



Trace Elements Removal from Waster water by *Ceratophyllum demersum*

^{1*}MARYAM FOROUGHI; ²PAYAM NAJAFI; ³SAJJAD TOGHIANI

^{1*} Young Researchers Club Islamic Azad University, Khorasgan Branch, Isfahan, Iran; Foroughi.maryam@yahoo.com

² Assistant professor, department of Soil Sciences, Islamic Azad University, Khorasgan Branch, Isfahan, Iran
payam.najafi@gmail.com

³ Young Researchers Club Islamic Azad University, Khorasgan Branch, Isfahan, Iran; stoghiani@yahoo.com

ABSTRACT: Trace element contamination in aquatic ecosystems is one of the most important concerning of environmental health. Submerged aquatic plants can be used for the removal of Trace elements. The aim of this study was to investigate how *Ceratophyllum demersum* could affect on wastewater quality for recycling the wastewater to reuse for other purposes in agriculture and industrial fields. In this survey, two treatments in four replications were designed. The treatments were included raw municipal wastewater (RMW) and treated municipal wastewater (TMW). The experiment performed in outdoor of Khorasgan University area without aeration through 18 days period. In this study Fe, Zn, Mn, Ni, Pb and Cd were measured in wastewater through experiment. The average of removal efficiency of Fe, Zn, Mn, Ni, Pb and Cd from TMW were 40%, 47.5%, 90.82%, 96.55%, 100% and 100% respectively. Removal efficiency of Fe, Zn, Mn, Ni, Pb and Cd from RMW were 67.5%, 37.5%, 94.21%, 94.21%, 100% and 97.77% respectively. The results indicated that *Ceratophyllum demersum* had high capabilities to remove trace elements directly from the contaminated water. Therefore it can conclude that *Ceratophyllum demersum* could be used for refining the wastewater. @JASEM

Key words: Trace elements, Aquatic ecosystems, *Ceratophyllum demersum*, wastewater

Pollution of the environment with toxic metals has been attracting considerable public attention over the past few decades (Li and Thornton, 2001). Heavy metals are one of the most detrimental fractions, being persistent accumulates in water, soil, sediment and living organism (Miretzky et al., 2004).

Heavy metals may come from various industrial sources such as electroplating, metal finishing, textile, storage batteries, lead smelting, mining, plating, ceramic and glass industries. Zinc, copper and lead are common contaminants of industrial wastewaters. Because they pose serious environmental problems and are dangerous to human health, (Cheung et al, 1997; Sternberg and Dom, 2002)

Occurrence of toxic metals in plants and water bodies adversely affects the lives of local people since they utilize this water for daily requirements. These heavy metals can be incorporated into food chain and their levels can increase through biological magnification (Cardwell et al., 2002).

Heavy metals are highly toxic elements that can accumulate and concentrate in live tissues. Lead, copper and especially cadmium can become a sanitary and ecological threat to drinking water resources, even at very low concentrations. Cd and Zn are common industrial pollutants. Both Cd and Zn are harmful to plant at relatively low concentrations (Chakravarty and Srivastava, 1992). Thus, clean alternatives must be developed in order to remove heavy metals from effluents (Volesky, 2003).

The methods for removal of many heavy metals include precipitation, oxidation, reduction, ion exchange, filtration, electrochemical treatment, membrane technologies, reverse osmosis and solvent extraction (Cheung et al, 1997; Sternberg and Dom, 2002) The traditional methods for the removal of heavy metals from water are generally expensive or inadequate to treat highly dilute solutions. Biosorption is a cost effective alternative that can be appropriate for treating effluents with low metal concentrations and can also be used to remove other contaminants such as dyes and organic compounds. (Volesky, 2003).

This technique is now recognized as an alternative method for the treatment of wastewaters containing heavy metals (Aksu and Akpınar, 2000; Kaewsarn, 2002). It has been long known that aquatic plants, both living and dead, are heavy metal accumulators and, therefore, the use of aquatic plants for the removal of heavy metals from wastewater gained high interest (Kuyucak and Volesky, 1989; Lacher and Smith, 2002). Some freshwater macrophytes including *Potamogeton lucens*, *Salvinia herzogii*, *Eichhornia crassipes*, *Myriophyllum brasiliensis*, *Myriophyllum spicatum*, *Cabomba* sp., *Ceratophyllum demersum* have been investigated for the removal of heavy metals (Wang et al, 1996; Schneider et al, 1999).

