Suitability of vetiver (*Vetiveria zizanioides*) for removal of Cr (III) from tannery effluent using floating bed and rhizofiltration systems

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How to Cite  

Abstract  
Various physico-chemical methods have been employed in remediating heavy metals from wastewater, but most of them are expensive. While phytoremediation, is one cost-effective and eco-friendly technology, proves to be an alternate amongst which Vetiver, a unique tropical plant, is recognized for its large biomass and dense root system and has been proven for various remediation studies. The current research was conducted to assess the potential for Vetiver rhizofiltration of chromium. A pilot study was conducted in rhizobox wherein Vetiver was grown using sand as a medium and samples were collected from rhizobox port 1 and rhizobox port 2. Subsequently, the study was upscaled to a floating bed experiment. In both studies, Vetiver were grown under 500 mg L\(^{-1}\) Cr (III) solution and tannery effluent had a chromium concentration of 379 mg L\(^{-1}\) and the results were compared to control. Between the samples collected from port 1 and 2, the removal of chromium in port 1 was recorded to be higher than that of port 2. Moreover, the removal of chromium ions from the tannery effluent was relatively higher than the spiked solution. In both the ports, the highest removal of chromium concentration was recorded in T\(_5\) (Sand + Vetiver + Cr (III) @ 500 mg kg\(^{-1}\)) with a removal percent of 12.59 and 10.38% in port 1 and 2, respectively. Hence, Vetiver grass has a great potential in removing pollutants like chromium from the wastewater.

Keywords: Chromium, Floating Bed, Rhizobox, Tannery, Vetiver

INTRODUCTION  
The concentration of Cr in tannery waste is approximately 20,000 ppm, approximately 1800 ppm in sludge and 200 ppm in composite effluent and these are disposed of without any treatment (Sundaramoorthy *et al.*, 2010; Genawi *et al.*, 2020). The recent findings are still more alarming, as the Cr fractions in the groundwater...
have increased 10-fold in the same region (maximum of 36.7 mg/L). In the Erode and Coimbatore basins, the impact of tanneries is becoming acute in terms of groundwater and river contamination. Nearly 60 lakh people, including tannery workers, are reported to have severe health impacts in Erode. Various technologies have been under research to remove and recover chromium from contaminated ecosystems through different approaches to reduce adverse environmental impacts. Rhizofiltration involves the use of root exudates and associated microbes to influence metal availability. The changes in the rhizosphere vary with the plant species growing in each soil biome (Krishnasamy et al., 2021). The exudation of organic acids depends on the level of metals in the soil Meier et al., (2012). Rhizofiltration is primarily used to remediate groundwater, surface water and wastewater with low contaminant concentrations (Raskin and Ensley,2000) and can be used for the removal of lead, cadmium, copper, nickel, zinc and chromium (Moosavi and Seghatoleslami, 2013). The main advantage of rhizofiltration is that heavy metals accumulate in the roots instead of transferring them to the shoots. Vetiver grass has been reported to withstand extreme environmental conditions due to its unique morphological, physiological and ecological characteristics, making it suitable for phytoremediation/rhizofiltration studies (Yebao et al., 2015; Kafil et al., 2019; Masinire et al., 2021). It has a massive and deep root system, tolerant to extreme climatic variations such as prolonged drought, flooding, emergence, fire, frost, and heat waves and a wide range of soil acidity, alkalinity, salinity, sodicity, and elevated levels of Al, Mn, and heavy metals. The vetiver has more potential to remove 77% nickel Mudhirizha et al. (2015), 606 mg/L Pb and 23,285 mg/L Zn (Aksorn and Chitsomboon 2013). Vetiveria zizanioides (Linn) and Vetiveria memorialis have the capability to remove 89% and 86% of chromium in HRT-conducted wetlands Srisatit and Sengsai (2003). Rhizobox studies using Vetiver sp. resulted in the accumulation of nearly 40% of Cr in roots, followed by Ni and Pb. Hence, the present study aimed to evaluate the performance and potential usefulness of vetivers for the removal of Chromium (III) from tannery effluent.

