HEAVY METAL IONS DEPOLLUTION BY MARINE NATURAL PRODUCTS

IOANA-RALUCA BUNGHEZ[1,2], RODICA-MARIANA ION[1,2], IRINA DUMITRIU[1,2], RADU-CLAUDIU FIERASCU[1,2]

[1] *National R&D Institute for Chemistry and Petrochemistry – ICECHIM Bucharest, 060021, Bucharest, Romania*

[2] *Valahia University of Targoviste, 130082, Targoviste, Romania*

Abstract: *Many industrial processes produce large amounts of wastewater, which have detrimental effects on human life and environment. The major pollutants in wastewater and marine ground 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.*
Algae have been found to be potential suitable biosorbents due to their cheap availability, relatively high surface area and high uptake capacity. Algae are able to eliminate different forms of heavy metals by chelating, complexe formation, catalysis or adsorption [1,2].
In the present study, we used a green algae as biosorbent. It has been studied the adsorption kinetics of metal ions using marine plants from synthetic solutions over different time intervals and various concentrations. The results have been processed by ICP-AES spectroscopy.

Keywords: *heavy metals, biosorbtion, algae, marine plant, wastewater treatment*

1. INTRODUCTION

Heavy metals are major pollutants in marine ground industrial and even treated wasters. Furthermore, in developing countries, many industries are operated at small or medium scale. These smaller units can generate a considerable pollution load which, in many cases, is discharged directly into the environment without any facilities for wastewater treatment. Metals can pose health hazards if their concentrations exceed allowable limits. Even when the concentration of metals does not exceed these limits, there is still a potential for long-term contamination, since heavy metals are known to be accumulative within biological systems. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc. [4].

In recent years, increasing awareness of the environmental impact of heavy metals has prompted a demand for the purification of industrial waste waters prior to discharge into natural waters. Research interest into the production of cheaper adsorbents to replace costly conventional methods of wastewater treatment methods are attracting attention of scientists. Conventional methods for example, ion-exchange, chemical precipitation, ultrafiltration, or electrochemical.

Many heavy metals (Fe, Cu, Mn, Zn) are essential micronutrients for algal metabolism and they may limit algal growth at low concentrations. In contrast the heavy metal, Au, Ag, Pb and Cd have no known metabolic function, but may be toxic towards algae. The most common overall toxicity sequence to algae is Hg> Cu> Cd>, Ag > Pb. Metal ions, either alone or in complexes, have been used for centuries to disinfect fluids, solids and tissues. Fundamentally bacteria and algae show low resistance to Ag, Cu and Zn ions which have been used for a long time in the biomedical field. Many new methods of purifying water from algae, fungi and bacteria include these metals [3].

The presence of heavy metals in aquatic environments is known to cause severe damage to aquatic life, beside the fact that these metals kill microorganisms during biological treatment of wastewater with a consequent delay of the process of water purification. Most of the heavy metal salts are soluble in water and form aqueous solutions and consequently cannot be separated by ordinary physical means of separation.

Physico-chemical methods, such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange, and membrane technologies have been widely used to remove heavy metal ions from industrial wastewater. These processes may be ineffective or expensive, especially when the heavy metal ions are in solutions containing in the order of 1-100 mg dissolved heavy metal ions/L. Biological methods such as biosorption/bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods. The use of adsorbents of biological origin has emerged in the last decade as one of the most promising alternatives to conventional heavy metal management strategies. Because of the absence of rational method for a priori prediction of the biosorption potential of a microorganism, the only method for identifying and developing newer and efficient biosorbents is the sustained screening of microbes. Biosorption of heavy metals by microbial cells has been recognized as a potential alternative to existing technologies for recovery of heavy metals from industrial waste streams. Many aquatic microorganisms, such as bacteria, yeast and algae can take up dissolved metals from their surroundings onto their bodies and can be used for removing heavy metal ions successfully. Equilibrium studies, that give the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which is usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium [5,6].

Cr, Zn, Cd are toxic heavy metals whose toxicity is atributed in part to its ability to accumulate in tissues.

