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Investigation of Heavy Metal Removal by a Submerged Aquatic Plant (*Myriophyllum spicatum*) in a Batch System

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The experimental results regarding the performance of a laboratory scale wetland in removing heavy metals (Zn^{2+}, Cu^{2+}, Cd^{2+}) were presented. A total of ten glass aquaria were used to constitute the wetland. River sand was placed at the beds of the aquaria to keep the plants in an upright position. After establishing the experimental conditions, five aquaria were planted with *Myriophyllum spicatum* and the other five control aquaria were left unplanted. Heavy metals were used at 1, 2, 4, 8 and 16 mg/L concentrations. Operating took two weeks. Removal of metals occurred in 1–5 d. Removal rates ranged from 87.3–99.9% for Zn, 90–98.5% for Cu and 58.9–90.3% for Cd. The results show that the *M. spicatum* system, which was able to remove Zn^{2+}, Cu^{2+} and Cd^{2+} has a good removal capacity.

Key Words: Heavy metal, Removal, Submerged plant, *Myriophyllum spicatum*, Batch system.

INTRODUCTION

Human industrial activities produce pollutants that can be hazardous to aquatic life in the receiving water. Depending on the nature of the industry and the projected use of the water of the receiving stream, various waste constituents may have to be removed before discharge. These may be toxic organics, suspended solids, soluble organics, heavy metals etc.[1] Heavy metal pollution in water bodies is a serious environmental problem threatening not only the aquatic ecosystems but also human health, through contamination of drinking water[2]. Although, the toxic effects of heavy metals have been known for a very long time, water pollution by heavy metals has only become acute in recent years[3]. The wastewaters including heavy metal ions have low BOD concentrations, and generally exhibit acid and inorganic characteristics. The heavy metals causing pollution are lead, chromium, nickel, copper, iron, zinc, arsenic, mercury and cadmium in general. Among these metals, copper can be found in copper mine drainage waters, electroplating plants, paper, petrol and dye industry wastewaters. Zinc is the other pollutant that can be discharged from electroplating plants, steel works and fibre plants[1]. Some environmentalists focused on cadmium due to its most toxic properties. The major sources of cadmium release by wastewaters into the receiving streams are electroplating, smelting, alloy manufacturing, pigments, plastics, battery, mining and refining processes[4].

Waters contaminated with toxic metals need an effective and affordable technological solution. Because of the non-degradability properties of heavy metals, conventional biological treatment methods are not effective for heavy metal removal. To accomplish complete heavy metal removal, immediate alternative technologies will be necessary which suit the situation of low capital availability, minimum manpower and can also save on energy consumption in the future[3]. Even though chemical methods have been applied for heavy metal removal, certain amount of heavy metals may still remain in the effluents and polishing or advanced treatment methods may be necessary.

On the other hand, natural and constructed wetlands are considered low-cost alternatives for treating municipal, industrial and agricultural effluents[5]. In natural wetlands, plants have a very broad diversity of species. Also wetland plants have variable adaptations to the physical and chemical environments in wetlands such as water depth, dissolved oxygen, salinity, air temperature and sunlight[6].

In the constructed wetlands, submerged aquatic macrophytes have their photosynthetic tissue entirely submerged. These plants are able to assimilate nutrients from polluted waters. The prime potential use of submerged aquatic macrophyte-based wastewater treatment systems is for "polishing" secondarily treated wastewaters. The presence of these plants depletes dissolved carbon in the water and increases the content of dissolved oxygen during the periods of high photosynthetic activity. The use of submerged macrophytes for wastewater treatment is still at an experimental stage, with species like *Egeria densa*, *Elodea canadensis*, *Elodea nuttallii*, *Ceratophyllum demersum*, *Hydrilla verticillata* being the most promising[7]. *M. spicatum* (Eurasian water milfoil) is a submerged aquatic perennial herb that reproduces primarily by vegetative fragmentation. These fragments are produced during much of the year with the roots often developing on a fragment. Plants may grow in water from 0.5 to 10 m deep; however, most plants appear to grow in water 0.5 to 3.5 m deep. It is rooted in the bottom and grows to the surface. When the surface is reached, the plant branches profusely to form a dense canopy. Flowering and seed production are common; however, the seeds exhibit prolonged dormancy and their germination is erratic[8]. Present knowledge suggests that their prime area of application will be as a final step in multistage systems[9].