Aquatic plants like *Ceratophyllum demersum* are known to accumulate industrial radionuclides and also heavy metals (Ornes and Sajwan, 1993; Bolsunovskii et al, 2002). especially Cd at low concentrations (0.1–

*Email: Foroughi.maryam@yahoo.com

Table 1. The initial physico-chemical parameters of TMW and RMW quality of experimental water.

parameters	TMW	RMW
NH ₄ (me/L)	90	135
NO ₃ (me/L)	60	60
TOP(me/L)	4.48	13.68
Fe(mg/l)	0.036	0.04
Zn(mg/l)	0.033	0.04
Mn(mg/l)	0.063	0.083
Ni(mg/l)	0.29	0.383
Cd(mg/l)	0.036	0.036
Pb(mg/l)	0.58	0.59
COD(mg/L)	260	664
EC(ds/m)	1.34	2.68
pH	8.14	6.28

TOP = total dissolved phosphorus, N = ammonium nitrogen, NO₃-N = nitrate nitrogen, COD = chemical oxygen demand, EC = Electrical Conductivity.

0.5 ppm). Cadmium (Cd) is a non-essential and toxic element (Vallee and Auld, 1990). *C. demersum* (Coontail or hornwort) is a completely submersed plant and commonly seen in ponds, lakes, ditches, and quiet streams with moderate to high nutrient levels (Johnson et al., 1995). It does not produce roots, instead it absorbs all the nutrients it requires from the surrounding water. If it is growing near the lake bottom, it will form modified leaves, which it uses to anchor to the sediment. However, it can float free in the water column and sometimes forms dense mats just below the surface. The main purpose of this study is to investigate the adsorption of heavy metals such as lead, cadmium, zinc, iron, nickel and manganese form *Ceratophyllum demersum* in the natural situation.

MATERIALS AND METHODS

Ceratophyllum demersum plants were collected from Zayanderood river in spring season of 2009 (Isfahan, Iran, 32° 38' 30" N, 51° 39' 40" E). Samples were thoroughly washed with distilled water to remove any soil /sediment particles attached to the plant surfaces. The plants were then placed in urban wastewater and Khorasgan University's sewage water in 8 bottles. The weather of Khorasgan University during this study was between 28 and 32 degree centigrade. However, the temperature of wastewater, which plants were located in them, was between 24 and 26 degree centigrade. The experimental were performed in outdoor of Khorasgan University area under natural daylight for 18 days without aeration. Preliminary tests were run on the raw municipal wastewater (RMW) and treated municipal wastewater (TMW) at the beginning of the experiment (Table 1).

Samples were collected for three periods of six days at noon and compared with primary sample (before using *C. demersum*). After each collection from samples, volume of TMW and RMW that were evaporated was replacement with equal amount of distilled water. No₃

and NH₄ were measured according to standard method (Keeney and Bremner, 1966).

Standard Testing Method: Phosphorous were determined according to the estimation of available phosphorous in the soil (Olsen et al., 1954). EC was measured according to comparison and extracts with saturation extracts (Hogg and Hurey, 1984), and COD was measured by COD meter. For analyses the data of this study and for investigating the significant of heavy metals, Randomized Complete Block Design was used. Statistical analyses of experimental data were performed using SPSS Version 16 statistical software package. Fe, Zn, Mn, Ni, Cd and Pb were measured according to Analytical method for Atomic Adsorption Spectrophotometer (AAS) (Perkin Elmer, 1982).

RESULTS AND DISCUSSION

1. Fe concentration in RMW and TMW: Amount of Fe concentration adsorbed by *C. demersum* during 18 days in RMW and TMW was illustrated in figure 1. After 18 days, the concentration of Fe in RMW and TMW decreased from 0.04 (at first day) to 0.022 mg/l (after 18 days) and from 0.036 (at first day) to 0.02 mg/l (after 18 days) respectively. The amount of Fe, which was removed by *C. demersum* after 18 days, was 40% from TMW and 67.5% from RMW. The maximum amount of Fe that would remove by *C. demersum* from RMW and TMW was after 6 days. Based on Fig 1, the most adsorption occurred after 6 days and the final stage of research (18th day), a part of Fe returned to wastewater again. Unrooted submerged vegetation such as *Ceratophyllum demersum* requires nutrient uptake from the water (Mjelde and Faafeng, 1997).

