A PRELIMINARY STUDY OF REMEDIATION OF CHROMIUM FROM TANNERY EFFLUENT

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INTRODUCTION

The environment is contaminated by a variety of heavy metals which commonly results from human activities. The effluent and sludge disposed from the leather industries into the rivers are the sources of Cr in the environment. Cr(III) and Cr(VI) are two stable oxidation states that are present in the environment. They show different chemical and biochemical reactivity. Cr(VI) compounds are more soluble, mobile and bioavailable than Cr(III) [1]. Cr(VI) is acutely toxic, mutagenic and carcinogenic in contrast to Cr(III), which has low toxicity and is immobile under moderately alkaline to slightly acidic conditions [2]. Remediation of contaminants by chemical methods has some disadvantages. They are; high cost, need expensive equipment, incomplete removal of contaminants, inability to recycle the products and possible environmental effects posed by the products.

Phytoremediation involves the use of plants to remove toxic substances from the environment. It is a green technology and is more favoured than the conventional methods because it costs less and is environmental friendly and the pollutants absorbed by plants can be extracted for commercial purposes (phytomining).

Plant species are selected for phytoremediation based on their potential to accumulate metals, growth rates and yields and depth of their root zone. This ability of plant species can be used to remediate heavy metals from the contaminated sites [3].

In the leather industry, Cr(III) salts and chromic acid are widely used as chrome tanning agents. During the process, polynuclear Cr(III) complexes bridge the neighboring proteins by coordinating with carboxyl groups. This toughness prevents putrefaction of leather. Effluents discharged into water streams, on standing generate Cr(VI) through oxidation by dissolved oxygen. Conversion of Cr(III) to Cr(VI) is thermodynamically feasible and poses an environmental hazard [4].

The objectives of the study were: to determine the characteristics of tannery waste, to optimize the conditions to sustain growth of *Lemna minor*, and to determine the efficiency of *Lemna minor* to remove chromium from tannery waste.

METHODOLOGY

The aquatic plant *Lemna minor* was collected from a canal in the Rajagiriya area and acclimatized in a fresh water tank in a mesh house.

The industrial effluent was collected from a leather tanning factory in Colombo. The physical parameters of the effluent were measured using calibrated instruments (Hanna pH 211), and conductivity (Hanna EC 215); total Cr concentration of the effluent was determined using Atomic Absorption Spectrophotometry (AAS – Varian AA280 FS).

In experiment 1, a litre of each of the diluted raw effluent samples was placed in black plastic basins. *Lemna minor* (6-8 g) was added to each basin which were kept in the mesh house for four days. The initial fresh weight of *Lemna minor* and the pH of the mixture were recorded.

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This experiment was carried out with 2- fold, 5- fold 10- fold and 20- fold diluted raw effluents. A set of effluent samples were withdrawn at 24 hour intervals for four days. The final fresh weights of the plants were recorded each day. Effluents were analyzed for Cr content by using an Atomic Absorption Spectrophotometer.

In experiment 2, the same procedure was carried out with the effluent of which the pH was adjusted, by adding dilute NH_4OH drop wise, to the optimum pH for growth of *Lemna minor*. In this case both effluent samples and plants were analyzed for chromium content by AAS. Plants in distilled water served as the control.

During the experiment, the sample mixture was replenished by adding distilled water daily to maintain the initial volume of the sample.

All experiments were run in triplicate.

Relative growth of plants in control and experiments were calculated each day during the experimental period as,

$$\text{Relative Growth} = \frac{\text{Final fresh weight (g)}}{\text{Initial fresh weight (g)}}$$

RESULTS AND DISCUSSION

The tannery effluent was greenish blue in colour. The physical and chemical parameters of the effluent are as follows:

Conductivity = 99.4 ± 0.01 µS

pH = 3.92 ± 0.01

Total chromium content = 1.52×10^3 ppm

All plants treated in the raw effluent diluted to two-fold and five-fold dilution showed toxic symptoms within a few hours. This is probably due to the high concentration of Cr(VI). Therefore the experiment was carried out in more diluted effluent: ten- and twenty-fold dilutions.

The plants in the control experiment were fresh and normal throughout the experiment.

