*. for adsorption of Cr metal ions. Algal biomass can be used for biosorption process in live or dead form. However, in practical applications, the use of nonliving biomass is more practical and advantageous because living biomass cells often require the addition of fermentation media which increases the biological oxygen demand or chemical oxygen demand in the effluent. In addition, non-living biomass is not affected by the toxicity of the metal ions, they can be subjected to different chemical and physical treatment techniques to enhance their performance. Physical treatment methods such as heat, acid and base treatments have usually shown an increase in biosorption capacity of biomass due to re-organization of cell wall structure.[8,9]

The cell wall of algae consists of chitin, lipids, polysaccharides and proteins. These macromolecules provide different functional groups, such as thioether, carboxyl, imidazole, hydroxyl, carbonyl, phosphate, phenolic, etc., which can form coordination complexes with heavy metals. *Cladophora glomerata* have a branched flamentous structure and its cell wall is composed of different layers such as chitin, pectose, and cellulose and these constituents provide functional groups as mentioned above capable of binding various heavy metals.[10]

In this study, the biosorption of Pb(II) and Cu(II) on powdered non-living *Cladophora glomerata* from single and binary mixtures are investigated. Also the effect of the system parameters such as pH, initial metal concentration and acid/heat-treatment on the biosorption capacity of biomass investigated.

2. Experimental

2. 1. Biomass

Cladophora glomerata was collected from the coasts of Kızılırmak in Turkey. Samples were washed twice with distilled water. The washed biomass was oven-dried at 50 °C for 24 h, crushed with an analytical mill, sieved (size fraction of 0.5–1 mm) and stored in polyethylene bottles until use.

2. 2. Biosorption Studies

The biosorption experiments were conducted in Erlenmeyer flasks containing 50 ml of heavy metal solutions and 0.1 g of algal biomass. The flasks were agitated on a shaker at 150 rpm constant shaking rate for 6 h to ensure equilibrium was reached. Studies were performed at a constant temperature of 25 °C to be representative of environmentally conditions. At the end of experimental period metal solutions were separated from the algae by centrifugation at 4000 rpm and analyzed using Atomic Adsorption Spectrometer (GBC 933 AAA). The amount of metal biosorbed, Qm (mg/g), was calculated according to the following equation:

$$Qm = (Ci - Ceq)\,V / m, \qquad (1)$$

where V is the volume of metal solution (ml), m is the mass of dry algae (g), Ci and Ceq are the initial and equilibrium concentration of metal in solution (mg/l), respectively.

Also the effect of solution pH on biosorption of metal ions was studied. For this purpose aqueous solutions adjusted to the predetermined pH values (ranging from 2.0 to 6.0) were used. To determine the effect of initial metal concentration on biosorption capacity of *Cladophora glomerata* five different Pb(II) and Cu(II) concentrations (25–200 mg/l) of metal solutions were prepared.

2. 3. Competitive Biosorption

The competitive biosorption of both divalent cations was tested through batch experiments. For this purpose, the binary mixtures composed of 100 mg/l Pb (II) and Cu (II) were prepared. Biosorption of metal ions with binary aqueous solutions containing fungal biomass were carried out similarly as in a single-component metal systems, but only at pH 5.0 and 4.0.

2. 4. Modication of Biomass

The algal biomass was treated with 2% hydrochloric acid for 2 h while continous stirring at 150 rpm on the water bath at 80 °C. So the algal biomass was treated with acid and heat conditions together. Treated biomass were filtered, washed with deionized water and dried in oven at 50 °C. Biosorption experimets repeated with acid/heat treated biomass as mentioned above.

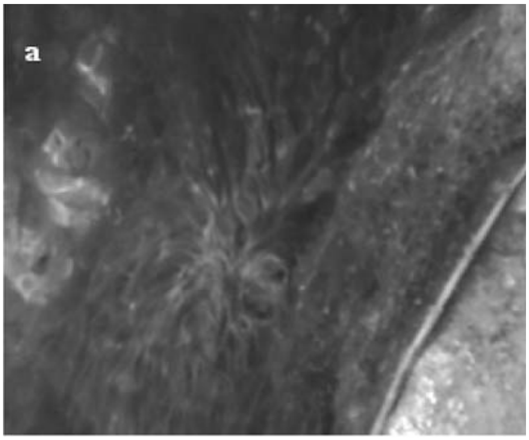
3. Results and Discussion

Figure 1a and 1b shows the general morphology and surface properties of *Cladophora glomerata*.[11] From the figures, *Cladophora glomerata* have a flamentous structure. This property of algal biomass provides broad surface area for biosorption of metal ions, so the biosorption capacity increased importantly.

