A SIMPLE GREEN REMEDY OF CHROMIUM FROM LEATHER TANNERY EFFLUENT

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INTRODUCTION

Pollution of aquatic systems results mainly due to industrial effluents in Sri Lanka. The tanning industry in Sri Lanka is relatively a small scale industry. There are about 16 private tanneries in Sri Lanka and mostly situated in and around Colombo. Of the 16 tanneries only one has an effluent treatment plant, but even this does not function effectively due to the inappropriate design, inadequate maintenance and inefficient operations (Mubarak, 1998).

Leather tanning is the process of converting the raw hides/ skins into leather. During this process, Cr (III) is oxidized to Cr (VI). Reducing agents are used to reduce excess Cr (VI) to Cr (III) in the effluent. Mostly all the tanneries discharge their untreated effluent into inland waterways and / or marsh lands. This causes a considerable amount of pollution in the water bodies (Ileperuma, 2000).

Cr (III) is the main component in the tannery wastewater. Although Cr (III) is an essential micro-nutrient, it is hazardous at relatively high concentrations. However Cr (VI) is very harmful. It is carcinogenic, mutagenic and also more toxic than Cr (III). Chromium (III) is relatively stable and slowly oxidized to the much more toxic Cr (VI). The conversion of Cr (III) into Cr (VI) is thermodynamically feasible in water bodies ($\Delta G^\circ =$ - 150 kJ/ mol). Hence, there is a need to remove the chromium from the wastewater or reduce it to an acceptable level, before discharging into water bodies.

Biosorption is now recognized as a green remedy of heavy metals from wastewater. *Cabomba caroliniana*, an aquatic plant was selected for this study as it is known to adsorb both Cr (III) and Cr (VI) (Chathuranga *et al.* 2012).

The objective of this study is to investigate the feasibility of application of *Cabomba* caroliniana to remove Cr (III) from leather tannery effluent.

METHODOLOGY

CHARACTERIZATION OF LEATHER TANNERY EFFLUENT

Effluent (50 litres) was collected from a leather factory in Mattakkuliya, Colombo 15. The physical parameters (colour, pH, conductivity and temperature) and the chemical parameter (total chromium content) were measured by using calibrated instruments in the laboratory.

DIGESTION OF TANNERY EFFLUENT

The tannery effluent (25.0 cm³) was pipetted into a test tube of the heating digester. Conc. HNO_3 (5 cm³) and conc. H_2SO_4 (5 cm³) were added to the above sample inside the fume hood. The mixture was heated to 120 °C, until white dense fumes of SO₃ gas appeared. Then 0.5% v/v HNO_3 (15 cm³) was added. The mixture was heated again until the brownish color fumes disappeared. Mixture was allowed to cool. The solution was transferred to a 50 cm³ volumetric flask, and the volume was made up to 50.0 cm³ by using distilled water. The digested samples were stored in a refrigerator until the determination of the total chromium content (Gatew and Mersha, 2013).

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PREPARATION OF BIOSORBENT

Healthy and mature *Cabomba caroliniana* were collected from a water stream in Horana. Plants were thoroughly cleaned and air dried for 2 days and oven dried for 3 days at 60 °C. Dried plant samples were ground to a powder and were sieved through a sieve with pore size 710 μ m.

BIOSORPTION EXPERIMENT

The successful biosorption process is greatly affected by ambient conditions such as pH, dosage of biomass, contact time, initial concentration of metal solution, agitation speed *etc*. In order to improve the biosorption process it is essential to optimize these conditions. These conditions were optimized for the biosorption of Cr(III) from the tannery effluent (Ariharan and Thayaparan -manuscript preparation in progress) and reported as pH 4.5, contact time- 45 minutes and dosage of the biomass 4.0 g/100 cm³ of 1500 ppm of tannery effluent. These parameters were used in this experiment which was carried out in two ways as follows.

EXPERIMENT – I

Biomass (7.0 g - calculated from the experiment which was carried out for optimization of biomass) was introduced to one litre of 40 fold diluted effluent (150 ppm). The pH was maintained at the optimized pH 4.5 and ambient temperature was 34 °C in the mesh house. The suspension was mixed thoroughly with a glass rod and kept for 2 hours in the mesh house under natural conditions. Samples from the residual solution were withdrawn at 45 minutes intervals (Figure I) over 2 hours and analyzed total chromium using Atomic Absorption Spectrometry (AAS).