There are several studies with laboratory scale wetlands for removing nutrients[10, 11]. Also metal removal experimentation was established and researchers demonstrated that macrophytes like *Typha latifolia*, *Phragmites australis*, *Schoenoplectus lacustris* and *Iris pseudacorus* can be used for heavy metal removal[12]. Consequently, wastewater treatment capability of wetlands became known in many parts of the world. Although, Shutes[13] had suggested that aquatic plants could be used as sewage treatment facilities, there is scarce study about heavy metal removal capacity of submerged aquatic plants. In order to contribute to the studies on the removal of heavy metal with submerged aquatic plants, the present study has been made to show the effectiveness of the *M. spicatum* system, in retaining heavy metals (Zn^{2+}, Cu^{2+}, Cd^{2+}) with respect to different heavy metal concentrations in a batch system of the laboratory scale constructed wetland.

EXPERIMENTAL

The aquatic plant, *M. spicatum,* was collected from agricultural drains near Seyhan river (Adana, Turkey). The plants were kept separately in a cement pond containing tap water prior to the start of the experiments. The plants were washed carefully with tap water. The experiments were performed in ten glass aquaria and batch system. River sand was placed at the bed of the aquaria to keep the plants in a vertical position. Air pumps were used to supply dissolved oxygen that is required for the plants' survival. General view of the system is shown in Fig. 1.

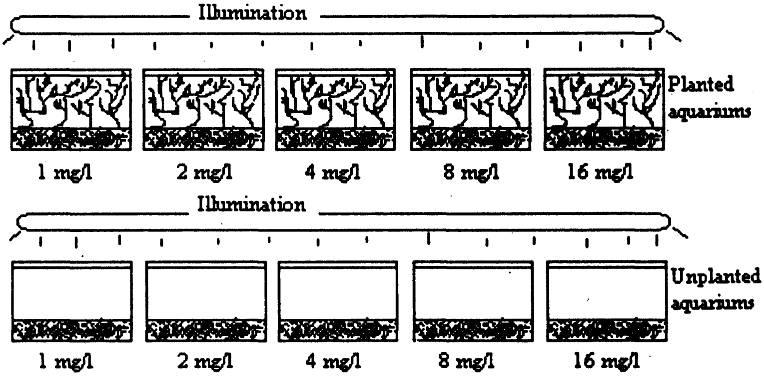

Fig. 1. The scheme of the experimental wetland

Laboratory scale wetlands were constructed in a batch mode with 80W fluorescent lamps simulating daylight conditions. Ten aquaria, measuring 50 cm long, 23 cm wide and 38 cm deep, were each filled with river sand up to 5 cm height. The volume of the water for each aquarium was 35 L. Five aquaria were planted with *M. spicatum*. The other five aquaria were left unplanted as controls. The planted aquaria were left for one week to adapt the plants to the new environment. The plants were fed with 5% Arnon-Hoagland solution during the adaptation period[14] (Table-1).

After the adaptation period, the plants were exposed separately to the mixed solutions of Zn^{2+}, Cu^{2+}, Cd^{2+} ions at 1, 2, 4, 8 and 16 mg/L. Samples were collected from each aquarium at the 1st, 3rd, 5th, 7th, 9th, 11th, 13th and 15th days after adding heavy metals. The samples were filtered and stored at 4°C until laboratory analyses. These samples were analysed for Zn^{2+}, Cu^{2+}, Cd^{2+}. pH measurements were done with pH-meter in the aquaria (Hanna Instruments pH 211 microprocessor pH-meter). Dissolved oxygen was measured with oxygen-meter (YSI 51B). To determine the metal concentrations in the samples and plants, atomic absorption spectrophotometer was used (Perkin-Elmer model 3100) according to standard methods[15]. Removal efficiency was calculated for Zn^{2+}, Cu^{2+} and Cd^{2+} parameters. Water temperature was measured with thermometer. The biomasses were not quantitatively controlled but plant growth was observed and recorded during the experiment period. All heavy metal removal data were subjected to univariate analysis of variance.

