Removal of Cr(III) and other pollutants from tannery wastewater by *Moringa stenopetela* seed

M D Islam¹, A Rahaman², M M Mahdi²,³*, D Mallik⁴

¹Department of Applied Chemistry and Chemical Engineering, University of Dhaka, Dhaka-1000, Bangladesh
²,³,⁴Institute of Leather Engineering and Technology, University of Dhaka, Dhaka-1209, Bangladesh

*Email: miz40.mahdi@gmail.com

**Abstract.** The tanneries release a substantial amount of trivalent chromium with wastewater that bring about serious environmental pollution problem and health hazards without proper treatment. Therefore, the chromium concentration should be kept permissible in tannery effluent. In this study, the dried *Moringa stenopetela* seed was used as bio-adsorbent for the removal of Cr(III) from tannery effluent. Different adsorption parameters viz. pH, adsorbent dosage, initial chrome concentration, etc. were studied for optimizing the adsorption process. The sorption mechanism was described by various isotherm models and physicochemical parameters like turbidity, conductivity and TDS were also tested after treatment. The analyses showed that the percentage of Cr(III) removal (82.93%) was obtained at pH 3, adsorbent dosage 20g(mg/l), initial concentration 1123.3mg/l, for contact time 12hours at ambient temperature. The adsorption process followed Langmuir isotherm model. Additionally, the reduction in physicochemical parameters e.g. turbidity (67.68%-72.70%), conductivity (72.88%-80.99%) and TDS (71.96%-83.33%) was found satisfactory and the values were closed to the permissible limit set by DoE. Therefore, dry *Moringa stenopetela* seeds can be successfully used as a low-cost tannery effluent treatment agent to reduce the environmental threats caused by harmful tannery effluents.

1. **Introduction**

In recent years, the contamination of water by heavy metals has become a major environmental pollution problem. Extensive discharge of heavy metals and other pollutants with industrial wastewater has increased water pollution that results in the scarcity of fresh drinking water in many countries. Among heavy metals, chromium is considered as a potent toxic metal despite having several industrial applications [1]. In nature, chromium exists in two oxidation stages e.g. +3 and +6 [2]. It has been stated that the oxidation states of Cr are not stable in water and trivalent chromium can be easily converted into hexavalent chromium even in presence of mild oxidizing agent like MnO₂ which may form chromate (CrO₄²⁻) and dichromate (Cr₂O₇²⁻) ions that show more toxic symptoms (500-1000 times) than any other valence state [3, 4, 8]. Hence, it is imperative to remove chromium from industrial wastewaters before discharging them into soil/water.

Among industries, leather industry is recognized as a potential source to generate a significant amount of chromium into the environment. In the leather industry, chromium is used as Basic chromium sulfate (BCS), a trivalent chromium salt, which has been the most popular leather-tanning
agent for over a century [5]. Ahmed et al., (2017) [6] showed that the pickled pelts consume only 60% of the total applied chromium salt during chrome tanning and the residual 40% salt remains unreacted and discharged with wastewater into the environment. Scholars have found that the amount of chromium in spent chrome liquor is ranged 2656-5420mg/L which is beyond the permissible limit of Cr(III) (5mg/l) in industrial effluent [7, 8]. Moreover, the discharge of chrome-tanning effluent can contaminate agricultural soil, surface water and irrigation channels, deposit chromium in the vegetative parts of various vegetables through bioaccumulation and finally the accumulated chromium is transported to the human food chain by the consumption of those vegetables [9]. Several toxicological studies have showed that the daily intake of Cr with daily diet at an excess rate (>50-200µg/day) might show carcinogenic, mutagenic and teratogenic effects on human health. Moreover, the drinking of chrome-containing water causes several harmful diseases such as skin irritation, dermatitis, nausea, vomiting and even lung cancer on prolonged exposure [10, 11]. Therefore, the concentration of Cr(III) in tannery effluent should be kept up to the threshold limit.

Many attempts have reported to treat Cr(III) containing tannery wastewaters such as ultrafiltration, adsorption, ion exchange, ozonization, membrane filtration, photocatalysis [12]. Among them, adsorption is preferred due to its low-cost, high efficiency and less secondary pollution [13]. However, the increasing price of commercial adsorbents (activated carbon), adsorbent variety, low adsorption capacity and less recyclability (clay) has compelled researchers to look for cost-effective and efficient wastewater treatment agents [8, 13]. In recent years, biomass-based adsorbents such as rice husk, fruit shells, animal bones, chitosan, etc. have been suggested for metal removal from industrial effluents for their abundant availability, cheap price and excellent adsorptive affinity but still the literature is very limited [14-17].

