

# **HEAVY METALS REMOVAL WITH WATER MILFOIL (MYRIOPHYLLUM SPICATUM) IN CONSTRUCTED WETLAND**

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## **ABSTRACT**

Toxic heavy metals contamination is often detected in wetlands, impoundments, estuaries, coastal areas and other ecosystems. The sources of metal contamination are usually from marina or harbor activities, boat and shipping industry, canal run-off, sewage effluent, industrial waste discharge, etc. Conventional remediation methods such as precipitation chemical oxidation or reduction, ion exchange, filtration, membrane technologies or evaporation process are generally impractical or ineffective to be applied in an ecosystem. The use of living plant biomass for removing metals from an ecosystem provides a potential for cleanup of the wetland or estuarine coastal environments.

## **INTRODUCTION**

Growing public awareness and increased scientific knowledge have enunciated environmental problems such as coastal water pollution, loss and degradation of habitats, contaminated water and sediment in ecosystems and the continuing conversion of open land to urban development. Stormwater runoff from urban sites and other non-point source pollution that carries heavy metals, oil, hydrocarbons, pesticides, nutrients and other suspended solids have degraded water quality in many of the nation's wetland ecosystems. One of the key elements of the U.S. Environmental Protection Agency Stormwater runoff regulation is the promotion of the use of best management practices for controlling non-point pollution sources (Yu, 1995). These management practices include detention ponds, infiltration basins, vegetative stripes and constructive wetlands. Pollutant removal through constructive wetland or detention ponds are mainly by gravitational particle-settling, chemical precipitation of metals, filtration of organic matter, and biological uptake or adsorption by aquatic vegetations. Using aquatic plants for bioremoval of pollutants plays an important role in wetland ecosystem remediation.

Aquatic plants are known to accumulate metals and other toxic elements from contaminated water (Wolverton and McDonald, 1975; Muramoto and Ohi, 1983; Green and Bedell, 1990; Wilde and Benemann, 1993). Bioremoval process using aquatic plants often exhibits a two-stage uptake process: an initial fast, reversible metal binding process (biosorption), followed by a slow irreversible, ion sequestration step (bioaccumulation). The initial biosorption by different parts of cells can occur via complexation, coordination, chelation of metals, ion exchange, adsorption and microprecipitation. The second state of bioaccumulation process is an active mode of metal accumulation by living cells. This process of sequestration is dependent on the metabolic activities of the cell, which in turn can be affected by the presence of the metallic ions (Wilde, W.E., and Benemann, J.R., 1993).

Plants exhibit large variability in their capacity to sequester toxic elements. The adsorption capability varies with its physiological state, age, growing water quality as well as other environmental conditions during the actual biosorption process such as pH, temperature, and presence of certain co-ions. Therefore, a plant screening program is the required first step in development of a bioremoval process in a constructed wetland systems. A successful candidate would exhibit (1) capability to reduce metal concentrations to the required regulatory level; (2) high specific metal adsorption capability; (3) capability of removing several metal ions, simultaneously; and (4) high productivity in a low cost cultivation system; ease of harvesting, processing, storage, transportation and disposal.

The objective of this study is to describe methods to identify promising aquatic plants which possess the best characteristics for use in metal removal process in the wetland or detention pond. This was accomplished by first screening a number of potential plants and then choosing the promising plants to establish adsorption isotherms in order to obtain the maximum specific adsorption capability (mg metal adsorbed/kg of dried biomass) and bioconcentration factor (the ratio of specific adsorption to residual metal concentration) of the plants.

## METHODS AND PROCEDURES

A small scale biomass metal contacting experiment was performed to screen the optimal plant species. With 50 mL of metal solution and any desirable amount of biomass added to 125 mL polyethylene flasks, the flasks were placed in a shaker and allowed to contact for a sixty minute period. At the end of each experiment, the content of flasks were filtered or centrifuged to separate the biomass from the solution. Both biomass and the filtrate were analyzed to determine metal contents. The experimental results were used to calculate (1) percent of metal remaining in solution; (2) percent metal recovered by biomass; (3) specific adsorption per unit weight of biomass; (4) bioconcentration factor. These parameters evaluated the metal adsorption characteristic to select suitable plant for treating stormwater runoff in the wetland ecosystem. After initial screening of plant species, a series of experiments were performed with various metal concentrations in the selected plants. The obtained specific adsorption was plotted against the residual metal concentration to define the sorption characteristic for the plant biomass. The maximum adsorption was calculated using the Langmuir adsorption equation (Volesky, 1990).  $C/Y = C/Y_m + 1/kY_m$ , where  $Y_m$  was the

maximum adsorption;  $k$ , the equilibrium constant related to the affinity of the binding site; and  $Y$ , the specific adsorption at residual metal concentration  $C$ . From a plot of  $C/Y$  vs.  $C$ , the slope ( $S = 1/Y_m$ ) gave  $Y_m$  and the intercept ( $I = 1/kY_m$ ), gave  $k$  constant. Each metal biomass adsorption characteristic was evaluated with  $Y_m$ ,  $C$  and  $k$  values. The maximum adsorption capability and residual metal concentration were important features shown in the sorption isotherms. A steep isotherm from the origin at low residual concentration indicated high affinity of the biomass for the given metal species.