3. 1. Effect of pH

pH has a very significant effect on biosorption of metal ions from solutions. It is known that the solution of pH affects the surface charge of the biomass, the speciation of the functional groups such as carboxylate, phosphate, hydroxyl and amino groups of the cell wall.[12,13] Figure 2 shows the biosorption of Pb(II) and Cu(II) on *Cladophora glomerata* as a function of pH.

The maximum Pb(II) biosorption is reached at pH 4.0 and the maximum Pb(II) adsorptions of 22.5 mg/g was recorded. In the case of Cu(II) biosorption, maximum biosorption capacity was 15 mg/g at pH 5.0. As can be depicted from Figure 2, the biosorption of Pb(II) and Cu(II) metal ions by *Cladophora glomerata* was strongly affected by pH. A sharp increase in metal uptake was observed with increasing pH. This results can be explained using the fact that with increasing pH, functional groups avai-



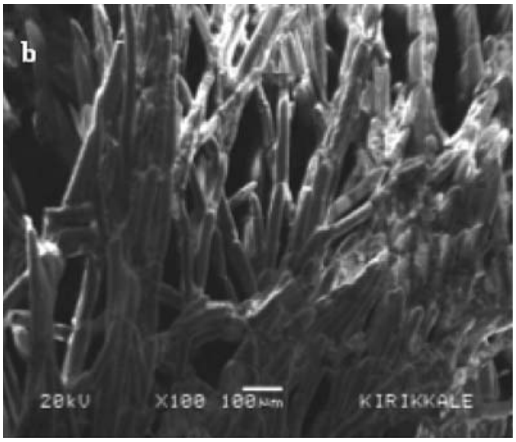


Figure 1. (a) General, (b) surface morphology of *Cladophora glomerata*[11]

lable on algal surface would be exposed and thus negative charges will result. So the attraction between the negative charged cell wall and the metals would increase. Another reason for increasing biosorption of metal ions with increasing pH is that the the zero-point charge of algal biomass (pH 2.9–3.0).[14,15] At pH values above the zero-point charge, the algal cells would have negative net charge and the electrostatic attractions between positively charged cations such as Pb(II) and Cu(II) and negatively charged binding sites on algal surface enhanced. All these reasons explains the significant increase of the binding efficiency by increasing the pH from 3.0 to 5.0. At pH below 3, biosorption capacity of Pb(II) and Cu(II) were negligible, probably due to the cation competition effects with hydronium ion H_3O^+. Furthermore, at pH 6.0 biosorption of metals decreased probably because of chemical precipitation.[16,17]

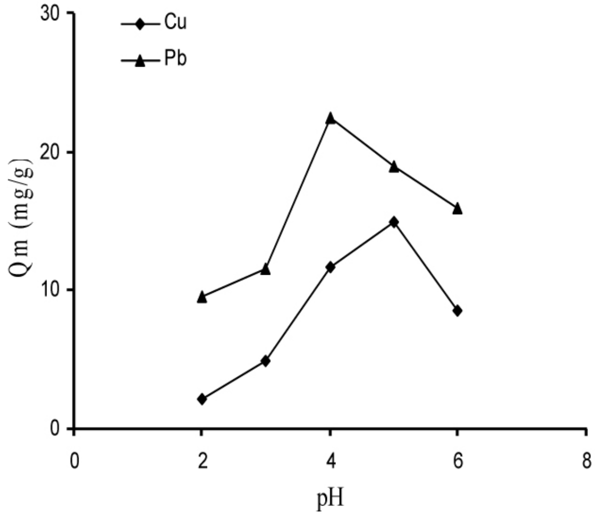


Figure 2. Effect of pH on biosorption of Pb (II) and Cu (II) metal ions

3. 2. Initial Metal Concentration

The metal distribution between the algae and the aqueous solution at equilibrium is of importance in determining the maximum biosorption capacity of the algae for Pb (II) and Cu(II) metals. The effect of initial metal concentration on the biosorption capacity was investigated at pH 4.0 for Pb(II) and pH 5.0 for Cu(II) metal ions. In Figure 3, biosorption of Pb(II) and Cu(II) increased much quickly with increasing initial metal concentration from 25 to 100 mg/l.