TABLE-1
THE CONTENTS OF ARNON-HOAGLAND NUTRITIVE SOLUTION

Component	Concentration (g/L)	Component	Concentration (mg/L)
KNO_3	1.020	H_3BO_3	2.86
$Ca(NO_3)_2$	0.492	$MnCl_2 \cdot 4H_2O$	1.81
$NH_4H_2PO_4$	0.230	$H_2MoO_4 \cdot H_2O$	0.09
$MgSO_4 \cdot 7H_2O$	0.420	$FeSO_4 \cdot .7H_2O$ 0.5	0.60
		Tartaric acid 0.4	

RESULTS AND DISCUSSION

Water temperature in the aquaria remained relatively constant at 21–23°C. Neutral pH values was obtained at 1, 2 and 4 mg/L concentrations. But 6.6–6.0 pH values were measured at 8 and 16 mg/L concentrations, respectively. Dissolved oxygen level did not decrease under 5.2 mg/L. The removal percentage exhibited the Zn, Cu and Cd removal capability of the *M. spicatum* (Tables 2–4).

TABLE-2
ZINC REMOVAL PERCENTAGE OF PLANTED AND UNPLANTED AQUARIA AT VARIOUS CONCENTRATIONS

Days	Concentrations (mg/L)									
	1		2		4		8		16	
	Control	Planted	Control	Planted	Control	Planted	Control	Planted	Control	Planted
1	29.5	94.1	55.4	98.0	28.8	99.1	43.8	95.2	66.1	78.9
3	44.6	97.0	65.2	99.7	33.1	99.3	47.1	97.7	66.6	84.2
5	51.8	96.4	66.9	97.7	43.1	99.9	55.0	97.9	66.6	87.3
7	51.1	97.0	62.6	97.7	62.7	99.6	58.6	98.6	66.8	87.9
9	55.7	96.4	61.4	99.3	66.2	99.6	59.1	98.2	66.4	91.8
11	60.3	97.4	63.1	99.3	63.4	99.6	70.5	98.6	67.2.	92.4
13	60.4	99.3	63.1	99.3	63.4	99.6	70.5	98.6	67.2.	92.4

TABLE-3
COPPER REMOVAL PERCENTAGE OF PLANTED AND UNPLANTED AQUARIA AT VARIOUS CONCENTRATIONS

Days	Concentrations (mg/L)									
	1		2		4		8		16	
	Control	Planted	Control	Planted	Control	Planted	Control	Planted	Control	Planted
1	16.0	40.0	43.0	86.0	14.5	70.5	8.5	78.0	28.3	41.2
3	20.0	58.0	67.0	97.0	58.5	98.0	71.2	97.7	55.0	71.2
5	40.0	90.0	70.0	98.0	63.5	98.5	72.7	98.2	53.2	96.1
7	42.0	94.4	70.0	98.0	69.5	99.0	78.0	98.5	53.1	98.1
9	56.0	96.0	73.0	98.0	72.0	99.0	80.0	98.7	63.7	99.1
11	58.0	96.0	74.0	98.0	76.5	99.0	86.5	98.7	78.8	99.1
13	58.0	96.0	74.0	98.5	76.5	99.0	86.6	98.7	86.1	99.1