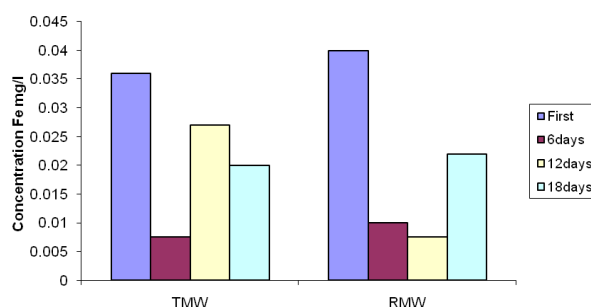


Fig1. Concentration of Fe (mg/l) in RMW and TMW during 18 days.

2. Zn concentration in RMW and TMW: Zn concentration after 18 days in RMW and TMW and amount of removal by *C. demersum* was shown in figure 2. Amount of removal Zn from RMW was 0.04 to 0.02 mg/l and from 0.017 from 0.033 mg/l for TMW after 18 days.

The measured Zn in RMW and TMW has decreased 47.5% from TMW and 37.5% from RMW. The maximum amount of Zn that would remove by *C. demersum* from treatments was after 6 days. Aquatic submerged plant *C. demersum* could be an effective biosorbent for zinc, removal under dilute metal conditions. Batch adsorption studies showed that *C. demersum* would adsorb zinc, lead and copper (Keskinan et al., 2004).

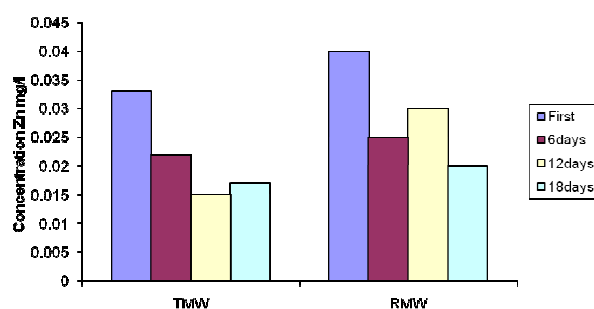


Fig2. Concentration of Zn (mg/l) in RMW and TMW during 18 days.

3. *Mn concentration in RMW and TMW*: The amount of Mn that was removed by *C. demersum* was 90.82% from TMW and 94.21% from RMW. The maximum adsorption of Mn related to first 6 days of experiment. It has been long known that aquatic plants, both living and dead, are heavy metal accumulators and, therefore, the use of aquatic plants for the removal of heavy metals from wastewater gained high interest (Kuyucak and Volesky, 1989; Lacher and Smith, 2002).

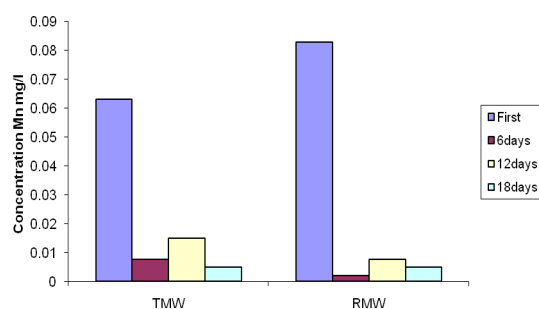


Fig3. Concentration of Mn (mg/l) in RMW and TMW during 18 days.

4. *Ni concentration in RMW and TMW*: Analysis of Ni in samples showed that concentration of Ni in TMW decreased from 0.29 to 0.0075 mg/l and from 0.38 to 0.005 mg/l in RMW for first three periods of six days (Fig 4). Result showed that amount of Ni which was removed by *C. demersum* after 18 days was 96.55% from TMW and 94.21% from RMW as compared to initial value after 18 days. The maximum adsorption of Ni related to first 6 days of experiment. *Ceratophyllum*

demersum is a submerged freshwater macrophyte of major importance in aquatic ecosystems for at least two reasons: (i) it is known to produce allelochemicals that influence the development of phytoplankton (Hilt and Gross, 2008; van Donk and van de Bund, 2002); (ii) it is an indicator of environmental pollutants such as heavy metals or phytotoxins (Lewis, 1993).

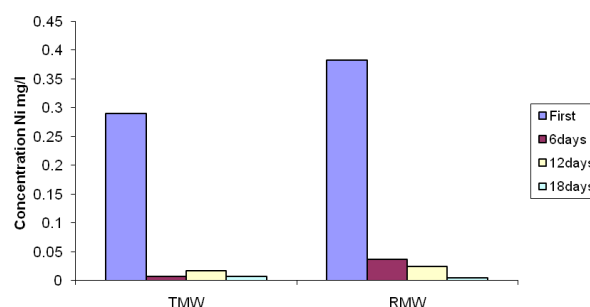


Fig4. Concentration of Ni (mg/l) in RMW and TMW during 18 days.

