Removal of Heavy Metals from Tannery Wastewater by using Sawdust and Spent Tea Leaves as an Adsorbent

Abu Sayid Mia MD\textsuperscript{1,\textdegree,*}, Uzzal Ali MD\textsuperscript{1}, Nur-E-Alam MD\textsuperscript{3}, Mafizur Rahman MD\textsuperscript{4} and Zahangir Alam MD\textsuperscript{2}

\textsuperscript{1}Institute of Leather Engineering and Technology, University of Dhaka, Bangladesh
\textsuperscript{2}Department of Applied Chemistry and Chemical Engineering, University of Dhaka, Bangladesh
\textsuperscript{3}Leather Research Institute (LRI), Bangladesh Council of Scientific and Industrial Research (BCSIR), Bangladesh
\textsuperscript{4}Department of Civil Engineering, Bangladesh University of Engineering and Technology (BUET), Bangladesh

*Corresponding author: Abu Sayid Mia MD, Institute of Leather Engineering and Technology, University of Dhaka, Dhaka 1209, Bangladesh, Tel: 01927907551; Email: emsayid@gmail.com

Abstract
Innovative processes for treating tannery wastewater containing heavy metals often involve technologies for reduction of toxicity in order to meet standards. Adsorbent is the most frequently studied and widely applied for the treatment of metal-contaminated wastewater. The removal of heavy metals e.g., chromium, nickel and lead from tannery wastewater at low concentrations is a recurring challenge, especially in developing countries. Batch studies were performed to evaluate the influences of various experimental parameters like adsorbent dose, contact time and pH. The removal of dyes from effluent using adsorption process provides an attractive alternative treatment, especially if the adsorbant is inexpensive and readily available. In this study, the low-cost adsorbant spent tea leaves and saw dust were used for removal of heavy metals from waste effluent of leather tanning industry. The adsorbants were found to be capable of removing heavy metals from wastewater; the metals removal capacity for spent tea leaves was approximately 99% at optimum dose, contact time and pH.

Keywords: Adsorption; Spent tea leaves; Saw dust; Tannery wastewater; Heavy metal

Introduction
Water is the most vital element among the natural resources and is crucial for the survival of all living organisms. The increasing urbanization and industrialization of Savar, Dhaka, have negative implications on water quality as well as other environmental issues [1]. The pollution from industrial and urban waste effluents and from agrochemicals in some water bodies and rivers has reached alarming levels. There are numerous ill effects of pollution, each type of pollutants having different effect, on human and animal health and ecology [2]. Chromium which largely used in tanning process, is one of the water pollutants which is a micronutrient required by our body in minute quantity. The form of trivalent chromium or Chromium-3 is safe [3]. Chromium also exists in another very rare form known as Hexavalent chromium or Chromium-6 [4]. This is usually introduced into ground water when chemical industries using chromium discharging wastewater without proper treatment [5]. Hexavalent chromium-6 is poisonous and should be removed from all kinds potable water. It causes cancer, anuria, nephritis, gastrointestinal ulceration, perforation in partition of nose. It penetrates cell membrane and badly affects central nervous system, causes respiratory trouble, and lung tumors when inhaled [7]. Trace amount of Cr (III) is essential for normal glucose, protein and fat
metabolism and hence it is an essential trace element in diet [8-10]. Lead, nickel and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc [11,12]. Unlike organic wastes, heavy metals are non-biodegradable and can be accumulated in living tissues, causing various diseases and disorders; therefore, they must be removed before discharge.

Chromium metal ions are usually removed by precipitation although ion exchange and adsorption are also used for its removal. The hydroxides of heavy metals are usually insoluble, so lime is commonly used for precipitating them. There are various methods to remove Cr including chemical precipitation, membrane process, ion exchange, liquid extraction and electrodialysis [13]. These methods are non-economical and have many disadvantages such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment [14]. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost [15].