TABLE-4
CADMIUM REMOVAL PERCENTAGE OF PLANTED AND UNPLANTED AQUARIA AT VARIOUS CONCENTRATIONS

Days	Concentrations (mg/L)									
	1		2		4		8		16	
	Control	Planted	Control	Planted	Control	Planted	Control	Planted	Control	Planted
1	2.5	5.6	22.9	47.5	5.7	10.7	17.2	17.8	45.5	46.3
3	28.2	82.5	41.8	82.5	29.3	87.7	25.0	68.0	47.4	54.6
5	29.1	85.2	45.3	88.6	31.5	90.3	30.5	78.5	48.2	58.9
7	33.5	85.2	45.7	88.6	47.5	90.6	37.2	82.7	48.8	62.2
9	46.6	86.0	58.4	88.6	50.7	91.0	49.0	82.7	49.3	62.5
11	48.4	88.3	62.3	89.5	56.7	92.3	62.7	85.6	50.4	65.2
13	48.6	88.7	62.3	90.8	57.0	92.3	62.8	86.7	50.6	67.9
15	48.8	88.8	62.3	91.0	57.0	92.3	63.1	87.5	50.7	68.1

The amounts of metals removed by *M. spicatum* as a function of treatment duration are shown in Figs. 2–16. The 15th day concentrations of all aquaria were lower than the first day concentrations. There was a significant difference ($p < 0.05$) between control and planted aquaria. But it can be said that a great portion of heavy metals were removed in 1–5 days. While Zn removal rate was 94.1–99.17% for the 1.0–8.0 mg/L concentrations in first day, Cu removal rate was 90.0–98.5% for the 1.0–16.0 mg/L concentrations over the first 5 days. In addition, Cd removal rate was 85.2–90.3% for the 1.–04.0 mg/L concentrations over the first 5 days. This indicated that there was a fast removal process in the first 5 days.

According to this study, *M. spicatum* system was capable of reducing 99.6% Zn level from pond water within 15 d of treatment for 4 mg/L concentration while Cu was removed at 99.12% rate for 16 mg/L concentration. Also Cd was removed by *M. spicatum* at 92.3% rate for 4 mg/L concentration during the same duration. It was considered that adsorption capability of *M. spicatum* caused the heavy metal concentration difference between planted and unplanted aquarium waters. As a matter of fact heavy metal adsorption capabilities of the *M. spicatum* and other various aquatic plants were reported by various researchers[16–20].

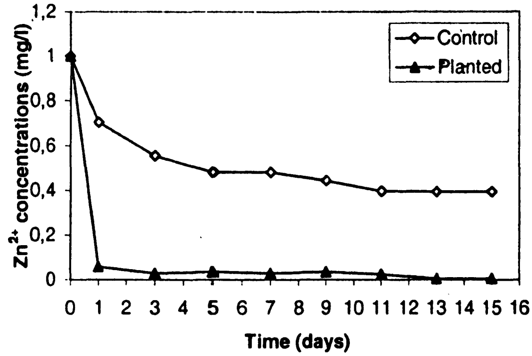

Fig. 2. Zinc concentrations in planted and unplanted aquarium waters in relation to time at 1 mg/L initial concentration

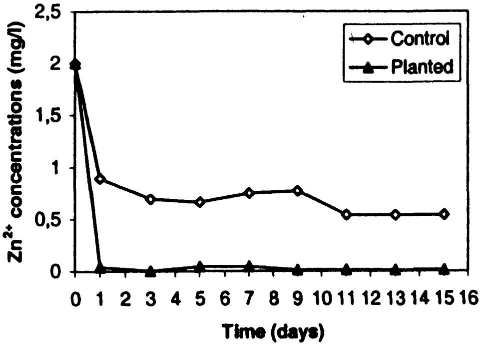

Fig. 3. Zinc concentrations in planted and unplanted aquarium waters in relation to time at 2 mg/L initial concentration