5. *Pb concentration in RMW and TMW*: The measured Pb values in RMW and TMW have decreased from 0.58 mg/l to ns (not seen value by AAS) and from 0.59 mg/l to ns (not seen value by AAS) for all three periods respectively (Fig 5).

The average removal efficiency of Pb was almost 100% from both treatments by *C. demersum* after 6 days. (Fig 5). It means that *C. demersum* has most capability adsorption for Pb as compared to other kinds of trace elements.

Aquatic plants have shown greater potential in ameliorating the metal load of wastewater by active uptake and surface adsorption (Chigbo et al., 1982). Zimels et al. (2009) showed that aquatic plants can be used for design calculations regarding expected removal of pollutants by aquatic floating plants

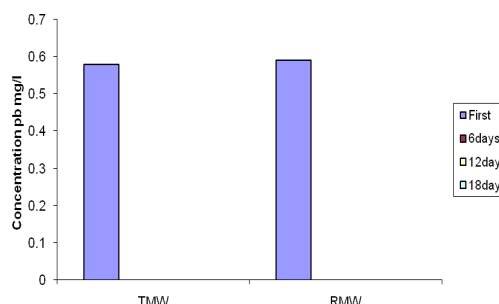


Fig5. Concentration of Pb (mg/l) in RMW and TMW during 18 days

6. *Cd concentration in RMW and TMW*

Results of Cd in two treatment indicated that the Cd reduced from 0.036 mg/l to (not seen by AAS) in both treatments for all three periods of time (Fig 6).). About

100% Cd were removal from both treatments after 6 days. It is related to low values of Cd in initial wastewater samples and the capability of *C.demersum* for adsorption of this kind of metal.

Submerged macrophyte has a high capacity for vegetative propagation and biomass production even under low nutritional conditions, which removes excess nutrients and cadmium from stagnant waters (Best, 1977; Pomogyi et al., 1984).

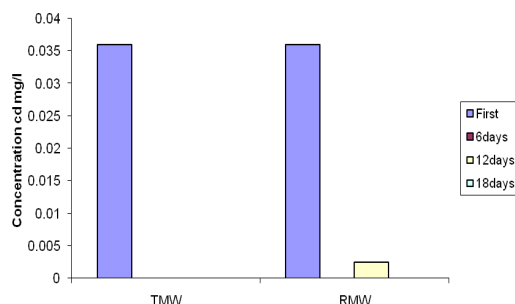


Fig 6. Concentration of Cd (mg/l) in RMW and TMW during 18 days.

Conclusion: The concentration of Fe, Zn, Mn, Ni, Cd and Pb decreased in TMW and RMW after 18 days. Based on the results of this research, most adsorption of trace elements occurred after 6 days. Longer contact wastewater with plants, had reverse effects on adsorption of some elements. In addition, the capability of *C.demersum* for removal Pb, Cd and Ni were more than Fe, Mn and Zn. This study showed that *C. demersum* could be as a major role in the environmental conditions of stagnant and flowing waters and this plant could adsorb elements and decrease pollution of wastewater.