In this present study, the feasibility of dry Morina stenopetela (MS) seed as a low-cost bio-adsorbent was investigated for the removal of Cr(III) from tannery wastewater. Morina stenopetela is a perennial plant and indigenous in tropical and sub-tropical countries. In Bangladesh, it grows widely in road sides, back yards and non-agricultural lands. Its pods are enriched with essential proteins and nutrients like vitamins and minerals [18]. Though MS seed extract has potential application as a coagulating agent in water purification [19], most of the people are not aware of its importance and usually throw them away after vegetable consumption. As a result, the waste seeds often create solid waste disposal problem and sometimes bring about serious odor pollution problem when they mix up with domestic wastes and get putrefied. Therefore, the study aims to reduce the waste disposal problem and provide an alternative adsorbent for tannery effluent treatment. Additionally, the effect of different adsorption parameters such as pH, adsorbent dose, contact time, etc. on the adsorption process and sorption mechanism were also evaluated as specific objectives.

2. Materials and methods

2.1. Materials and chemicals

Morina stenopetela (MS) seeds were collected in airtight polyethylene bag from a local nursery shop to use as bio-adsorbent. Analytical grade standard sodium hydroxide (NaOH) and hydrochloric acid (HCl) solution were purchased from Sigma-Aldrich, USA. Deionized water was used to perform all the experiments in this study.

2.2. Wastewater collection

A sufficient amount of chrome-tanning effluent was collected from the discharge point of four export-oriented tanneries (randomly selected) in sealed HDPE bottles (marked as S1, S2, S3, and S4 respectively). The bottles were disinfected by 10%HNO3 solution to avoid contamination during sample collection. The collected tannery effluent samples were filtered by Whatman No. 1 to remove suspended matters and the filtrates were stored at 4˚C temperature to prevent any chemical changes/metal leaching. The pH of the effluent samples was adjusted by 0.5M NaOH or 0.5M HCl
solutions before conducting adsorption experiments and it was measured by a digital pH meter (Hanna Instruments).

2.3. Adsorbent preparation and characterization
The MS seeds were thoroughly washed with tap water after brining to the laboratory to remove water soluble impurities and surface adhered coarse particles. The seeds were sundried for a week, powdered by a grinder and sieved with a nylon mesh to obtain particle size ranged 250-400µm. For chemical activation, the seed powder was soaked overnight into 0.5M NaOH solution at 1:1 weight ratio, washed with deionized water to remove surplus alkali until a neutral pH was achieved and oven-dried at 105°C temperature for 3hours in the next morning. Finally, the dried adsorbent was kept in a desiccator for cooling until further experiments. Consequently, the prepared adsorbent was subjected to assess by a Fourier transform infrared (FT-IR) spectrophotometer to test the characteristics of existed functional groups in the adsorbent.

2.4. Adsorption tests
All the adsorption experiments were performed in batch mode at ambient temperature to find out the Cr(III)-MS seed interaction and the influence of different adsorption factors on the adsorption process. In each experiment set, 250ml chrome-tan effluent of known concentration (1123.3-1904.7mg/l) was treated with a certain amount of adsorbent (2-20g) in a 500ml Erlenmeyer flask at desired pH (2-8). The mixture was agitated in a rotary shaker for a predetermined time (30-180minutes) at ambient temperature. After desired time, the mixture was centrifuged at 1000rpm for 3minutes to settle down the adsorbent. Finally, the mixture was filtered by Whatman No. 42 paper, and the residual quantity of chromium in spent chrome-tan liquor was measured by a flame atomic absorption spectrophotometer (FAAS) (Perkin Elmer PinAAcle™500) with air-acetylene flow. The following equations were used to estimate the removal percentage of chromium from chrome-tanning effluent:

\[
\text{Removal} (\%) = \frac{C_0 - C_f}{C_0} \times 100 \tag{1}
\]
\[
\text{Capacity} (q_e) = \frac{C_0 - C_f}{1000 \times m} \times V \tag{2}
\]

Where, \(C_0\) = initial concentration of chromium in effluent (mg/l), \(C_f\) = residual concentration of chromium after treatment (mg/l), \(q_e\) = amount of adsorbed chromium (mg/g), \(V\) = volume of chrome-tan effluent (ml), \(m\) = adsorbent mass (g).

2.5. Wastewater analysis
The wastewater discharged from chrome tanning and after treated with prepared adsorbent from MS seed were assessed. Several physicochemical parameter viz. total dissolved solid (TDS), conductivity, turbidity, dissolved oxygen (DO) of the wastewater samples were tested by calibrated instruments as per their standard testing methods. A digitalized potentiometer (metrohon 906 Toledo) and turbidity meter (Hach 2100Q) were used measure TDS and turbidity of the wastewater samples respectively. Meanwhile, conductivity was calculated by electrometric method and DO was estimated by a DO meter (Mettler Toledo).

