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Biosorption of Pb and Zn from pulp and paper industry effluent by water hyacinth (*Eichhornia crassipes*)

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Lead and zinc uptake by water hyacinth (*Eichhornia crassipes*) was studied in the laboratory conditions to investigate a low cost natural aquatic treatment system for pollutant removal from pulp and paper industry effluent. Bioaccumulation of Pb and Zn by water hyacinth was found concentration and duration dependent. The plant possessed ability to neutralize the effluent. It could effectively absorb Pb (0.28-1.39 mg/l, 17.6-80.3%) and Zn (0.26-1.30 mg/l, 16.6-73.4 %) after 20 days of treatment. Metal removal efficiency was found to be maximum (80.3% for Pb; 73.4 % for Zn) at 20 % effluent concentration, thus highlighting that phytoremediation could be used along with and/or in some cases as a substitute of expensive cleanup technologies in industrial sector.

Keywords: Bioaccumulation, Phytoremediation, *Eichhornia crassipes*, Langmuir isotherms

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Introduction

Heavy metals (Zn, Cu, Cr, Pb, Cd) present in wastewater are hazardous to the environment[1]. Pulp and paper mill, categorized as one of the 12 most polluting industries in India, releases environmentally hazardous[2] liquid effluent containing heavy metals and other organic toxicants. To remove toxic metals, industries employ several physico-chemical processes, which often require high capital and recurring expenditure[3]. To overcome these problems, environmental and public health engineers have been searching for an inexpensive and efficient technology. Several macrophytes and other biological entities as micro algae, bacteria, fungi and protozoa have also been tested to accumulate heavy metals from contaminated sites/artificial solutions[4,5]. The accumulation of metals by these organisms involves uptake into the intracellular components by an energy dependent process and passive attachment onto the body surface (adsorption)[6]. Generally, two mechanisms are responsible for plant survival in heavy metal polluted sites: (a) Their ability to decrease metal uptake, e.g. by inducing pH change around roots; and (b) Their ability to accumulate and translocate metal into the plant body. Besides, an ideal plant for bio absorption of heavy metals should also exhibit good tolerance to metal accumulated, high growth rate, highly effective metal accumulating biomass and accumulation of metals in above ground parts for easy harvest[7].

Most of the metal biosorption studies have been conducted taking very high concentration (1000 ppm) of heavy metals and sorbents[8,9], which seldom exist. Therefore, it is appropriate to carry out metal sorption studies at low and/or natural concentration of the metals in industrial effluent as well. Hence, the present investigation examines the feasibility of using water hyacinth (*Eichhornia crassipes* Solms), a floating aquatic macrophytic plant abundantly occurring in meso and eutrophic water reservoirs for removal of Pb and Zn from pulp and paper industry effluent.

Materials and Methods

Effluent

The pulp and paper mill effluent was collected from Century Pulp and Paper Mill, Lalkuan, Uttranchal in February, May and July. The effluent, collected in clean plastic containers from R G P (Rayon Grade Pulp) effluent drain, was stored at 4 ^{o}C until further experiments.

Plant Material

E. crassipes, collected from a natural pond adjacent to the Kesar Enterprises, Baheri, was washed thoroughly with running tap water followed by

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distilled water to avoid any surface contamination. The plant matter was cleaned with blotting paper for any surface moisture, avoiding damage to root and leaf apices and was grown and maintained in the laboratory for acclimatization.

Analytical Methodology

Using APHA method[10], pH, COD, TS, TDS, TSS, Na, Ca, Mg and K of the samples were determined. Digested plant samples were analysed for Na, Ca, Mg and K. Colour units of the effluent were measured[11]. G B C Australia atomic absorption spectrophotometer was used to determine concentration of Pb and Zn in digested plant and effluent samples.

Biosorption Studies

Experiment was performed with six sets in quadruplicate plastic tubs (capacity, 5 l; diam, 36cm). In one set, each tub was filled with distilled water (3 l) and in other five sets; tubs were filled with three litres of pulp and paper industry effluent (5, 10, 15, 20, and 25 % each). Uniform size roots (3) were immerged in each set of tubs. The plants, allowed to grow in different concentrations of effluent, were harvested and analysed for biomass and heavy metal content at 5, 10, 15 and 20 days of experiment. The effluent (50 ml) samples from each treatment were also withdrawn from the respective tub and analysed for various physico-chemical parameters. The lost effluent on account of its analysis was made good by adding equal amount of distilled water in each tub.

