Removal of Heavy Metal from Polluted River Water Using Aquatic Macrophytes Salvinia sp

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Concentrations of trace metallic element as well as macronutrients were measured in water and plants from pond water. The aquatic macrophyte Salvinia sp. was evaluated for its trace metals removal potential in river water under laboratory conditions. The experiment were performed using several healthy acclimatized plants Salvinia sp. The water and grown plants were collected from ponds. For the trace element removals test, 30-35 grams of fresh aquatic plants were grown in river water into a greenhouse for ten weeks. Control plants were also grown during the experiment. Every two weeks, both plants and water samples were collected. After the end of each experiment, the growth rate was calculated. Trace element concentrations in plants and pond water were obtained using TXRF techniques. Values for the elements (K, Ca, Ti, Fe, Cr, Mn, Cu, Zn and Sr) concentrations in plant dry weight have been obtained after deducting metal contents of control plants. For each trace element, the aquatic Salvinia sp. plant showed to possess different affinity for the incorporation of the metals in its biomass. Results suggest the use of aquatic macrophytes Salvinia sp. for metal abatement in dilute wastewaters.

I. INTRODUCTION

In natural aquatic ecosystems, metallic compounds use to occur in low concentrations, normally at nanogram to microgram per liter level. Heavy metals may come from natural sources, leached from rocks and soils according to their geochemical mobility or come from anthropogenic sources, as the result of human land occupation and industrial pollution. Depending on their solubility, these metals may eventually become associated to suspended particulated matter and/or accumulate in the bottom sediments.

The increase of industrial activities has intensified environmental pollution problems and the deterioration of several aquatic ecosystems with the accumulation of metals in biota and flora. Although trace metals at low concentrations are essential to life, at high concentrations, may become hazardous.

Since early 1970s several works have demonstrated that aquatic macrophytes can be used to partially strip trace metal in the wastewaters. Aquatic macrophytes are known to remove metals by surface adsorption and/or absorption and incorporate them into their own system or store them in a bound form [1]. The uptake of trace metals by the root systems of aquatic plants depend both on the kind of metal and on the species of plant absorbing the metal [2].

The imposition of stricter environmental regulations increases the demand for more competitive, effective and economically treatment methods for removal and recovery of toxic metals from industrial effluents which is a scientific challenge.

The aim of this work was to obtain the removal rate of trace metallic ions by the Salvinia sp. from pond water for treatability study. The present study provides useful information of aquatic plants on upgrading of water resources affected by point and non-point source pollution.

II. MATERIALS AND METHODS

A. Sample collection

The experiment was performed using several free-floating healthy acclimatized plants Salvinia sp. The plants were collected from artificial ponds used to grow fishes in water of So Francisco river, localized in Brazil, and were transferred to the laboratory in polyethylene bags. Plants of similar shape, size and weight ($30 \pm 5g$ wet mass) were selected. Six of these plants were chosen as a blank to determine their initial metal ion concentrations before the experiments.

The other plants were left to grow in an upright position in five polyethylene boxes of 30x20x10 cm^3 containing 5 l of pond water (from the So Francisco river) for ten weeks into the greenhouse. The number of aquatic plants in each polyethylene boxes was six. The total fresh weight of the plants in each boxes were measured before starting each growing time: 18, 32, 46, 61 and 76 days. The total of the river water was kept constant by adding deionized water to compensate for water lost through plant transpiration and evaporation. After the end of each experiment, the growth rate was calculated.

B. Digestion of plants

After every two weeks, the plants were collected from one of the polyethylene boxes and washed well using tap water and distilled water and weighted. All entire plant samples (in-

cluding blanks) were dried in an electric furnace at 80 ^{o}C during 72 hours. The ratio of fresh to dry weight for all the plants was approximately 16:1. To ensure uniform distribution of metals in the sample and also to facilitate organic matter digestion, the material was pulverized in an electrical mill. The finely ground material was stored in sealed polyethylene bags at room temperature until wet digestion.

A sample of approximately 0.5 g of ground plant was weight. Plant samples were digested with concentrated nitric acid and hydrogen peroxide mixtures (10:1 by volume) during which temperatures were raised to about 95^{o}C. To avoid the remaining undigested sample, the digestion times was extending overnight. The digests were diluted with distilled water to a total of 10 ml and prior to analysis for trace element content by TXRF. A reagent mixture blank was carried out following the same procedure as the plant samples.