In experiment 1 with ten fold dilution, plants were fresh and normal on Day one and thereafter, the plants started to show morphological changes. But in experiment 2 with ten fold dilution; most plants were fresh and normal. Compared to experiment 2, significant Cr toxicity was observed from Day two onwards in experiment 1. This may be due to the high concentration of Cr(VI) in the effluent which was toxic to *Lemna minor*. In experiment 2, when the pH was adjusted to the optimum value for plant growth (pH 6.18), most of the Cr(III) precipitated as $Cr(OH)_3$. This depletes $Cr(III)_{aq}$ in the effluent and hence the Cr(VI) bioavailable to plants. As a result, plants did not show growth (nor increase in biomass) and hence, an increase in Relative Growth (Figure 1).

In experiments 1 and 2 of twenty fold dilution, plants were fresh and normal up to Day two, but thereafter started to show morphological changes. Both experiments 1 and 2 showed similar morphology and relative growth, possibly because the pH values are similar in both experiments, and amounts of Cr(III) and Cr(VI) bioavailable were the same (Figure 2).

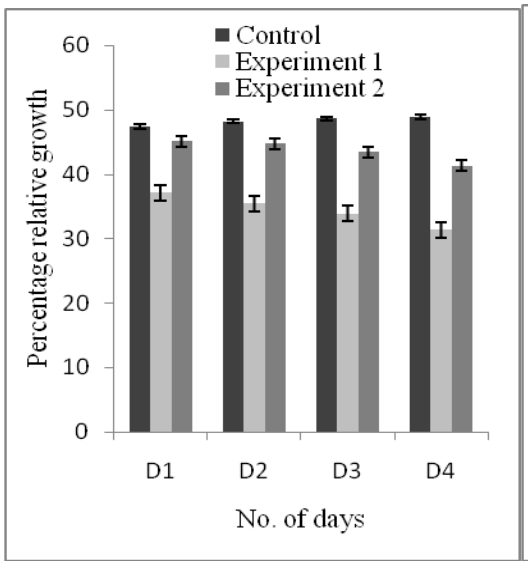

Figure 1 Percentage relative growth of *Lemna minor* In Ten – fold diluted effluent.

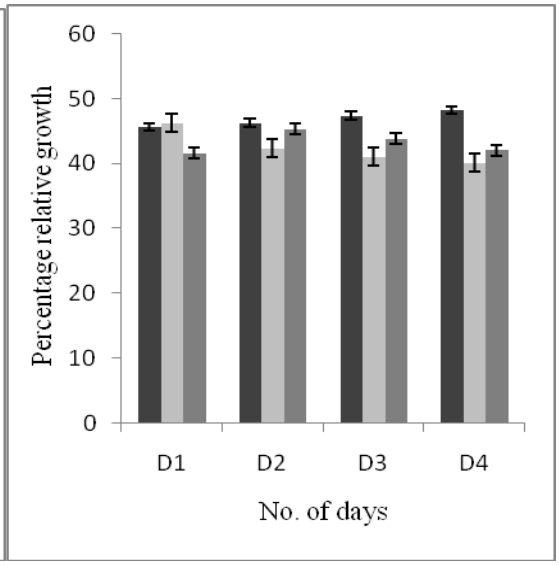

Figure 2 Percentage relative growth of *Lemna minor* in Twenty – fold diluted effluent.

Control- Plants in distilled water; Experiment 1- Plants in diluted raw effluent; Experiment 2 – Plants in diluted and pH adjusted (pH 6.18) effluent.

Variation of absorption of chromium by *Lemna minor* with time in the ten- and twenty-fold diluted effluents in experiment 2 during the experimental period is shown in Figure 3. In this study, Cr was not detected in the control experiment. According to Figure 3, in experiment 2 of ten fold dilution, the maximum absorption of Cr(VI) was 41.6 x 10^3 mg/kg DW on Day one. There was no significant difference in Cr(VI) absorption with time. This is because, when the effluent was adjusted for an optimum pH, 6.18, aqueous Cr(III) present in the effluent precipitated as $Cr(OH)_3$, an insoluble form which will not undergo aerial oxidation to form Cr(VI). Therefore bioavailable Cr(VI) is depleted for *Lemna minor*.