Development of Sorption Isotherm for Pb and Zn

Langmuir isotherm for Pb and Zn sorption by water hyacinth was developed based on the assumption that only a definite number of homogeneous binding sites are present on the plant surface having affinity for metal ions. Initial concentration of the metal was taken as the concentration added and the concentration of metal left after 20 days of treatment was taken as residual concentration in each treatment. The relationship between the added (initial) to residual metal concentrations in the effluent was established and Langmuir isotherm of Pb and Zn was drawn to interpret the experimental data. Langmuir equation is

$$\frac{X}{M} = \frac{XmC}{K + C}$$

And its linear form is

$$\frac{C}{X/M} = \frac{1}{Xm}(C) + \frac{K}{Xm}$$

Table 1 — Physico-chemical characteristics of pulp and paper industry effluent
[values (± SE) except for pH and colour are in ppm]

Parameters	Values
Colour (CU)	3807.69 ± 1.25
pH	7.96 ± 0.17
COD	4160 ± 12.10
TS	4013 ± 6.39
TDS	2300 ± 3.84
TSS	1713 ± 3.76
Na	230.07 ± 11.82
Ca	83.50 ± 4.21
Mg	18.00 ± 1.70
K	32.00 ± 2.20
Fe	18.50 ± 1.60
Zn	1.30 ± 0.01
Pb	1.39 ± 0.01

where, *X/M* is weight of sorbate (metal) per unit weight of sorbent (plant biomass). *Xm* is the sorption capacity, *K* is Langmuir constant and *C* is equilibrium concentration[8].

Results and Discussion

Pulp and paper mill effluent was dark brown and slightly alkaline (pH 7.9). Most of the physico-chemical parameters (Table 1) exhibited higher values than their permissible limits[12]. Heavy metal content of the effluent was also found (Pb, 1.39; Zn, 1.30 mg/l) more than permissible limits[12].

Sorption Kinetics

During the treatment, residual heavy metal content of the effluent was determined periodically (Table 2). The results indicated that the heavy metal removal is not only a function of treatment time but also being influenced by the metal concentration in the effluent (Figs 1a & 1b). Metal uptake by water hyacinth was higher at low effluent concentration (up to 20 %) and decreased thereafter with increase in effluent concentration due to the toxicity at higher effluent concentration. Similar nature of metal uptake was also noted in water lettuce and water hyacinth for Cd and also in water lettuce for As[8,9]. Metal reduction for Pb and Zn was almost same upto 15 days of treatment (Figs 1a & 1b) but afterward reduction for Zn declined as compared to that of Pb. This might be due to metal binding sites at the plant root surface got shield with relatively large size Pb ion than Zn ion. Reduction in metal content was found maximum

Table 2 — Change in Pb and Zn content of pulp and paper Industry effluent during treatment with water hyacinth (± SE)

Time Days	Metal ppm	Concentration of effluent, %					
		0	5	10	15	20	25
0	Zn	0	0.06 ± 0.030	0.13 ± 0.035	0.19 ± 0.030	0.26 ± 0.035	0.32 ± 0.030
	Pb	0	0.07 ± 0.003	0.14 ± 0.004	0.20 ± 0.004	0.28 ± 0.004	0.34 ± 0.003
5	Zn	0	0.05 ± 0.020	0.10 ± 0.030	0.16 ± 0.035	0.20 ± 0.035	0.27 ± 0.030
	Pb	0	0.06 ± 0.003	0.10 ± 0.003	0.16 ± 0.004	0.21 ± 0.003	0.28 ± 0.004
10	Zn	0	0.03 ± 0.035	0.07 ± 0.030	0.10 ± 0.035	0.12 ± 0.030	0.19 ± 0.035
	Pb	0	0.05 ± 0.003	0.07 ± 0.004	0.10 ± 0.003	0.13 ± 0.003	0.19 ± 0.004
15	Zn	0	0.02 ± 0.035	0.04 ± 0.030	0.08 ± 0.030	0.09 ± 0.035	0.16 ± 0.030
	Pb	0	0.03 ± 0.004	0.04 ± 0.003	0.08 ± 0.003	0.09 ± 0.003	0.17 ± 0.004
20	Zn	0	0.02 ± 0.030	0.038 ± 0.035	0.70 ± 0.030	0.06 ± 0.030	0.13 ± 0.030
	Pb	0	0.02 ± 0.003	0.03 ± 0.003	0.69 ± 0.003	0.73 ± 0.003	0.13 ± 0.003

Table 3 — Relationship between the initial (added) to residual metal concentrations (ppm ± SE) in the effluent (contact period 20 days)

