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# Efficiency of *Tamarindusindica* Seed Charcoal for Chromium Removal from Tannery Wastewater

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**ABSTRACT**
In this study, chromium sorption ability of the prepared *Tamarindusindica*seedcharcoal is presented.The prepared charcoal was characterized by Fourier Transform Infrared Spectroscopy (FT-IR).The effectiveness of charcoal adsorbent for chromium sorption efficiency was examined investigating: charcoal dose, contact time, and relative pH.Chromium content in the raw wastewater and after treatment in the filtrate was 3415.02 mg/L and 27.7mg/L, respectively. The chromium removal efficiency was obtained at 98.9%. The reduction of chloride was 17.2% and pH was (7.7) with the discharged level (6-9).The use of native *Tamarindusindica*seedcharcoal adsorbent could be achoice to remove chromiumfrom tannery wastewater.

Keywords: Tannery wastewater, Chromium, Environment, Adsorbent

## 1. Introduction

Worldwide growing amount of waste produced from the anthropogenic activities has a huge impact on the environment. Many industries dispose of their industrial production waste to the environment without any treatment. Increasing industrialization enhances the disposing of mine tailings and metallurgical slags [1, 2].Henceforth, sediment/soil is contaminated with toxic metalsfrom where possible mobilization of metals into groundwater or enter human food chain. Existence of these wastes in the natural environment can cause significant impacts on ecosystem.

The fraction of discharged waste chrome liquor is directly mixed with the water body, which causesserious environmental pollution. Again, afraction of chromium is settled in the lagoon or adsorbent by sediment/soil. About 90% of tanneries use basic chromium sulfate as a tanning agent to obtain better quality leather [3].On average only 60%chromium is uptaken by the pickled pelt and 40% chromium remain in the liquid as wastage of chrome liquor [4]. Conventionally,chrome tanning wastewater contains 1500-3000 mg/L chromium [5]. Hashem et al. [6] reported that chromium content in the wet blue waste chrome liquor ranges from 2656-5420 mg/L.

Balamurugan et al. [7] reported that chromium (III) in the environment under certain legend conditions leads to the cell to death and modification of its own structure of proteins. Solubility and pH appear to be the primary determinants of the capacity of individual chromium compounds to stimulate an allergic response [8]. In humanbody function,chromium (III) is considered as an essential trace element [9] but a long-term exposure to chromium (III) is acknowledged to cause allergic skin reactions and cancer [10]. On the other hand, chromium (VI) can be toxic and carcinogenic [11].

In past few decades, numerous researchers try to remove chromium from the tannery wastewater using stone cutting solid waste [12], bone charcoal [13], using indigenous adsorbent [14], *syzygiumcumini* bark adsorbent [15] and eggshell and powered marble [16].These approaches are well, but in some cases they are not potentially efficient or are not virtually possible or not cost effective. In some cases it takes long contact time to remove high percentage of chromium [3,13].

In this present study,an attemptwas made the use of *Tamarindusindica* seed charcoal chromium from the tannery wastewater. This seed used in cuisines around the world. In Bangladesh, India,Colombia, Cuba, PuertoRico, Venezuela, Italy, Spain, Caribbean, almost all over the world, it is available and low cost.

The objectives of this study is to remove chromium from the chrome tanning wastewater using*TamarindusIndica* seed charcoal.

## 2. MATERIALS AND METHODS

**2**.1 Sample collection

The chromium-containing wastewater water was collected from the SUPEREX LEATHER Ltd. Khulna Bangladesh. Just after the chrome tanning operation, chrome-tanningwastewater was collected in high-densitypolyethylene (HDP)container, which was washed with diluted nitric acid and instantly deported to the laboratory for experimentation.The*Tamarindusindica*seed was collected from Jessore, Bangladesh.

2.2 Charcoal preparation

**Fig. 1** shows the *Tamarindusindica*seed and prepared charcoal.The *Tamarindusindica*seeds were sun-dried.


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**Fig.1***Tamarindusindica* seeda) and prepared seed charcoalb)

After sun drying, the seed was burnt at 450-500$^0$C and chafing to make a powder using a mortar.After shaking on a sieve,the charcoal with the required size was obtained.

2.3 Reagents

The reagents perchloric acid (Merck, India), sulphuric acid (Merck KGaA, Germany), nitric acid (Merck KGaA, Germany), ammonium iron(II) sulphate hexahydrate (Merck, India), and*N*-phenylanthranilicacid (LobaChemie, India)were procured from a local scientific store, Khulna, Bangladesh. Also, the anti-bumping agent glass bed (LobaChemie, India), and filter paper (Whatman No. 1) were procured from a local scientific store, Khulna, Bangladesh.