MATERIALS AND METHODS

Study area
Effluent and water source
The physico-chemical characteristics of the tannery effluent and water source utilized in the column study were analyzed as per the standard methods. The total dissolved and suspended solid were determined by following the method given by Gupta et al. (2000), while pH, electrical conductivity, calcium, magnesium, sodium, chloride, and sulfate were estimated using the protocol given by Jackson (1973). The BOD and COD were determined by the method given by Young et al. (1981) and Moore et al. (1949) while the carbonate and bicarbonate ions were determined using the procedure given by Piper (1966).

Designing vetiver-based wastewater treatment methods for Cr removal
A pilot-study using rhizobox was performed to assess the efficiency of the removal of Cr (III). The study was carried out in a PVC made rhizoboxes with a height of 30 cm and diameter of 4.5 inches. The inner column has a diameter of 2.5 inches and the distance between the outer and inner column was 3 cm. Two different ports were made at different heights to collect the sample (Fig.1). The boxes were loaded with acid washed sand (3.2 kg/box). Vetiver plants containing one tiller with uniform weight (10.0±2.0 g) were planted in the inner layer of rhizobox designed as rhizosphere region. Chromium solutions of 500 ppm concentration and tannery effluent with a chromium concentration of 379 mg L⁻¹ were added to the inner layer of each rhizoboxes to based on the water holding capacity of the sand. The experimental setup was incubated for 15 days. The moisture content of the rhizoboxes were maintained by replacing the evaporation loss with deionised water (Kim et al., 2010). The wire mesh (0.2mm) and muslin cloth were placed at the bottom of each layer to avoid contact between the amendments. Nine different treatments with three replicates were studied which included T₁ (Sand + water), T₂ (Sand + Cr (III) @ 500 mg L⁻¹), T₃ (Sand + Tannery Effluent), T₄ (Sand + Vetiver + Water), T₅ (Sand + Vetiver+ Cr(III) @ 500 mg L⁻¹), T₆ (Sand + Vetiver+ Tannery Effluent). The soil solution was collected in the bulk sand zone of rhizobox via port 2 and the aqueous solution zone via port 3 (Fig.1). The Cr concentration in the aqueous solution were analyzed using AAS (Perkin Elmer AA400) at regular time intervals.

Vetiver floating beds for the removal of Cr in tannery effluent
A floating bed experiment was performed to assess the efficiency of the removal of Cr (III). The study was carried out in 15-litre water tubs filled with an aqueous solution. A chromium solution of 500 ppm was prepared using deionized water. Either 8 liters of Chromium solution or tannery effluent was added to each water tub. Five vetiver plants containing one tiller with uniform weight (10.0±2.0 g) were inserted into the polystyrene sheets and allowed to float freely on the surface of the solution. A schematic illustration of the floating vetiver system is depicted in Fig. 2. The treatment details include T₁ (water), T₂ (Cr III @500 mg L⁻¹), T₃ (Tannery Effluent), T₄ (Water + Vetiver), T₅ (Cr III @500 mg L⁻¹ + Vetiver), T₆ (Tannery Effluent + Vetiver). The experimental setup was incubated for 7 days. After seven
days from the tubs, water samples were collected and analyzed using AAS (Perkin Elmer AA400) to determine the Chromium concentration.

Data analysis
Statistical analysis of experimental data from the experiment was carried out to determine the effect of treatments and other factors through ANOVA for a completely randomized design (batch experiment) by the statistical software SPSS. The interpretation of data was performed using the critical difference (CD) value calculated at the 0.05 probability level by ANOVA. Analysis of variance was calculated as suggested by Panse and Sukhatme (1967).