C. Target Preparation

Standard stock solution ($11.6\text{x}10^3 mg\ l^{-1}$) of yttrium was prepared dissolving quantitatively 50 g Merck package $Y(NO_3)_{3.6}H_2O$ in Ultra Pure Milli-Q water. The solution was stored in an acid-washed volumetric flask.

To investigate the trace element content in plant samples, a 5 ml aliquot of digest was taken and 5 μl of the yttrium stock solution (11.6 $g\ ml^{-1}$ yttrium) was added as an internal standard. Aliquots of 5 μl were then pipetted on a pre-cleaned 3 mm thick acrylic disks and left to dry at ambient temperature in a clean box. The sampling, drying, and thin target preparation processes for digests, pond water and standard samples were identical.

D. Analysis of samples

The elemental content in both plants and pond water were estimated using the TXRF technique. The STXRF measurements were carried out using the polychromatic X-ray beam, with maximum energy of 20 keV, of the XRF line, at the National Laboratory of Synchrotron Light (LNLS), located in Campinas-SP [3]. A Si(Li) detector, with 160 eV FWHM@Mn-K$_\alpha$ line, surrounded by tantalum collimators and placed at 90^o to the incident beam, was used for X-Ray detection. X-ray spectra were analyzed using the AXIL program [4]. Typical X-ray spectra for STXRF obtained from plant and pond water sample are shown in Figure 1, with prominent peaks for the K X-ray lines of K, Ca, Cr, Mn, Fe, Ni, Cu, Zn and Y, the internal standard element.

Working standard solutions with different concentrations of several elements with atomic number in the range of interest were used to determine the elemental sensitivity curve of the STXRF system. All standard solutions were spiked with the Yttrium stock solution as well as the digested plant solutions.

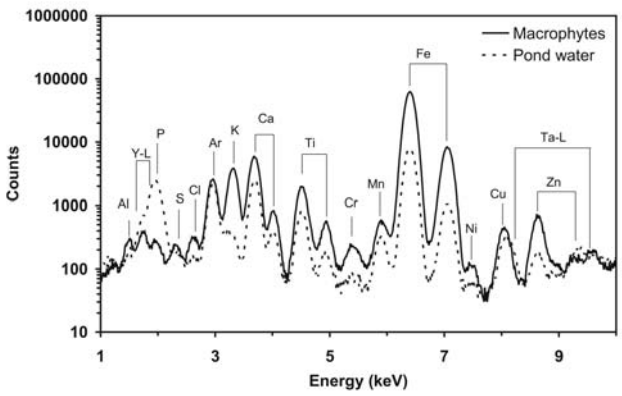


FIG. 1: Typical STXRF spectra for aquatic macrophytes and pond water.

III. RESULTS

The growth rate for aquatic macrophytes Salvinia sp. in each growing time are plotted in Figure 2 to show how the growing decreases with increasing time due to a decreasing of essential macro and micro nutrients for the plant in the pond water.

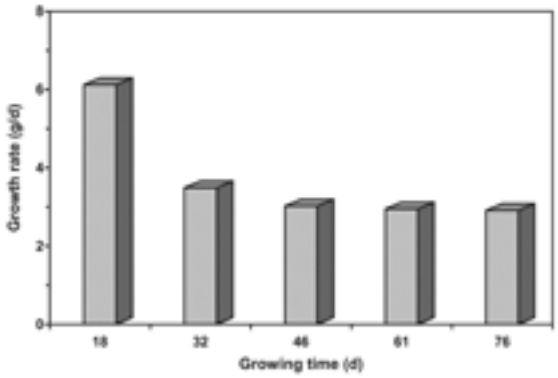


FIG. 2: Growth rate for aquatic macrophytes Salvinia sp. (in g/d) during the growing time.

Backgrounds were subtracted in the K_α areas that were used to calculate the elements concentrations of the samples.

The relative elements concentrations were calculated using the following relation [5]:

$$C_Z = \frac{I_Z}{I_S}\frac{Y_S}{Y_Z}C_S$$

where Y_S/Y_Z is a ratio derived from effective yield curve, I_S/I_Z is a ratio representing the relative-to-Yttrium fluorescence intensity of the element, C_Z is the element concentration ($\mu g\ ml^{-1}$), and C_S is the Yttrium internal standard concentration (11.6 $\mu g\ ml^{-1}$).