2.4 Characterization of Wastewater

The physicochemical properties of wastewater were measured in terms of chromium, pH, total dissolved solids (TDS), electrical conductivity (EC), salinity, and chloride ($Cl^-$) content.

2.4.1 Chromium Determination

Chromium content in the chrome tanning wastewater and after treatment in the filtrate was determined by the titrimetric method following the official methods of analysis of Society of Leather Technologist and Chemists [17] official method of analysis (SLC 208). A 50 mL sample volume was taken in 500 mL conical flask. A 20 mL of concentrated nitric acid was added followed by 20 mL ofperchloric acid/sulphuric acid mixture. Then,the flask was gently heated and boiled until the mixture had become a pure orange-red colour and continue boiling for one minute. The flask was removed from the heating source and as soon as ebullition has ceased. Rapidly, the flask was cooled by swirling in a cold water bath. Carefully, 100 mL of distilled water was added with a few glass beads and boiled for 10 minutes to remove free chlorine. Then, 10 mL 30% (v/v) sulphuric acid was added and cooled to room temperature. The mixture was titrated with freshly prepared 0.1N ammonium iron(II) sulphatesolution with six drops of *N*-phenyl anthranilic acid as an indicator. The endcolour was indicated by a colour change from the violet to green.

2.4.2 Determination of pH

pH of the raw chrome tanning wastewater and treated liquor was measured using pH meter (UPH-314, UNILAB, USA). Before measuring pH, the meter was calibrated with the standard solutions.

2.4.3 Determination of TDS, EC and salinity

TDS, EC and salinity were measured using the conductivity meter (CT-676, BOECO, Germany). Before measuring the parameters, the meter was calibrated with standard solutions.

2.4.4 Chloride ($Cl^-$) determination

Chloride content in the chrome tanning wastewater and after treatment in the filtrate was measured by APHA standard argentometric method [18]. A 100 mL water sample was taken in a conical flask and pH was adjusted in the range of 7 to 10. After that, 1.0 mL potassium chromate ($K_2CrO_4$) indicator was pipetted. Then, the solution was titrated with silver nitrate as titrant (0.0141N) to a pinkish yellow endpoint. The titrant was standardized by the sodium chloride (0.0141 N) solution.

2.5 Charcoal characterization

Chromium loaded charcoal and pure charcoal were analyzed using Fourier transform infrared spectrometer (FTIR, Spectrum 100, PerkinElmer, USA) with an attenuated total reflectance (ATR) accessory. Infrared spectra were recorded at a resolution of 4 $cm^{-1}$ and 20 spectra were averaged to reduce the noise.

2.6Treatment of chromium-containing wastewater

Batch-wise chromium removal test was conducted with the prepared charcoal. The scheme for the treatment of chrome tanning wastewater is shown in **Fig. 2**. Firstly, the physicochemical parameters of the untreated chromium-containing wastewater were analysed and filtered through a 0.45 µm pore size filter. Secondly, 70mL of filtrate wastewater was mixed with the prepared charcoal. The charcoal mixed wastewater was stirred over a fixed period of time and the mixture was then allowed to settlefor a fixed time. After settling, the mixture was filtered through 0.45 µm pore size filter and again chromium content measurement was performed.

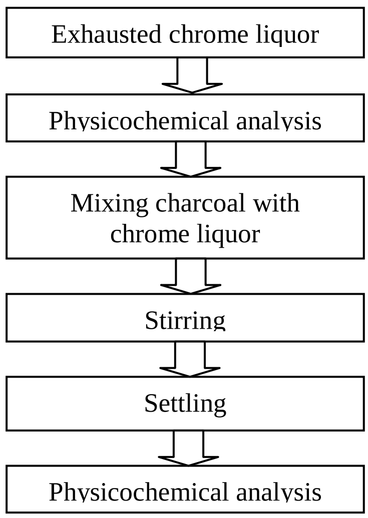


**Fig.2** Schematic flow chart for chromium removal treatment process

2.6 Process optimization

The treatment process was optimized to obtain maximum chromium removal efficiency. Tests were carried out to optimize the chromium removal parameters: adsorbent dose, contact time and relative pH. The optimized conditions were recognized based on thechromium removal efficiency.

## 3. RESULTS AND DISCUSSION

### 3.1FT-IR analysis

**Fig. 3** depicts the FT-IR spectrum of charcoal before and after the adsorption of chromium. The figure reveals thechanges in the peak intensity. Since FT-IR ascertains different surface functional groups, it can be said that different functional groups of the pure charcoal were responsible for adsorption and removal of chromium.