3. Results and discussion

3.1. Adsorbent nature
The FT-IR spectra (Figure 1) showed the prominent nature and presented functional groups in the adsorbent. The strong absorption peak was found at 3446.79cm\(^{-1}\) that attributed to the H bonded alcohol group (-OH) and amine group (-NH). The spectrum band at 2927.94cm\(^{-1}\) represented C-H stretching and at 1629.85cm\(^{-1}\) indicated bending in primary amine. However, the band range at
1446.61 cm$^{-1}$ is due to C=C vibration in the aromatic ring. Weak absorption from 1379 to 1317 cm$^{-1}$ is due to C-N Stretching. There is C=O stretch due to the spectrum band at 1076.28 cm$^{-1}$. The broad-spectrum band ranging from 769.6 to 514.99 cm$^{-1}$ may represent an out of plane -NH bending vibration for primary and secondary amines.

**Figure 1.** FT-IR spectrum of *Moringa stenopetela* seed.

### 3.2. Optimization of adsorption process

#### 3.2.1. Effect of pH

The optimization of solution pH is one of the major factors in the adsorption study. Chromium can exist in various forms such as HCrO$_4^-$, CrO$_4^{2-}$, and Cr$_2$O$_7^{2-}$ depending on the pH and concentration of the aqueous phase. In the pH range 2.5-4.5, Cr exists in solution primarily as bi-chromate (HCrO$_4^-$) ion, whereas the dichromate (Cr$_2$O$_7^{2-}$) ion predominates at lower pH values and higher concentration [20]. The favorable pH for the adsorption of Cr was observed in weakly acidic medium (2.5-4.5). In weakly acidic medium, the bi-chromate anion forms an ion-pair electrostatic bond with the positively charged adsorbent surface. According to Pearson’s classification [21], chromium is categorized as a hard acid and nitrogen is classified as a hard base (adsorbent used in this study contain primary and secondary amines shown in the Figure 1). This can be used to explain the variety of complex ion reactions. As they are both strong, good interaction between the positively charged protonated amine group of chitosan and negatively charged bi-chromate anion can be expected. In this study, effluent was treated at various pH ranging from 2 to 8 and found that removal efficiency was gradually reduced with increasing pH of the solution (Figure 2(a)).

#### 3.2.2. Effect of Adsorbent dosage

Figure 2 shows the effect of adsorbent dose on the chromium removal efficiency. In this study dose effect was studied for two different concentration solutions. It has been found that for both concentrated solution with increasing the adsorbent dose (2 to 20 gram sample in 250 ml effluent), chromium removal percentage also increased. This is due to increasing the amount of certain amount of dose; the number of active sites also increased thus surface area for metal binding sites increased resulting increment of percentage of chromium from the solution [22]. The optimal dose for this adsorbent is 20 gram. But further increasing of the dose decrease uptake of metal; which is due to
increase of adsorbent, agitation of the metal binding active site might occur and the removal efficiency could be hampered (remain level or decreased) [23].

3.2.3. Effect of initial concentration
In adsorption processes, the initial concentration of metal ions plays an important driving force for mass transfer between the effluent solution and the solid phase (adsorbent) [24]. In this research, effluent from four different tannery industry (contamination level by chromium was different) was collected and investigate initial concentration effect on chromium removal. As shown in Figure 2(c), the removal efficiency was reduced by increasing the initial concentration of chromium ion, so that the removal efficiency at the concentration of 1123 and 1904 ppm was 92.0 and 81.0 %, respectively. At low metal concentration, the ratio of the active sites of the adsorbent to the metal ion in the solution is high and lower availability of metal ion for the active sites results reduction of removal efficiency [25].

3.2.4. Effect of contact time
Contact time is an important parameter of adsorption which also reflects adsorption kinetics of an adsorbent for a solution with a given concentration and pH values. The batch studies were carried out at 30°C with initial concentration of Cr of 1150 and 1900 ppm 250 ml solution, pH of 2.0 using 20 gram adsorbent at various contact time period. Figure 2(d) shows the effect of contact time on the chromium removal percentage by the adsorbent. The results shows that percentile removal increases with increasing contact time from 30 to 120 min and after 120 min efficiency remain constant or slightly reduced and attain equilibrium condition, which indicates that 120 min of contact time is enough for the maximum removal of Cr ions from aqueous solution under these experimental condition. Equilibrium adsorption achieved may be due to the accumulation of Cr ions on the vacant sites and causes limited mass transfer of the adsorbate from the bulk liquid to the external surface of adsorbent [26]. Slight removal percentage results due to re-dissolution of Cr from the adsorbent site to aqueous solution.