## RESULTS

Water milfoil (*Myriophyllum spicatum*), hydrilla (*Hydrilla verticillata*), hygrophyllum (*Hygrophila polysperma*), water lettuce (*Pistia stratiotes*), and alligator weed (*Alternanthera phiuxeroides*) were initially examined in the screening program. Water milfoil was found to be one of the most promising plants in the study. The initial screening results show that with biomass density of 0.01 kg/L in a solution containing 0.51 mg/L of Cd and 3.97 mg/L of Zn, the plant exhibited the specific adsorption of 525 and 4,770 mg/kg and bioconcentration factor of 4,770 and 2,615 for Cd and Zn, respectively. With these promising results, five metals, Cd, Zn, Ni, Pb and Cu were then used to establish adsorption isotherms with initial metal concentrations ranging from 2.5 to 20 mg/L and contact time at 60 minutes, the maximum adsorption capability for water milfoil were 8,200 mg/kg Cd; 13,500 mg/kg Zn; 55,600 mg/kg Pb; 5,800 mg/kg Ni and 12,900 mg/kg Cu. The initial pH in water solution was 3 and then quickly increased to pH 7.0 after biomass was added to the solution. Experiments were also conducted to test the ability of the biomass to lower the metal concentration below the EPA surface water discharge criteria. The results indicate that the minimum residual concentration for Cd, Ni and Cu was about 0.01 mg/L and for Zn and Pb were 0.1 and 0.004 mg/L, respectively. All the metals except Cd were within the EPA quality criteria (USEPA, 1986). The effect of contact time on Cd adsorption by water milfoil was tested at pH 7. More than 50% of the metal was adsorbed by the end of the first minute and 95% of adsorption was complete within 30 minutes.

## CONCLUSIONS

Water milfoil is naturally immobilized and is a very common component of many natural communities. Those characteristics as well as the high metal adsorption capability and relatively short adsorption time serve as an indication that this plant can be used for metal bioremoval process for a constructed wetland or detention pond.

Using Water milfoil for treating storm water runoff in wetland system offers some advantages such as: (1) metals at low concentration can be selectively removed to meet regulatory level. (2) this process can result in the recovery of the metals bonded by the biomass. The metal laden biomass can be reduced in volume by drying or incineration, thereby reducing the volume of hazardous waste. (3) Biosorption process can be performed in detention pond or constructed wetland with contaminated water flowing over plants for metal removal. (4) Water milfoil

biomass has a very low affinity for calcium and magnesium ions in natural water bodies. This serves as a very attractive characteristic for Water milfoil to treat stormwater. (5) The system offers low capital investment and low operating cost. They can be operated over the broad range of pH value (3-9) and temperature (4 to 90°C).

### LITERATURE CITED

- Green, B. and G.W. Bedell, Immobilize Algae for Metal Recovery in I. Akatsuka (ed.), Introduction to Applied Phycology, Academic Publishing, The Hagu, pp. 109-136, 1990.
- Kuyucak, N., Feasibility of Biosorption and Biosorbents in Removal of Heavy Metals, Ed., B. Volesky, CRC Press, Boca Raton, 371-398, 1990.
- Kuyucak, N. and B. Volesky, Biosorbents for Removal and Recovery of Metals from Industrial Solutions, Bioletters; 10:137, 1988.
- Muramoto, S. and Y. Ohi, Removal of Some Heavy Metals from Polluted Water by Water Hyacinth, Bull. Environmental Contam. Toxicol., 30:170-177, 1983.
- Yu, S.L., Innovative and Cost-Effective Practices for Controlling Nonpoint Source Pollution, International Chinese Environmental Protection Conference Proceedings, 8-58/8-65, 1995.
- USEPA, Water Quality Criteria for Aquatic Life, 1986.
- Volesky, B., Biosorption and Biosorbents in Biosorption of Heavy Metals, Ed., B. Volesky, CRC Press, Boca Raton, 1990, 3.
- Wilde, E.W., and J.R. Benemann, Bioremoval of Heavy Metals by the Use of Microalgae, Biotech Adv. 11, 781-812, 1993.
- Wolverton, B.C. and R.C. McDonald, Water Hyacinth and Alligator Weeds for removal of Lead and Mercury from Polluted Waters, NASA Report, 1975.