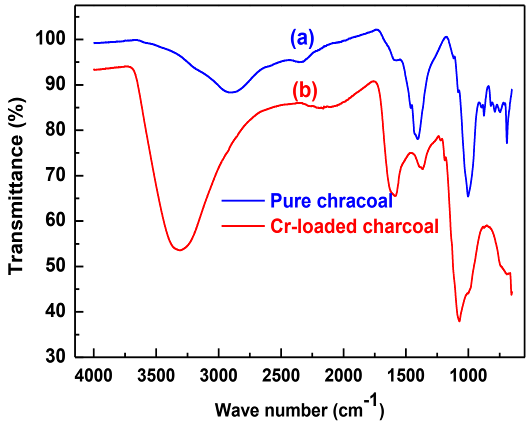


**Fig.3** FT-IR spectrum of pure charcoal **a**) and chromium-loaded charcoal**b**)

Fourier transform infrared absorption spectra studies exposed various types of chemical groups in the charcoal, which are likely to precipitate in the metal binding. Trivalent chromium precipitates by formation of sodium hydroxide at pH>5. The characteristics of the charcoal before and after treatment by using FT-IR analysis are shown in the following **Fig. 3** simultaneously.

FT-IR spectrum of chromium loaded and pure charcoal is depicted in Fig. 2. It shows a shift of peak intensity. The FT-IR was indicated the changes in frequency in the functional groups of the charcoal because of chromium adsorption. It provides an indication of the various functional groups which are responsible for the removal of chromium through charcoal adsorbent.

Fig. 3(a)indicates a broad spectrum around 3200-3600 cm$^{-1}$regionspresence the groups in charcoal of O-H, C-H, N-H.Also, it reveals that the appearance of C=O group around 1670-1820 cm$^{-1}$ region. These functional groups might be the reason of chromium adsorption as well as pH increase during treatment process.

Fig. 3(b) shows shift in peak intensity as well as new peak intensity like around 1500 cm$^{-1}$ region expressing C=C group. Moreover, the presence of C-N and =C-H group is noted around 1277 and 903.5 cm$^{-1}$ region respectively. The FT-IR data ensures the presence of different functionalgroup responsible for the removal of chromium through charcoal adsorbent.

### 3.2 Characteristics of the spent chrome liquor

**Table 1** shows the characteristics of the raw chrome tanning wastewater,after treatment (optimized) in the filtrate as well as ECR standard [19] ECR.

**Table 1** Data comparison with ECR standard

| Parameters | Raw sample | This study (optimum) | ECR [19] |
|---|---|---|---|
| pH | 3.5 | 7.7 | 6–9 |
| TDS (g/L) | 29.06 | 34.34 | 2.1 |
| EC (mS) | 66.8 | 79 | 1.20 |
| Salinity (ppt) | 40.3 | 48.6 | – |
| Cr (mg/L) | 3415.02 | 27.68 | 2.0 |
| $Cl^-$ (mg/L) | 15050 | 12460 | 600 |

It seems that that the chrome tanning wastewater had strong pollution loads in terms of higher quantities of pollutants e. g., higher concentration of chromium, total dissolved solids (TDS),strongly acidic (pH=3.5). The chrome tanning wastewater is threatening to the environment. Therefore, it is essential to treat the chrome tanning wastewater properly to reduce the pollution loads.

The physicochemical parameters of the treated were obtained e. g., pH, TDS, EC, salinity, chromium, chloride was 7.7, 34.3 g/L, 79mS, 48.6ppt, 27.7 mg/L, 12460 mg/L, respectively. The maximum chrome removal efficiency was 99.2%. After treatment pH was appeared within the discharge level (6-9)but other parameters were slightly increased. The reduction of chloride was of obtained 17.2%.

### 3.3Optimal charcoal dose

The dose of charcoal has a significant effect on the ability of chromium sorption. **Fig. 4** shows the effect of charcoal dose and relative pHchanges for the chromium sorption ability from chrome tanning wastewater.