REFERENCES

- Aksu, Z. Akpınar D. (2000). Modelling of simultaneous adsorption of phenol and nickel II onto dried aerobic activated sludge. *Sep Purif Technol*, 21: 87_9.
- Best, EPH. (1977). Seasonal changes in mineral and organic components of *Ceratophyllum demersum* and *Elodea canadensis*. *Aquat Bot*; 3:337–48.
- Bolsunovskii, AIA. Ermakov, AI. Burger, M. Degermendhzi AG. Sobolev AI. (2002). Accumulation of industrial radio nuclides by the Yensei river aquatic plants in the area affected by the activity of the mining and chemical plant, *Radiat. Biol. Radioecol.* 42: 194–199.
- Cardwell, AJ. Hawker, DW. Greenway, M. (2002). Metal accumulation in aquatic macrophytes from southeast Queensland, Australia, *Chemosphere*, 48: 653–663.
- Chakravarty, B. Srivastava, S. (1992). Toxicity of some heavy metal in vivo and vitro in *Helianthus annuus*. *Mutation Research*, 283, 287–294.
- Chigbo, FE. Smith, RW. Shore, FL. (1982). Uptake of arsenic, cadmium, lead and mercury from polluted waters by the water hyacinth *Eichhornia crassipes*, *Environ. Pollut. (A)* 27, 181-193.
- Cheung, CW. Porter, CF. McKay, G. (1997). Sorption kinetics for the removal of copper and zinc from effluents using bone char. *Sep Purif Technol*;19:55_64.
- Hilt, S. Gross, E.M. (2008). Can allelopathically active submerged macrophytes stabilise clear-water states in shallow lakes? *Basic Appl. Ecol.* 9, 422–432.
- Hogg, T and Huery, JL. (1984). Comparison and extracts with the saturation extracts in estimating salinity in saskatchewan soils. *Canadian Soil Science Jornal*, 64: 669- 704.
- Johnson, D, Kershaw, L, MacKinnon, A and Pojar J. (1995). *Plants of Western Boreal Forest and Aspen Parkland*. Lone Pine publishing, Vancouver, BC.
- Kaewsarn, P. (2002). Biosorption of copper(II) from aqueous solutions by pre-treated biomass of marine algae *Padina* sp. *Chemosphere* ;47:1081_5.
- Keeney, DR and Bremner, JM. (1966). Comparison and evaluation of laboratory methods of obtaining an index of soil nitrogen availability. *Agron. J.* 58:498-503.
- Keskinkan, O. Goksu, MZL. Basibuyuk, M. Forster CF. (2004). Heavy metal adsorption properties of a submerged aquatic plant (*Ceratophyllum demersum*). *Bioresour. Technol.* 92, 197–200.
- Kuyucak, N. Volesky B. (1989). Biosorbents for recovery of metals from industrial solutions. *Biotechnol. Lett.* 10, 137–142.
- Lacher, C. Smith, RW. (2002). Sorption of Hg by *Potamogeton natans* dead biomass. *Min Eng*;15:187_91.
- Lewis, MA. (1993). Freshwater primary producers. In: Calow, P. (Ed.), *Handbook of Ecotoxicology*, vol. 1. Blackwell Sci. Publ., Oxford, pp. 28–50.
- Li, XD. Thornton, I. (2001). Chemical partitioning of trace and major elements in soils contaminated by

- mining and smelting activities. Appl Geochem;16:1693–706.
- Miretzky, P. Saralegui, A. Fernandez, Cirelli A. (2004). Aquatic macrophytes potential for the simultaneous removal of heavy metals (Buenos Aires, Argentina). Chemosphere 57, 997–1005.
- Mjelde M. Faafeng BA (1997). *Ceratophyllum demersum* Hampers phytoplankton development in some small Norwe Gian lakes over awide range of phosphorus concentrations and Geographic allatitude. Fresh wat. Biol. 37:355–365
- Olsen SR, Cole CV, Watanabe FS and Dean LA. (1954). Estimation of ailaible phosphorus in soils by extraction with sodium bicarbonate. USDA Circular 939. U.S. Government Printing Office, Washington D.C.
- Ornes WH. Sajwan KS. (1993). Cadmium accumulation and bioavailability in coontail (*Ceratophyllum demersum* L.) plants, Water Air Soil Pollut. 69: 291–300.
- Perkin Elmer A. 1982. Analytical method for Atomic Adsorption Spectrophotometry.
- Pomogyi P. Best EPH. Dassen JHA. Boon JJ. (1984). On the relation between age, plant composition and nutrient release from living and killed *Ceratophyllum* plants. Aquat Bot; 19:243–50.
- Schneider, IAH, Rubio J. (1999). Sorption of heavy metal ions by the non living biomass of freshwater macrophytes. Environment Science Technology, 33: 2213–7.
- Sternberg SPK. Dom RW. (2002). Cadmium removal using Cladophora in batch, semi-batch and flow reactors. Bioresour Technol;81:249_55.
- Vallee, BL. Falchuk, KH. (1993). The biochemical basis of zinc physiology, Physiology Review, 73 : 79–118.
- Van, Donk E. van de Bund, WJ. (2002). Impact of submerged macrophytes including charophytes on phyto- and zooplankton communities: allelopathy versus other
- Volesky B. 2003. Sorption and Biosorption, BV Sorbex, Inc., St. Lambert, Quebec.
- Wang, TD. Weissman, JC. Ramesh, G. Varadarajan, R. Benmann, JR. (1996). Parameters for removal of toxic heavy metals by Water Milfoil (*Myriophyllum spicatum*). Bull Environment Contam Toxicology, 57: 779–86.
- Zimmels, Y. Kirzhner, F. Kadmon, A. (2009). Effect of circulation and aeration on wastewater treatment by floating aquatic plants. Separation and Purification Technology, Volume 66, Issue 3, 7 Pages 570-577.