The results of the elements concentrations in plant and water at various treatment durations are shown in Tables I and II, respectively. The uptake of macro (K, Ca, Ti, Fe) and trace elements (Cr, Mn, Cu, Zn, Sr) by the aquatic macrophytes from pond water have been obtained after deducting elements contents of control plant.

Concentration factor (CF) in plant was calculated [1] as the ratio between the metal concentration in plants ($\mu g\ g^{-1}$ dry weight) and the ambient metal concentration in pond water ($\mu g\ ml^{-1}$). Metal concentration factor at various treatment durations are shown in Table III. Aquatic macrophytes plants showed high CF values for all the metals. The values were initially very low but increased with increase in time. At treatment duration of 46 days, concentration factor have reached its highest value for all the metals, except for Sr.

	Concentration ($\mu g\ g^{-1}$ dry matter)				
	18d	32d	46d	61d	76d
K	218(23)x10	904 (95)	131(14)x10	848 (89)	938 (99)
Ca	111(11)x10	106(11)x10	122(12)x10	888 (90)	127(13)x10
Ti	94 (10)	154 (16)	489 (51)	66 (7)	121 (13)
Fe	454 (46)	678 (68)	802 (81)	490 (50)	746 (75)
Cr	0.94 (12)	2.31 (28)	2.16 (27)	0.66 (9)	1.80 (23)
Mn	3.03 (35)	4.41 (51)	8.08 (94)	3.22 (37)	6.70 (78)
Cu	1.42 (15)	1.96 (21)	2.45 (26)	1.04 (11)	4.38 (45)
Zn	6.80 (49)	5.86 (43)	7.50 (55)	4.93 (36)	5.41 (40)
Sr	1.82 (23)	1.19 (17)	0.97 (16)	0.67 (11)	2.34 (33)

TABLE I: Concentration ($\pm$ S.D.) (in $\mu g\ g^{-1}$ dry matter) of elements investigated in aquatic macrophytes Salvinia sp. at various treatment durations.

	Concentration ($\mu g\ l^{-1}$)				
	18d	32d	46d	61d	76d
K	385 (22)	989 (52)	373 (20)	449 (25)	967 (50)
Ca	284(14)x10	467(24)x10	238(12)x10	356(18)x10	552(28)x10
Ti	257 (13)	435 (22)	7 (1)	50 (3)	37 (2)
Fe	573 (29)	848 (43)	31 (2)	143 (7)	172 (9)
Cr	4.1 (4)	4.9 (6)	2.0 (2)	4.1 (5)	3.1 (3)
Mn	25.3 (14)	9.1 (6)	0.6 (1)	1.7 (3)	2.3 (2)
Cu	7.5 (5)	4.6 (4)	1.0 (1)	2.1 (3)	1.4 (2)
Zn	5.8 (4)	10.3 (6)	3.8 (2)	9.3 (5)	8.9 (5)
Sr	68 (5)	62 (7)	63 (4)	60 (5)	67 (4)

TABLE II: Concentration ($\pm$ S.D.) (in $\mu g\ l^{-1}$) of elements investigated in water at various treatment durations.

IV. CONCLUSION

The present work is a first attempt to determine the removal rate of metallic elements by the aquatic macrophytes Salvinia sp. Our data show that the plant concentrated a high amount of metals.

The aquatic plant Salvinia sp. have shown promising potential for the removal of metals from pond water. A combination of different types of plants could be useful for treatability studies. More work to optimize the design and management of an aquatic plant based system are also in progress.

	Concentration Factor ($\mu l\ \mu g^{-1}$)				
	18d	32d	46d	61d	76d
Ti	364	353	73483	1314	3303
Fe	793	799	26271	3416	4344
Mn	120	487	13839	1902	2882
Cu	193	406	2162	550	1366
Cr	232	474	1063	163	575
Zn	42	31	124	11	34
Sr	21	32	39	17	66

TABLE III: Metal concentration factor values (in $\mu l\ \mu g^{-1}$) of aquatic macrophytes Salvinia sp. in pond water at various treatment durations. Uncertainty is approximately 10 to 20 %.

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