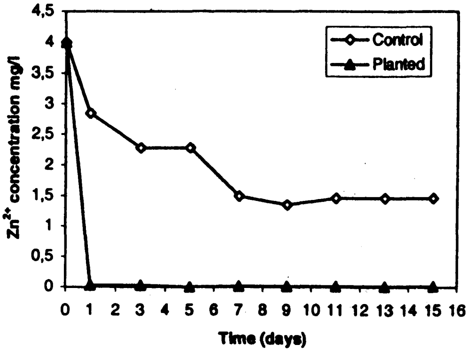

Fig. 4. Zinc concentrations in planted and unplanted aquarium waters in relation to time at 4 mg/L initial concentration

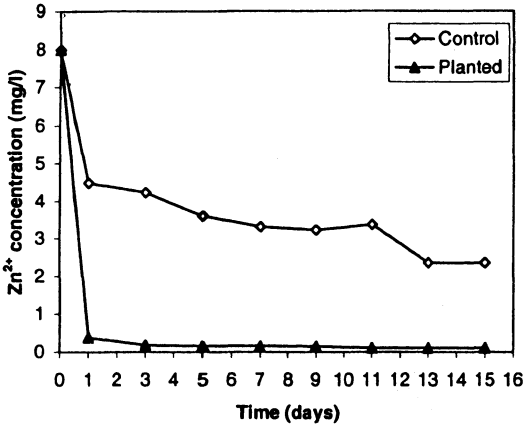

Fig. 5. Zinc concentrations in planted and unplanted aquarium waters in relation to time at 8 mg/L initial concentration

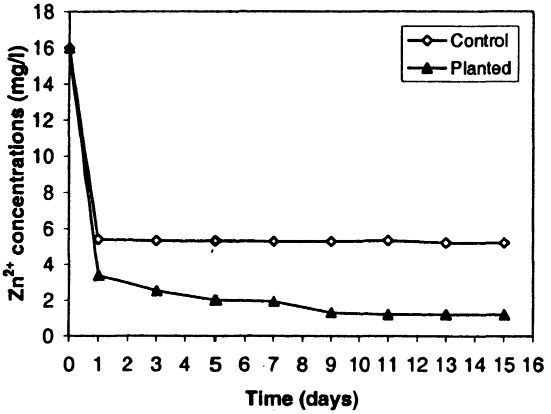

Fig. 6. Zinc concentrations in planted and unplanted aquarium waters in relation to time at 16 mg/L initial concentration

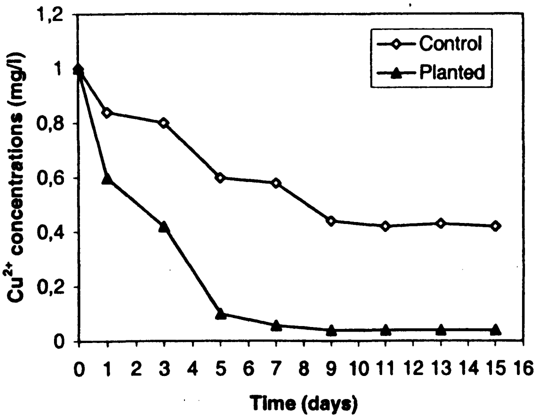

Fig. 7. Copper concentrations in planted and unplanted aquarium waters in relation to time at 1 mg/L initial concentration

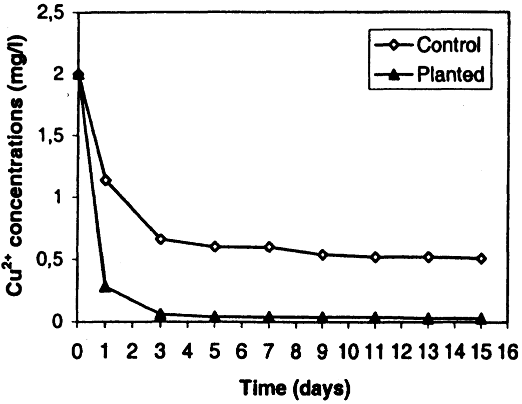

Fig. 8. Copper concentrations in planted and unplanted aquarium waters in relation to time at 2 mg/L initial concentration