RESULTS AND DISCUSSION
Characterization of tannery effluent
The characteristics of tannery effluent used for the study are presented in Table 1. Apparently, the pH, EC, TDS and TSS values were 4.53, 20.9 dS m⁻¹, 14000 mg L⁻¹ and 4200 mg L⁻¹ respectively. The BOD and COD values of the effluent were found to be 36.0 mg L⁻¹ and 276 mg L⁻¹. The values of calcium, magnesium, sodium, chloride and sulphate were 4.02 meq L⁻¹, 7.01 meq L⁻¹, 206 meq L⁻¹, 143 meq L⁻¹ and 50.40 meq L⁻¹ respectively. The heavy metal total chromium content was 379 mg L⁻¹, which was higher than the permissible limit to discharge into the inland surfaces or river. The tannery effluent is acidic (4.53). This might be due to the utilization of concentrated acids for tanning process. Divya and Vidya (2016) reported the use of salts such as calcium carbonate, sodium chloride and sodium dichromate in the transformation of animal skin to hide. Other effluent characteristics like BOD, COD, TSS, TDS, Na, Cl, SO₄²⁻ were also high which coincides with the evidences of several researchers Dilacocni et al. (2002); Louhab et al. (2008). Adding this, Cr concentration was found to be high, which might be due fact that only 60-70% of chromium salts utilized in
the tanning process retaliate with the skins and the remnant amount of 30-40% left in the exhaust bath to be discharged.

**Rhizobox study and Floating bed technology to evaluate the potential of vetiver in Cr removal**

The removal of chromium by Vetiver based biofilter is presented in Table 2 (Port 1). After two weeks of incubation, the concentration varied between 370.80 \((T_6)\) and 495.15 mg L\(^{-1}\) \((T_2)\), respectively. As the days progressed, a reduction in the concentration was observed. At the end of four and six weeks, the lowest concentration was recorded in \(T_6\) (Sand + Vetiver+ Tannery Effluent (379 mg/L)) with a reduction percent of 0.02 and 2.16 %, respectively. The role of Vetiver based biofilter system in removing chromium from port 2 is presented in Table 3 (Port 2). Generally, it was observed that in all treatments, the removal was significantly higher in port 1 than in port 2. During the second week, the chromium concentration ranged between 373.68 \((T_6)\) and 497.64 mg L\(^{-1}\) \((T_2)\), respectively. As like in port 1, the chromium concentration gradually declined as days progressed. At the sixth week, the highest removal percent of 1.40 % was observed in \(T_6\) (Sand + Vetiver+ Tannery Effluent (379 mg/L)). Furthermore, during both 4\(^{th}\) and 6\(^{th}\) week, the highest concentration was recorded in \(T_2\) (Control (Sand + Cr (III) @ 500 mg L\(^{-1}\)) as 492.64 and 469.36 mg L\(^{-1}\) in port 1; while in port 2, the concentration was found to be 490.82 and 487.41 mg L\(^{-1}\) respectively.

A hydroponic study conducted using Vetiver in the removal of chromium exhibited the superior nature of Vetiver in remediation (Table 4). Initially, the chromium concentration ranged from 377.38 \((T_6)\) to 499.34 mg L\(^{-1}\) \((T_2)\), respectively. After one week, a progressive decline in all treatments were observed with the highest reduction of 1.50 % in \(T_2\) (Sand + Vetiver+ Tannery Effluent) followed by \(T_6\) (Sand + Vetiver+ Tannery Effluent (379 mg/L)) with a reduction percent of 1.46 %.

**Table 1.** Characterization of tannery effluent (TE)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>4.53</td>
</tr>
<tr>
<td>2</td>
<td>Electrical conductivity (dS m(^{-1}))</td>
<td>20.9</td>
</tr>
<tr>
<td>3</td>
<td>Biological Oxygen Demand (mg L(^{-1}))</td>
<td>36.0</td>
</tr>
<tr>
<td>4</td>
<td>Chemical Oxygen Demand (mg L(^{-1}))</td>
<td>276</td>
</tr>
<tr>
<td>5</td>
<td>Total Dissolved Solids (mg L(^{-1}))</td>
<td>14,000</td>
</tr>
<tr>
<td>6</td>
<td>Total Suspended Solids (mg L(^{-1}))</td>
<td>4200</td>
</tr>
<tr>
<td>7</td>
<td>Calcium (meq L(^{-1}))</td>
<td>4.02</td>
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<tr>
<td>8</td>
<td>Magnesium (meq L(^{-1}))</td>
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<tr>
<td>9</td>
<td>Sodium (meq L(^{-1}))</td>
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</tr>
<tr>
<td>10</td>
<td>Chloride (meq L(^{-1}))</td>
<td>143</td>
</tr>
<tr>
<td>11</td>
<td>Sulphate (meq L(^{-1}))</td>
<td>50.40</td>
</tr>
<tr>
<td>12</td>
<td>Total chromium (mg L(^{-1}))</td>
<td>379</td>
</tr>
</tbody>
</table>