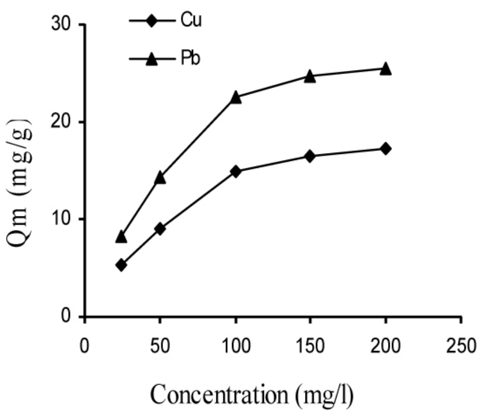


Figure 3. Effect of initial metal concentration on biosorption capacity

A higher initial concentration provides an important driving force to overcome all mass transfer resistances between the metal solution and algal cell wall, thus the biosorption capacity increases. In addition, the number of collisions between metal ions and biosorbent increases with increasing initial metal concentration so the biosorption process enhances.[18] Biosorption rate was decreased with increasing initial concentration from 100 to 200 mg/l due to the saturation of the biosorption sites on the algal surface.

3. 3. Competitive Biosorption

In real wastewaters, synergistic or antagonistic interactions can be caused by the presence of other cationic and anionic metal ions. So the competetive effect becomes important in wastewater treatment applications. The results of the competetive biosorption of the Pb(II) and Cu(II) metal ions on algal cells are shown in Figure 4.

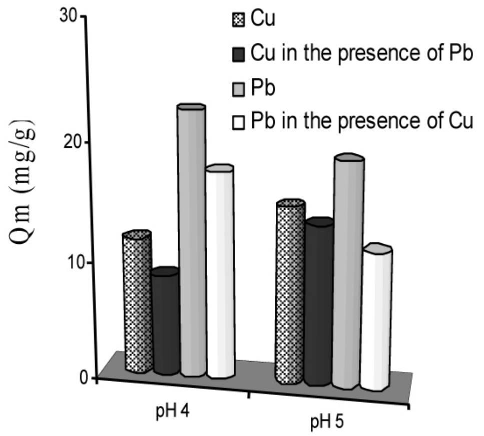


Figure 4. Competetive biosorption of Pb (II) and Cu (II) metal ions

The presence of another cationic metal resulted in a suppression of metal uptake. The biosorption capacity was decreased 22% and 40.7% in the competetive biosorption at pH 4.0 for Pb(II) and Cu(II) metal ions, respectively. At pH 5.0 biosorption capacity was decreased 38% and and 29% for Pb(II) and Cu(II) metal ions, respectively. The suppression in Cu(II) uptake in the presence of Pb(II) was much more significant than the suppressions in Pb(II) uptake in the presence of Cu(II) ions. These suppressions in competetive biosorption indicates an overlap in the biosorption site of algal cell wall. In the presence of another metal, chemical interactions between metal ions and a competition for the binding sites occured and the biosorption capacity decreased.[15] Since most of the functional groups present on the algal cells wall are non-specific for a metal so the different metals interact with the binding sites and the competetion occur. It has been reported that the biosorption process enhamces with the increasing ionic radii of metals, which follows the order Pb(II) > Cu(II). The differences in biosorption capacities may be explained by the differences in the electronegativity of the metal ions, which also follows the order Pb(II) > Cu(II). The greater the electronegativity, the greater is the affinity, which also explains the significant suppression of copper uptake in the presence of lead.[18–19]

3. 4. Modification of Biomass

Biosorption capacities of un-treated and acid/heat-treated biomass are shown in Figure 5. An increase in biosorption capacity was observed after acid/heat-treatment.