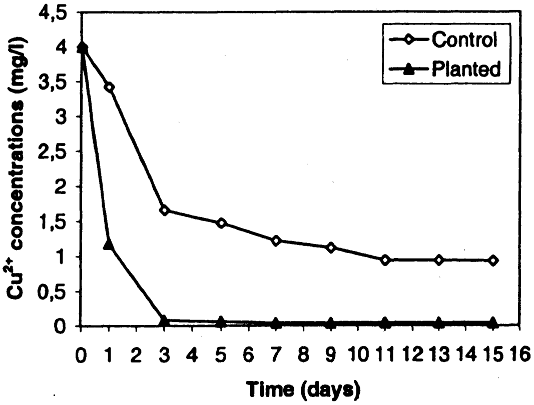

Fig. 9. Copper concentrations in planted and unplanted aquarium waters in relation to time at 4 mg/L initial concentration

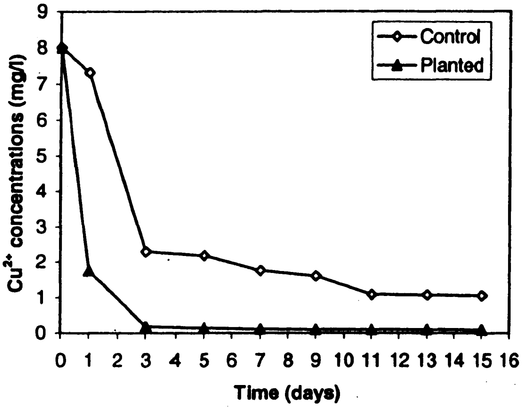

Fig. 10. Copper concentrations in planted and unplanted aquarium waters in relation to time at 8 mg/L initial concentration

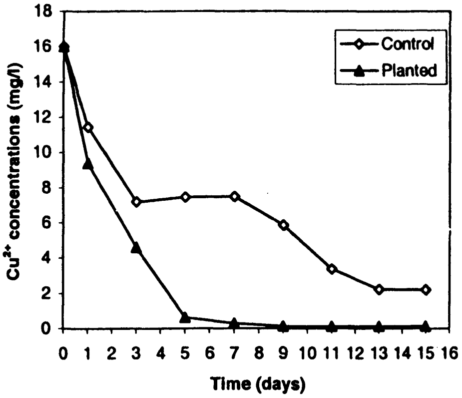

Fig. 11. Copper concentrations in planted and unplanted aquarium waters in relation to time at 16 mg/L initial concentration

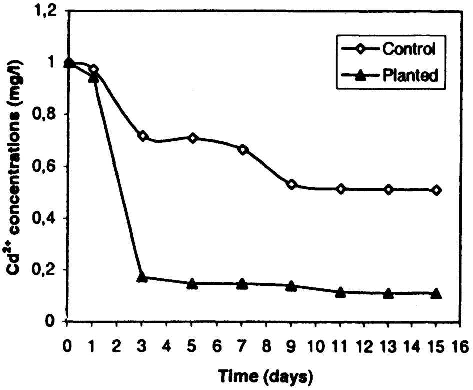

Fig. 12. Cadmium concentrations in planted and unplanted aquarium waters in relation to time at 1 mg/L initial concentration

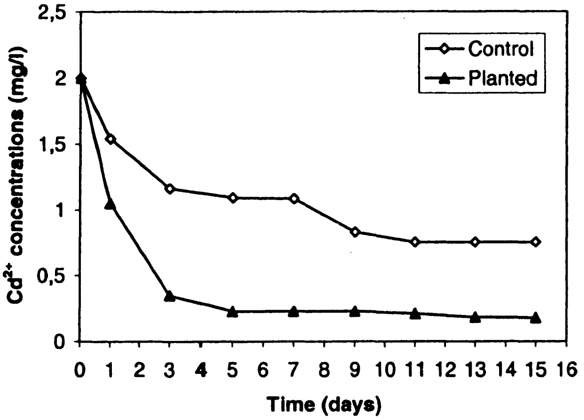

Fig. 13. Cadmium concentrations in planted and unplanted aquarium waters in relation to time at 2 mg/L initial concentration