	Metal	Concentration of effluent, %					
		0	5	10	15	20	25
Added conc.	Zn	0	0.06 ± 0.030	0.13 ± 0.035	0.19 ± 0.030	0.26 ± 0.035	0.32 ± 0.030
	Pb	0	0.07 ± 0.003	0.14 ± 0.004	0.20 ± 0.004	0.28 ± 0.004	0.34 ± 0.003
Residual conc.	Zn	0	0.02 ± 0.030	0.038 ± 0.035	0.70 ± 0.030	0.06 ± 0.030	0.13 ± 0.030
	Pb	0	0.02 ± 0.003	0.03 ± 0.003	0.69 ± 0.003	0.73 ± 0.003	0.13 ± 0.003

(73.4 % for Zn, 80.3 % for Pb) in 20 percent effluent concentration after 20 days of treatment. This could be due to a high metal concentration induced toxicity to plant metabolism in other treatments. Similar metal induced toxicity was reported in water hyacinth and channel grass and in water lettuce[8,13,14]. Removal of Zn (70.7%) from 10 per cent effluent concentration was found very close to the corresponding value (73.4%) observed from 20 per cent effluent concentration. This was primarily due to the lower concentration of Zn in the effluent that supported the plant growth and metabolism leading to its increased plant uptake[15].

Sorption Isotherm for Pb and Zn

The relationship between the initial (added) to residual metal concentration in the effluent is shown in Table 3. The data for Pb and Zn accumulation were filled in Langmuir isotherm (Figs 2a & 2b). The sorption capacity for Pb (1.50 mg/g) and Zn (1.75 mg/g) indicates that the plant can uptake and

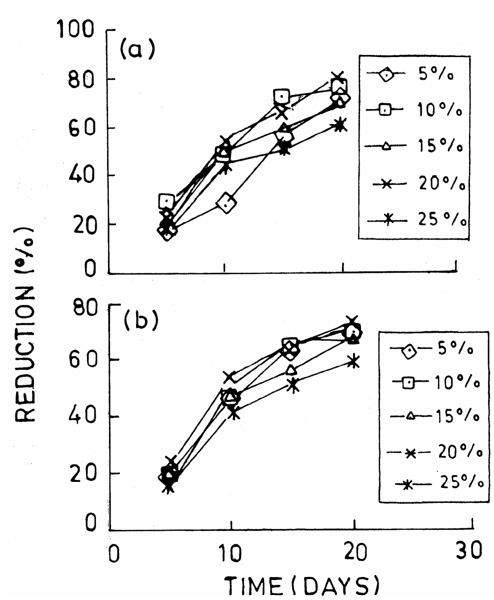

Fig. 1 — Removal of Pb (a) and Zn (b) from effluent by *Eichhornia crassipes*

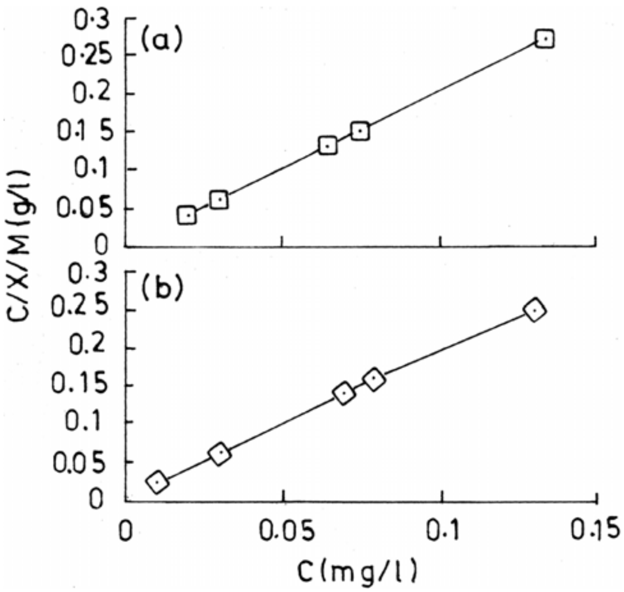

Fig. 2 — Langmuir sorption isotherm for Pb (a) and Zn (b)

absorb higher concentration of Zn than Pb. This is because of the growth promotry effect of Zn, which acts as a plant nutrient and facilitates the plant growth[16].

Conclusions

The present study reveals that water hyacinth has a strong potential to uptake and accumulate the toxic heavy metals from industrial wastewater and paves way for the development of an economically cheap technology for the removal of heavy metals from the industrial effluents (especially pulp and paper mill) by exploiting this plant, which often grows luxuriantly as weed in meso and eutrophic aquatic systems. However, this calls for detail pilot scale study.

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