We want to demonstrate in this study the biosorbtion capacity of *Mayaca fluviatilis* green marine plant, *Porphyra umbilicalis* and *Fucus vesiculosus* dried algae for heavy metal ions from aqueous solutions.

2. MATERIALS AND METHODS

2.1. MATERIALS

As biosorbents we used *Mayaca fluviatilis* (Fig. 1.) green marine plant, *Porphyra umbilicalis* (Fig. 2.) a red alga from Coreea, *Fucus vesiculosus* (Fig. 3.) a brown-green alga from China, and heavy metal ions removal was tested using synthetic solutions (certificate reference material of 1000 mg/L, MRC).

Fig. 1. Mayaca fluviatilis

Fig. 2. Porphyra umbilicalis-red dried alga

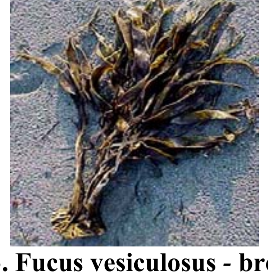

Fig. 3. Fucus vesiculosus - brown-green dried alga

Next step was to add the biomass of plant to the synthetic solution of heavy metal ions at different concentrations (20 mg/L and 5 mg/L). Then we have agitated continuous with a mechanic agitator for 120 min, at room temperature and pH = 5.5. We took out 10 mL at specific time intervals.

3. APPARATUS

A Varian Liberty 110 Series spectrometer was used for the ICP-AES analysis. A manual hydraulic press was used for the preparation of pressed pellets and a mixer for the blending of the materials. For the ICP-AES measurements, sub samples were cut off from the original sherds and were finely powdered in an agate mortar. Multielement, matrix matched standards were used for the quantitative determinations.

4. RESULTS AND DISCUSSION

The difference between the initial and remaining metal concentration was assumed to be taken up by the biosorbent.

Evolution of Cr, Zn, Cd in different time intervals and various concentrations showed that heavy metal ions significantly decreases, faster in the first 30 min from the beginning of the experiment, then was stabilized for next 60 minutes.

In Figs. 4 and 5 are represented evolutions of Cr and Zn concentration in artificial solutions, at 0, 15, 30, 45, 60, 75, 90, 120 minutes. In Fig. 6 it is represented evolution of Cd concentration in artificial solutions, at 0, 30, 60 and 120 minutes in an artificial solution with a 20 mg/L concentration.

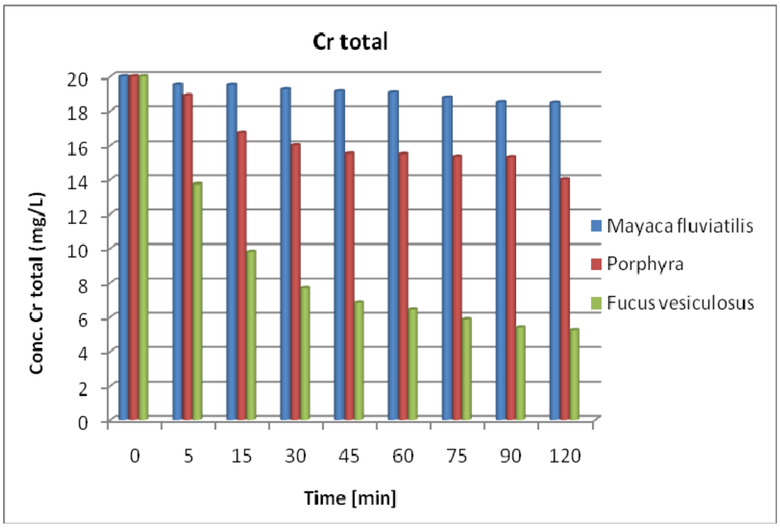

Fig. 4. Evolution of Cr concentration in time for initial solutions of different marine plants containing 20 mg/L quantities of chromium ions.