**Table 2.** Removal of Cr (III) by biochar based Vetiver biofilter system - Port 1

<table>
<thead>
<tr>
<th>Treatments</th>
<th>2 Week</th>
<th>4 week</th>
<th>6 Week</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1- Control (Sand + water)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>T2- Control (Sand + Cr (III) @ 500 mg/L)</td>
<td>495.15</td>
<td>492.64</td>
<td>489.36</td>
</tr>
<tr>
<td>T3- Control (Sand + Tannery Effluent (379 mg/L))</td>
<td>377.65</td>
<td>375.69</td>
<td>368.21</td>
</tr>
<tr>
<td>T4- Sand + Vetiver + Water</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>T5- Sand + Vetiver+ Cr(III) @ 500 mg/L</td>
<td>494.16</td>
<td>489.36</td>
<td>476.21</td>
</tr>
<tr>
<td>T6- Sand + Vetiver+ Tannery Effluent (379 mg/L)</td>
<td>370.80</td>
<td>366.75</td>
<td>348.45</td>
</tr>
</tbody>
</table>

**Table 3.** Removal of Cr (III) by biochar based Vetiver biofilter system - Port 2

<table>
<thead>
<tr>
<th>Treatments</th>
<th>2 Week</th>
<th>4 week</th>
<th>6 Week</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1- Control (Sand + water)</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>T2- Control (Sand + Cr (III) @ 500 mg/L)</td>
<td>497.64</td>
<td>494.37</td>
<td>491.72</td>
</tr>
<tr>
<td>T3- Control (Sand + Tannery Effluent (379 mg/L))</td>
<td>378.38</td>
<td>375.72</td>
<td>371.39</td>
</tr>
<tr>
<td>T4- Sand + Vetiver + Water</td>
<td>0.02</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>T5- Sand + Vetiver+ Cr(III) @ 500 mg/L</td>
<td>495.72</td>
<td>490.82</td>
<td>487.41</td>
</tr>
<tr>
<td>T6- Sand + Vetiver+ Tannery Effluent (379 mg/L)</td>
<td>373.68</td>
<td>370.54</td>
<td>367.95</td>
</tr>
</tbody>
</table>

study findings by Amenu (2015) indicated that total chromium was decreased up to 99.3% for an inlet average total chromium loading rate of 40mg/L. The difference in results between the planted and unplanted beds might be due to the Vetiver grass's ability to absorb metal. The most vital reaction zone for chromium removal is the root zone (rhizosphere), wherein physicochemical and biological processes happen (Stottmeister et al., 2003). The removal efficiency of chromium is achieved due to the uptake potential of Vetiver. Various researches and studies were conducted at both lab – and full scale on the removal efficiency of chromium by Vetiver (Aregu et al., 2021; Darajeh et al., 2019; Jayanthi et al., 2020 and Rajendran et al., 2019).

Conclusion

Chromium (Cr) poisoning of soil and water was caused by the indiscriminate dumping of wastes from tanning factories. The biofilter employing Vetiver was used with the intention of eliminating Cr (III) from the tannery effluent. Plants that can accumulate metal ions in their tissues are known as hyperaccumulators. The findings suggest that Vetiver may accumulate higher levels of chromium. As a result, the hydroponic Vetiver system may be employed as one of the wastewater treatment solutions for heavy metal-laden industrial effluents. This is a pilot-scale study being conducted for a shorter period. To fully maximise Vetiver's potential, more long-term and large-scale trials and research into the process of heavy metal removal by Vetiver are required.

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Conflict of interest

The authors declare that they have no conflict of interest.

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