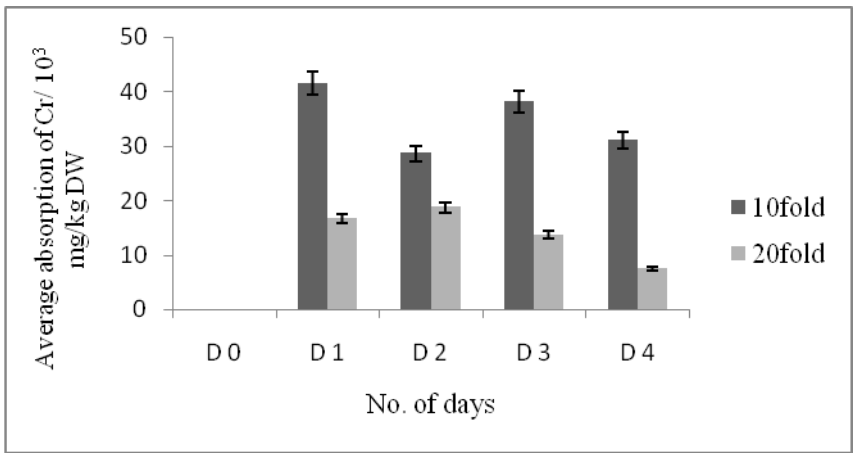

Figure 3 Absorption of chromium by *Lemna minor* from the ten- and twenty fold diluted effluent during the study period.

With twenty – fold dilution, the maximum absorption of Cr in experiment 2 was 18.8 x 10^3 mg/kg DW in Day two (Figure 3). There was no significant difference in absorption with time as in experiment 2 in ten- fold diluted effluent. Due to the conditions of experiments 1 and 2, Cr existed mostly as $Cr(OH)_3$ (pH 6.18) and the soluble form of Cr(III) was less and hence Cr(VI) bioavailable to plants were lower.

Variation of total chromium content of the remaining effluent in experiment 1 with time for both ten- and twenty – fold dilution is given in Figure 4.

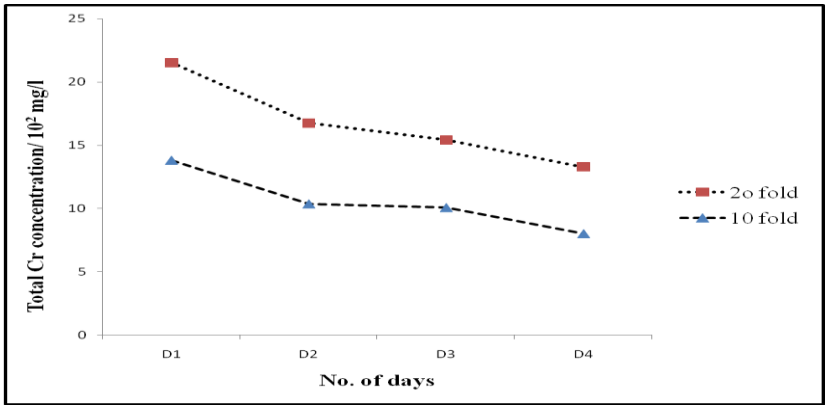

Figure 4 Variation of total chromium content remaining after uptake by *Lemna minor* in ten- and twenty- fold effluent without pH adjustment**.**

According to Figure 4, during the study period, the total chromium content of both ten- and twenty- fold diluted effluents decreased; plants absorbed Cr(VI) species present in the solution and the Cr(VI) species are formed by oxidation of Cr(III) by air and dissolved oxygen.

CONCLUSION

Tannery effluent was acidic (pH = 3.92) and contained a high chromium content and showed toxicity to *Lemna minor*. The two- and five -fold diluted effluent was toxic to *Lemna minor*, while ten- and twenty- fold diluted effluents showed considerable growth of *Lemna minor* as shown by the Relative Growth. When the pH was adjusted to 6.18, which is optimum for *Lemna minor*, Cr uptake was diminished because at pH 6, the predominant Cr species are Cr^{3+}_{aq} and $Cr(OH)_3$, which are not bioavailable for plants. Low Cr(III) content in effluent means lower bioavailable Cr(VI) and hence lower Cr uptake, less toxicity symptoms and higher Relative Growth.

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