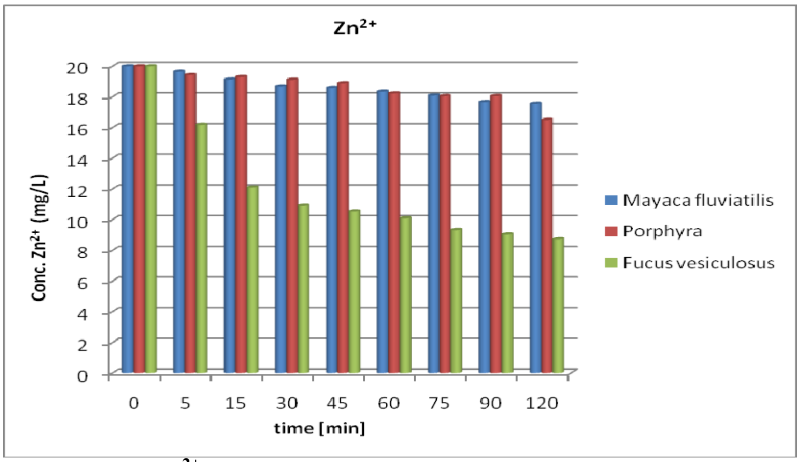

Fig. 5. Evolution of Zn^{2+} concentration in time for initial solutions of different marine plants containing 20 mg/L quantities of zinc ions.

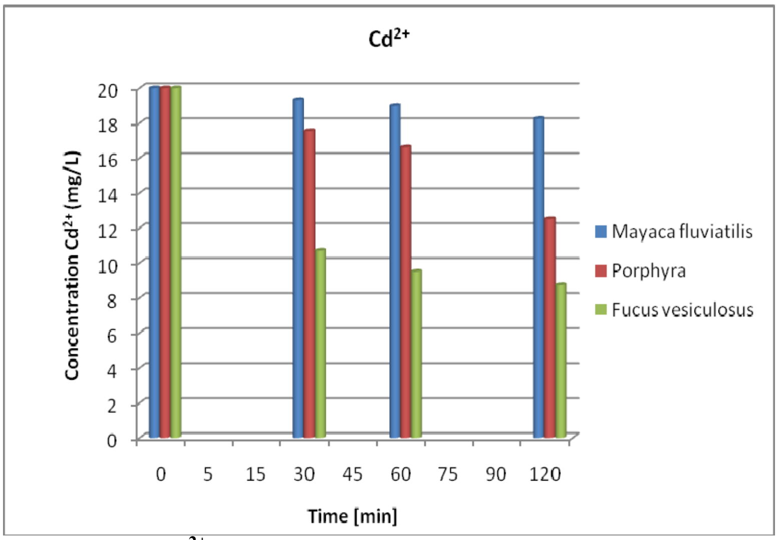

Fig. 6. Evolution of Cd^{2+} concentration at 0, 30, 60 and 120 minutes for initial solutions of different marine plants containing 20 mg/L quantities of zinc ions.

In Figs. 7, 8 and 9 it is presented the fact that at 5 mg/L concentration artificial solution, the decrease of heavy metal ions occurred like the same of 20 mg/L concentration. It is observed that *Fucus vesiculosus* decreases most rapidly, as happened at 20 mg/L concentration.

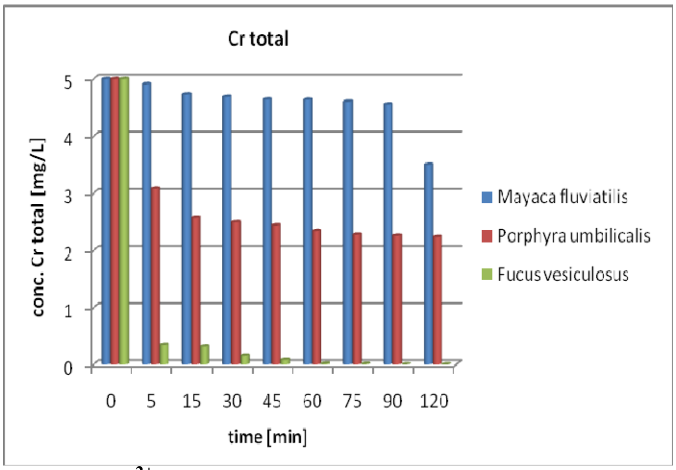

Figure 8. Evolution of Cr^{2+} concentration in time for initial solutions of different marine plants containing 5 mg/L quantities of chromium ions.