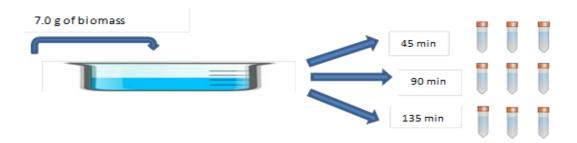


Figure 1. Schematic diagram for Experiment I

EXPERIMENT - II

Experiment I was repeated under the same experimental conditions and by introducing new biomass to the filtrate each time and samples were withdrawn at 45 minutes intervals over 2 hours (Figure 2). All the samples were analyzed for total chromium using AAS.

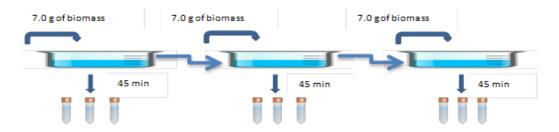


Figure 2. Schematic diagrams for Experiment II

DESORPTION EXPERIMENT

The biomass was loaded with raw tannery effluent under optimized conditions (pH 4.5 and contact time 45 minutes). Then biomass was separated by filtration and washed with tap water followed by distilled water. The filtrate was acid digested and analyzed for total Cr content using AAS. Cr loaded biomass was desorbed under the same experimental conditions with 0.1 M HNO₃, 0.05M H₂SO₄, 0.1 M HCl, 0.1 M EDTA, distilled water and tap water. Finally Cr content in the desorbing agents was analyzed using AAS. Desorption efficiency was calculated.

RESULTS AND DISCUSSION

CHARACTERIZATION OF LEATHER TANNERY EFFLUENT

The physical and chemical parameters are given Table1.

Table 1. The physical and chemical parameters of the Tannery Effluent

Parameters	Results
Colour	blackish Green
pH	3.72 ± 0.01 at 28.8 °C
Conductivity	57.7 \pm 0.01 mS / cm at 28.4 °C
Total chromium (undigested)	3068 ppm
Total chromium (digested)	6333 ppm.

The effluent is very acidic and contains a very high amount of total chromium (~6000 ppm).

BIOSORPTION EXPERIMENT

The result of both biosorption experiment I and II is shown in Figure 3.

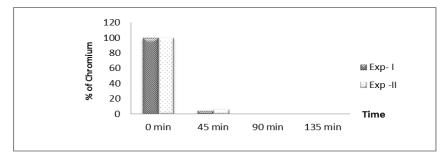


Figure 3. Percentage chromium remaining in the residual solution with time.

It was observed that after the first 45 minutes, the percentage of chromium in the residual solution of both experiments (Experiment I and II) was 4.72% and 6.66% respectively. No chromium was detected after 90 minutes in both experiments. This result indicated that 7.0 g biomass removed around 95% of the total chromium from the diluted tannery effluent (~150 ppm) at pH 4.5 and ambient temperature 34 °C within one hour.

DESORPTION EXPERIMENT

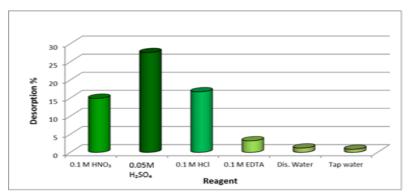


Figure 4. Desorption of Cr from Cr- loaded biomass with different desorbing agents

Among the acids used, H_2SO_4 desorbed more total chromium (27%) from the biomass (Figure 4). It may be due to the relative affinity of sulphate anion towards chromium. It is reported that percentage desorption can be increased by increasing acidic strength of sulphuric acid (Ferraz *et al.* 2004).

CONCLUSION

Leather tannery effluent contained a very high amount of total chromium (~6000 ppm). This method is simple and biosorption is very rapid. It can be applied to Industrial effluent / wastewater at the site as a cheap, eco-friendly green remedy. Adsorbed chromium can be recovered (~30%) using H₂SO₄ from the Cr-loaded biomass in one cycle. It may be possible to use *Cabomba caroliniana* as a biosorbent to remove Cr(III) from leather tannery effluent/ wastewater.

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