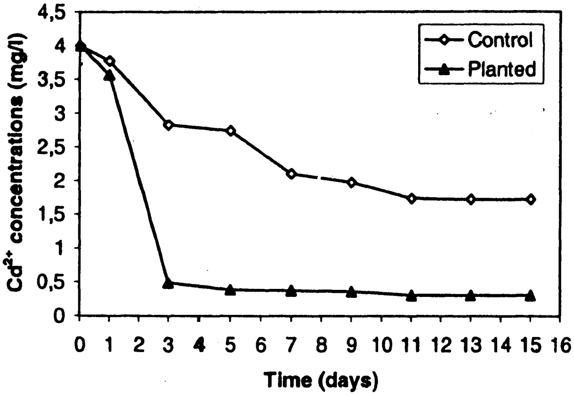

Fig. 14. Cadmium concentrations in planted and unplanted aquarium waters in relation to time at 4 mg/L initial concentration

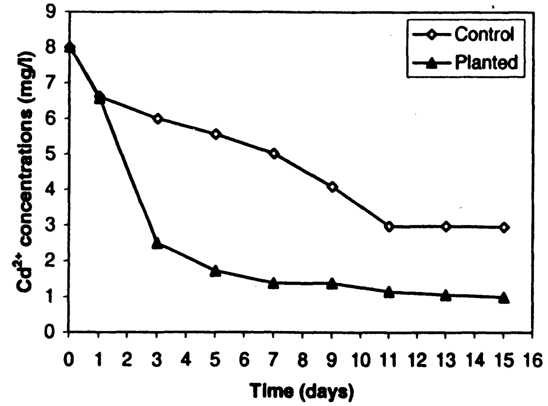

Fig. 15. Cadmium concentrations in planted and unplanted aquarium waters in relation to time at 8 mg/L initial concentration

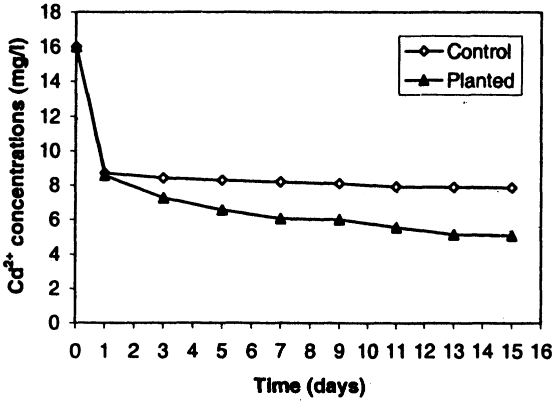

Fig. 16. Cadmium concentrations in planted and unplanted aquarium waters in relation to time at 6 mg/L initial concentration

The amounts of heavy metals removed from water were higher than taken by plants in controls. On the other hand, Kamal *et al.*[21] reported that heavy metals can be removed from water through a chemical pathway that involves the formation and precipitation of metal phosphates. In this study, 60.3 to 70.5% for zinc, 58 to 86.6% for Cu and 48.8 to 63.1% for Cd removal rates were obtained respectively in the unplanted aquaria. Kamal *et al.*[21] also reported that they obtained high metal concentrations on the *Mentha aquaticum*, *Myriophyllum aquaticum* and *Ludwigina palustris*.

Conclusion

Results of present study indicate that an appreciable amount of heavy metals was removed from aquarium water. It can be inferred that *M. spicatum* might be useful in such treatability studies. *M. spicatum* removed Zn, Cu and Cd effectively even at an 16 mg/L concentration. Wastewater treatment system effluents or wastewaters that contain low concentrations of Zn, Cu and Cd can be treated using *M. spicatum* in a batch system.

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