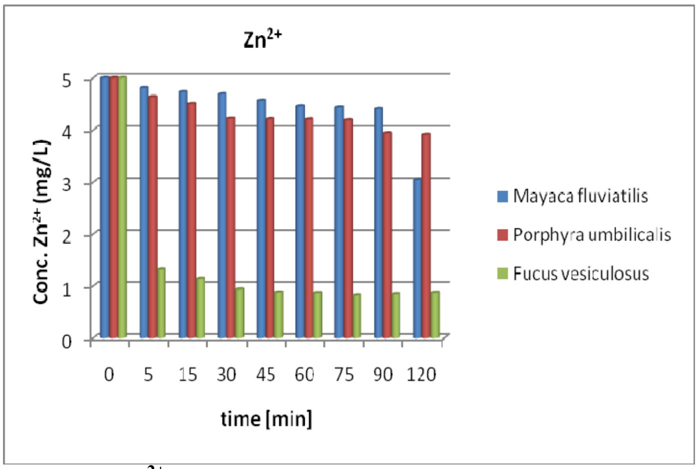

Figure 9. Evolution of Zn^{2+} concentration in time for initial solutions of different marine plants containing 5 mg/L quantities of zinc ions.

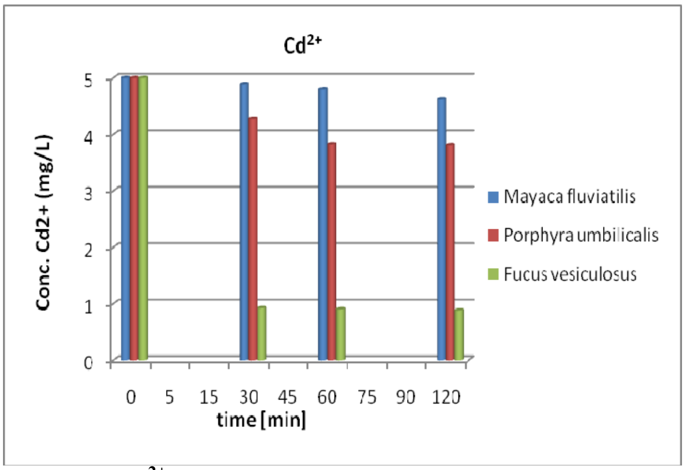

Figure 10. Evolution of Cd^{2+} concentration in time for initial solutions of different marine plants containing 5 mg/L quantities of cadmium ions.

5. CONCLUSIONS

The results indicates that the metals concentrations decreased during the first 30 minutes and remained nearly constant after 2 hours suggesting that the biosorption was fast and reached saturation within 2 hours for *Mayaca fluviatilis*. After this equilibrium period, the amount of adsorbed metal ions didn't significantly change with time.

The algae *Porphyra umbilicalis* and *Fucus vesiculosus*, decreased rapidly in the first 15-30 minutes, for all metal ions concentrations (Cr, Zn, Cd), then they became almost constant during the entire experiment. *Porphyra umbilicalis* is seen as better able to reduce chromium than the marine plant, *Mayaca fluviatilis.* Also, it is obvious that most effectively reduced metals is *Fucus vesiculosus*.

Mayaca fluvialis was the single plant from this study which hasn't significant decreases, result that it is not so efficient biosorbent for Cr and Zn ions like another two algae studied.

It can be concluded that this marine plant (*Mayaca fluviatilis)* and algae (*Porphyra umbilicalis* and *Fucus vesiculosus*) can be used in removal recovery of heavy metal ions from industrial waste water. The difference between the initial and remaining metal concentration was assumed to be taken up by the biosorbent.

Also we have seen that using live or dead algae and plant could be an effective biosorbents for the heavy metal ions from wastewaters. One possible explanation for using dead algae could be the metabolic extracellular products, which may form complexes with metals to retain them in solution.

Further studies are needed to increase the biosorbtion capacities of biomass and to develop appropriate technologies applicable in the treatment of wastewaters.

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