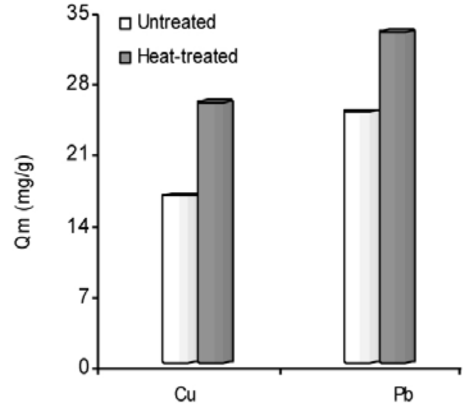


Figure 5. Effect of acid/heat-treatment on biosorption capacity of Pb (II) and Cu (II) metal ions

The bisorption capacity of Pb(II) and Cu(II) ions on the acid/heat-treated biomass was 1.38 and 1.45 times higher than untreated form, respectively.

Modification of biomass by heat and acid treatment results a re-organization of cell wall so the additional binding sites occured. Acid and heat treatment degrade some compenents of algal cell wall. The hydrochloric acid breaks the pectose down to pectin or pectic acid. By heating the filament of algae some compounds in cell wall dissolved and new binding sites formed.[20] And also proteins located in cell wall denaturated by treatment and structurel changes occured. All these cumulative effects of modification explain the increased biosorption capacity. The increase in biosorption capacity with modification may be a result of these changes in cell wall structure.

4. Conclusions

Biosorption technology, utilizing natural materials for effectively removing metals from aqueous media, offers an efficient alternative compared to traditional chemical and physical treatments. The goal of this work was to explore the potential use of *Cladophora glomerata* biomass as a low-cost sorbent for the removal of Cu(II) and Pb(II) heavy metal ions from aqueous solutions. Batch experiments showed that *Cladophora glomerata* have a remarkable ability to take up Cu(II) and Pb(II) heavy metal ions. The maximum biosorption capacity of heavy metal ions on *Cladophora glomerata* were 15.5 mg/g for Cu(II) and 25.5 mg/g for and the affinity order was Pb(II) > Cu(II). The results obtained showed that the pH and initial metal concentration affected the uptake capacity of the biosorbent. And also acid/heat modification affected the biosorption yield and metal uptake positively. In competetive biosorption the presence of other cationic metal ions significantly decreased efficiency of metal biosorption. Many workers have also investigated the performance of algae for the removal various heavy metal ions (Ni, Cu, Pb, Zn, Cd, and Al) from wastewater. Yu et al.[21] reported that capacities of macro marine algae for lead, copper, and cadmium were in the ranges of 1.0 to 1.6, 1.0 to 1.2 and 0.8 to 1.2 mmol/g, respectively. Munoz et al.[22] reported a 8.5 ± 0.4 mg/g maximum Cu(II) adsorption capacities of algal-bacterial biomass at an initial Cu(II) concentration of 20 mg/l. Mihova and Godjevargova[23] studied the biosorption of Cu heavy metal on different mikroorganisms and reported the higher adsorption capacity was found to possess S.cerevisiae (3.5 mg/g) than Ph.chrysosporium (2.5 mg/g). When compared the adsorption capacity values obtained by similiar metals in literature, *Cladophora glomerata* showed great promise for the removal of heavy metal ions. Also results obtained from this study can surely be used to design a practical and economical process for wastewater treatment.

5. References

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Povzetek

Raziskovali smo vpliv pH, začetne koncentracije kovinskih ionov ter modifikacije površine alge s toplotno in kislinsko obdelavo na biosorpcijo Pb(II) in Cu(II) z algo *Cladophora glomerata.* Izkazalo se je, da maksimalna kapaciteta biosorpcije znaša 15.0 mg/g pri pH 5.0 za Cu(II) in 22.5 mg/g pri pH 4.0 za Pb(II) ion. Toplotna in kislinska obdelava biomase poveča kapaciteto biosorpcije 1.38-krat za Pb(II) in 1.45-krat za Cu(II) ione v primerjavi z neobdelano maso. Odstranjevanje Pb(II) in Cu(II) iz odpadnih industrijskih vod z algo *Cladophora glomerata* bi bila torej učinkovita in poceni možnost.