Utilizing the waste material from sawmills can make treatment process economical and solve the solid waste disposal problem. Although it has been invented many years ago, saw dust and activated carbon is still the most popular adsorbents throughout the world due to their high adsorptive capacity [16]. Sawdust or wood dust is a by-product of cutting, grinding, drilling, sanding, or otherwise pulverizing wood or any other material with a saw or other tool; it is composed of fine particles of wood.

Tea is one of the most popular beverages and about 3.5 million tons of tea was consumed annually in the world [17]. The annual per capita consumption of tea in Bangladesh is 0.390 kg in 2013 [18]. After brewing, the spent tea becomes a waste which must be disposed of and that creates disposal problems. In present modern lifestyle, tea has become as essential drink due to improvement of people’s living standard and that results in the disposal of spent tea leaves which has gradually become an unavoidable challenge [19].

The present study was aimed at selection of low-cost adsorbents from sawdust and spent tea leaves, which can adsorb heavy metals from the tannery effluent effectively.

**Materials and Methods**

**Sample Collection**

Tannery wastewater was collected from tannery estate, Savar, Dhaka. Pre-washed plastic jars were used for sample collection.

**Preparation of Adsorbent**

Sawdust is solid waste product of sawmills. This sawdust was collected from sawmills of Don Chember, Narayanganj, Bangladesh. Sawdust was washed with water to remove dust, soil, silica and other contaminations. Then it was dried with sunlight and heated in oven to 105°C for 24 hours.

Spent tea leaves were collected from local tea stalls near University of Dhaka. It was used for the treatment as adsorbent. Surface impurities were removed from tea wastes by washing with boiling water. Color was also removed by repeating washing. The tea leaves were then oven dried for 6–8 h at 105°C.

**Adsorbent Size**

Sieving machine (retsch D-42459 HAAN, Germany) was used to separate the sample into desired size. Adsorbent was separated into different mesh size (30 to less than 40 and ≥40) by using sieving machine.

**Experimental Procedure**

In this study, the batch technique was performed in a series of beakers equipped with stirrers by stirring the tannery effluent. The batch technique was selected for its authenticity and simplicity [20]. After scheduled time, the suspension was filtered and the residual concentration of metal ions in the aqueous phase was measured by atomic absorption spectrophotometer (JEOL JSM-7600F). 250 mL of sample was conducted with varying adsorbent dose (1.5–17 g/L), contact time (30–150 min) and pH (4–10) at room temperature. Finally, Langmuir and Freundlich isotherms were also observed to determine the best model that characterizes the adsorption mechanism.

The physical parameters including total suspended solids (TSS), total dissolved solids (TDS), electrical conductivity (EC), pH, biological oxygen demand (BOD), chemical oxygen demand (COD) of raw tannery effluent and treated effluent were measured. Chemical parameter like sulfate (SO4^2-) and heavy metals such as Cr, Ni and Pb of raw and treated effluents were analyzed. Colors were measured in Pt–Co color unit.

**Results and Discussion**

**Characterization**

The investigated physico-chemical characteristics of
tannery effluents are shown in Table 1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw Effluents</th>
<th>Standard Limits (ISI-2000/ISW-BDS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour units (pt-c.)</td>
<td>1640</td>
<td>15</td>
</tr>
<tr>
<td>pH</td>
<td>7.3</td>
<td>6.0-9.0</td>
</tr>
<tr>
<td>EC (mS/cm)</td>
<td>21.45</td>
<td>0.288</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>5500</td>
<td>100</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>13000</td>
<td>2100</td>
</tr>
<tr>
<td>TS (mg/L)</td>
<td>18600</td>
<td>2200</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>1.2</td>
<td>4.0-6.0</td>
</tr>
<tr>
<td>BOD₅ (mg/L)</td>
<td>830</td>
<td>30/250</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>3790</td>
<td>250/400</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>3850</td>
<td>1000</td>
</tr>
<tr>
<td>Cr (mg/L)</td>
<td>25.60</td>
<td>02</td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>3.40</td>
<td>--</td>
</tr>
<tr>
<td>Ni (mg/L)</td>
<td>1.35</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 1: Characteristics of studied tannery effluent.