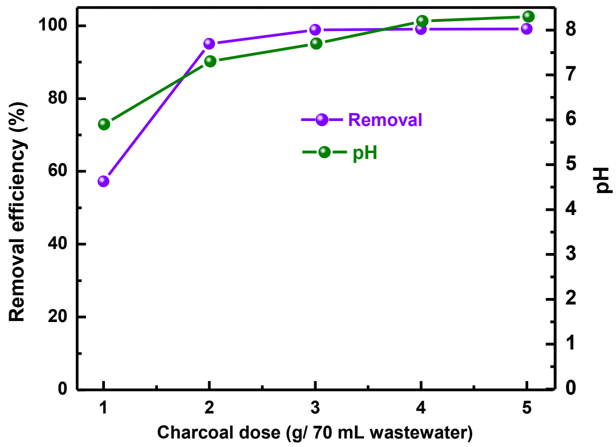


**Fig.4** Effect of charcoal dose and relative pH on chromiumsorption

**Fig. 4** implies that chromium sorption ability was increased with increasing the charcoal doses. Before

treatment (without charcoal) chromium content was in the wastewater was 3415.02 mg/L, the amount of charcoal doses (1 g to 5 g for every 70 mL wastewater) with contact time 10 min was kept constant. Chromium sorption ability was for 1 g, 2 g, 3 g, 4 g and 5 g for every 70 mL wastewater was 53.7%, 95.01%, 98.9%, 99.02% and 99.1%, respectively.
At charcoal dose 3 g for 70 mL wastewater, chromium sorption ability was 98.9%. After that, with increasing charcoal dose chromium sorption ability was not significantly changed. pHplays an role for the adsorption of metals ions because it is responsible for the protonation of metal (chromium)binding site. It establishes, chromium sorption by the*Tamarindusindica* seed charcoal was a function of solution pH. At lower pH, chromium sorption was obtained smaller than in the higher pH.Chojnacka et al. [20] reported thatthe higher the pH, adsorption of hydrolysis yields and precipitated chromium as colloidal insoluble chromium hydroxide, $Cr(OH)_3$. Therefore, it was anticipated that the maximum chromium sorption was occurred with 3 g charcoal dose for every 70 mL wastewater at pH 7.7.

3.4 Optimal contact time

Chromium sorption ability observed at a regular time interval to determine the optimal contact time, which implies in **Fig.5**. It seems that the chromium sorption ability for 2 min, 4 min, 8 min, 12 min and 16 min were 96.8 %, 97.8%, 98.9%, 99.2% and 99.3% respectively. It implies that chromium sorption ability increased with the increasing the contact time. It may be the reason is that more the contact time, metal ion (chromium) binds on the charcoal adsorption sites. Also, it is clear that after a certain time period e.g.,8 min chromium adsorption was extreme (98.9%) and there were no observable changes found (> 8 min). Hence, it was decidedthat the optimal contact time for sorption maximum chromium was 8 min.

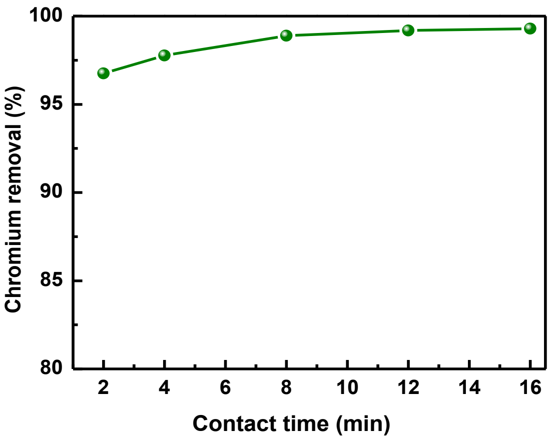


**Fig.5** Effect of contact time on chromium sorption

3.5Efficiency of treatment process

Obtained results of this treatment process at optimum conditions are depicted in**Table1**.The optimized conditions were: adsorbent dose 3g/70mL wastewater and contact time 8 min where pH was 7.7.

**Table 2**Data comparison with the previous study

| Removal efficiency (%) | Contact time | References |
|---|---|---|
| 90 | 30 min | [13] |
| 83 | 6 h | [3] |
| 99 | 14 h | [16] |
| 99 | 8 min | This study |

Before treatment, the chrome content in the wastewater was 3415.02 mg/L and after treatment with optimized conditions, the chrome content in the wastewater is 27.7 mg/L. Therefore, it observed that the maximum removal of chromium is obtained at 98.9%.
**Table 2** shows the comparison of chromium removal efficiency with the previous studies.It seems that with this present approaches chromium removal was obtained 99% with a short contact time (8 min). On the other hand, for example the efficiency of 90%, 83%, and 99% was obtained 30 min, 6 h, and 14 h, respectively. So, the efficiency of chromium removal percentage (99%) is very higher than other study within short time (8 min).

**Conclusion**

The present study reveals that *TamarindusIndica* seed charcoal is very effective to remove chromium from the chrome tanning wastewater. Batch-wise chrome tanning wastewater was treated to remove chromium from the chrome tanning wastewater. The removal chromium efficiency at optimized condition was obtained at 98.9% although others parameters were slightly increased. The reduction of chloride was obtained at 17.2%. This indicates that it will be an effective and low cost, in a word most preferable technique to reduce toxic substances that will minimize pollution load from the chrome tanning wastewater.

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