![Figure 2. Effect of (a) pH, (b) adsorbent dosage, c) initial concentration and (d) contact time on Cr removal.](image-url)
3.3. Isothermal studies
Adsorption isotherm models are usually investigated to describe the adsorption process and its mechanism [7]. Langmuir and Freundlich isotherms are two isotherms that are widely used models [2, 8, 11]. Langmuir isotherm is used by assuming the adsorption of a single layer on the adsorbent surface at equilibrium stage. The linear form of this equation is as followed [27, 28]:

\[
\frac{1}{q_e} = \frac{1}{K_L q_o} \cdot \frac{1}{C_e} + \frac{1}{q_o}
\]  

(3)

In the equation above, Ce is the concentration of metal ion in equilibrium state (mg/l) and q_e is the amount of metal ion adsorbed in equilibrium state per gram of the adsorbent. Furthermore, q_o and K_L are adsorption capacity (mg/g) and adsorption energy (L/g), respectively, which are constants of the Langmuir model.

The Freundlich isotherm [29] is a useful model to study the adsorption for dilute solutions. The adsorption on nonequivalent adsorption sites is well described by this empirical isotherm. The Freundlich equation takes into account the logarithmic decrease in the energy of adsorption with increasing surface coverage and this is attributed to the surface heterogeneity [29, 30]. The linearized form of this isotherm can be expressed as:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]  

(4)

Here, C_e is the equilibrium concentration of the Cr ion in mg/L, q_e is the amount of Cr adsorbed at equilibrium in mg/g, and K_F and n are the Freundlich constants, which indicate the adsorption capacity and the adsorption intensity, respectively. The values of K_F and n were obtained from the slope and intercept of the logarithmic plot of q_e/C_e.

In this study the regression coefficients for Langmuir and Freundlich are 0.9930 and 0.9886, respectively, which implies that Langmuir adsorption model is the best fit compared to Freundlich model. This observation implies that monolayer adsorption on homogenous surface may co-exist under the applied experimental conditions.

![Figure 3](image_url)

Figure 3. Isothermal study for Cr adsorption from effluent (a) Langmuir isotherm and (b) Freundlich isotherm

3.4. Removal of other physicochemical parameters
The test results of the assessed physicochemical parameters of the chrome tanning effluent samples were measured before and after treatment with 20g of adsorbent were shown in Table 1. From the results, it was observed that the values of each parameter were beyond than the marginal level set by
DoE in industrial effluents before treatment. As a result, it would bring threat to aquatic ecosystem and living organisms if these effluents were released without treatment. However, significant changes in these values were observed after treatment. The values such turbidity (67.68%-72.70%), conductivity (72.88%-80.99%), TDS (71.96%-83.33%) were reduced/nearly reduced to the maximum tolerable limit which might reduce the hazardous impact of these effluents as a result dissolved oxygen was found increased.

### Table 1. Characteristics of tannery samples before and after treatment.

| Sample id | TDS (mg/l) | Turbidity (NTU) | Conductivity (uS/CM) | Dissolved oxygen (mg/L) |
|-----------|------------|-----------------|----------------------|-------------------------|
|           | before     | After           | before               | After                   | before       | After       |
| S1        | 27101.5    | 5510            | 1050                 | 305                     | 53120       | 10100.8     | 2.5         | 3.7         |
| S2        | 30050.1    | 5010.2          | 720                  | 202                     | 57510.8     | 11012       | 3.2         | 3.4         |
| S3        | 36105      | 10123           | 950                  | 307                     | 70520.9     | 19127       | 2.7         | 3.5         |
| S4        | 31051.2    | 8121            | 923                  | 252                     | 62301       | 16523       | 2.8         | 3.9         |

### 4. Conclusions

In this present study, *Moringa stenopetela* seed was used as an adsorbent to remove trivalent chromium ions from harmful tannery effluent. The function of different operational parameters such as adsorbent dose, initial concentrating of metal ions were investigated in batch process. It was observed that the parameters viz. pH (3), adsorbent dosage 20g (mg/L), contact time (12 hours), and initial dye concentration (1123mg/L) were optimum for the highest Cr(III) adsorption (82.93%). The adsorption followed Langmuir isotherm model which indicated monolayer adsorption of trivalent chromium onto homogeneous surface of *Moringa stenopetela* seed. Moreover, the removal of other pollutants derived from the auxiliary chemicals used in chrome tanning were also examined. The findings showed that the reduction in several physicochemical parameters e.g. turbidity (67.68%-72.70%), conductivity (72.88%-80.99%) and TDS (71.96%-83.33%) were found satisfactory and the values were closed to the threshold limit after treatment that addressed the higher adsorption efficiency of MS seed towards other organic and inorganic pollutants as well. Based on findings it can be concluded that the *Moringa stenopetela* seeds can be an effective low-cost adsorbent for the metal removal and treatment of harmful tannery effluents to mitigate water pollution caused by toxic heavy metals.

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