**Effect of Contact Time**

This study was conducted by agitating 250 mL sample for different time period 30-150 min. After the predetermined time intervals, the samples were filtered and then analyzed. Figure 1 shows that the sorption increased at 60 min and it became almost constant at 150 min for all metal ions. At the beginning the metal ions uptake was high since all active sites of adsorbent were vacant. After that, only a very low increase in the metal ions uptake was occurred as there were few surface-active sites left on the adsorbent. The quick equilibrium time is due to the small particle size as the effective surface area is high for small particles.

![Figure 1](a) Effect of contact time on Cr, Ni and Pb removal by spent tea leaves (a) and sawdust (b) adsorbent.

**Effect of Adsorbent Dose**

The effect of adsorbent dose was conducted with varying amount of adsorbent starting from 1.5 to 17g/L. 250 mL of sample was treated with different number of doses of spent tea leaves and sawdust adsorbent. The effect of adsorbent dosage on the amount of the metal ions adsorbed shown in Figure 2.
The percentage of heavy metals removal is seen to increase with adsorbent dose up to 8 g/L for both samples. After that dose, very negligible uptake was happened.

**Effect of pH**

pH effect was performed taking a specific adsorbent dose and contact time. The pH was varying using dilute NaOH/HCL solution. The samples were agitated for specific time, filtered and then analyzed. Figure 3 revealed that the adsorption capacity of the metal ions by spent tea leaves is higher than that of sawdust, which is clearly affected by the pH. The dependence of metal uptake on pH related to the functional groups of the adsorbent and the solution chemistry [21]. The minimal adsorption at low pH may be due to the higher concentrations and high mobility of protons, which worked as a competitor and preferentially adsorbed rather than the metal ions on the active binding sites [22].
Comparison between Percentage of Removal

The comparison of percentage of heavy metals removal from tannery wastewater using sawdust and spent tea leaves as adsorbent is shown in Figure 4.

![Figure 4: % of removal (Cr, Ni & Pb) by spent tea leaves and sawdust adsorbent.]

For all the heavy metals removal from tannery wastewater, spent tea leaves as adsorbent shows the relatively better removal percentage than the sawdust.

Scanning Electron Microscope (SEM)

The SEM image is shown in the following Figure 5. Based on the surface of SEM image, spent tea leaf has porous structure and sawdust has smooth surface areas with long ridges.

![Figure 5: SEM images of spent tea leave (a) and sawdust (b).]

Adsorption Isotherms

Adsorption isotherm is an equilibrium plot of the solid phase ($q_e$) versus liquid phase concentration ($C_e$) at fixed temperature. Freundlich and Langmuir's isotherms are the simplest known relationships which describe the adsorption equation [23]. Freundlich and Langmuir adsorption isotherm parameters of spent tea leaves and sawdust are shown in Figure 6. The regression coefficient of Freundlich and Langmuir's isotherms of spent tea leaves and sawdust are close to each other and which are more than 0.9. Both Langmuir and Freundlich isotherms are followed by the...
adsorptions which indicate the formation of a monolayer of adsorbate on the outer surface of the adsorbent and the heterogeneity of the adsorbent.

**Figure 6:** Adsorption Isotherms of spent tea leaves and sawdust adsorbent.

**Conclusion**

Tannery effluents are not suitable for discharging into surface water bodies directly which pose potential threats to human health as well as to the environment. This study revealed that the spent tea leaves as well as sawdust using as adsorbent could reduce certain pollution levels of heavy metals like Cr, Ni and Pb from tannery wastewater. The adsorption can be influenced by several factors, such as, adsorbent mass, contact time, pH etc. Hence, there is a need to optimize these factors to maximize the treatment efficiency of adsorbents and minimize the treatment cost for tannery wastewater.

**Data Availability**

All information about the conducted research is available from the corresponding author, e-mail: emsayid@gmail.com.

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**Conflict of Interest**

On behalf of all authors, the corresponding author states that there is no conflict of interest.

**References**
