Paper ID: RT-252

Chromium Removal from the Wastewater Equipped *Artocarpus heterophyllus* Bark Charcoal

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Abstract

In this work, chromium removal of tannery wastewater using prepared charcoal from Artocarpus heterophyllus is described. The waste Artocarpus heterophyllus bark was collected from sawmill and prepared charcoal after drying and burning. The charcoal was characterized prior and post uses by Fourier transform infrared spectroscopy (FT-IR). Effectiveness of charcoal for chromium removal efficiency was examined investigating different parameters e.g., charcoal dose, contact time, and relative pH. In batch wise treatment process, 75 mL chromium containing wastewater was mixed with charcoal, stirred for fixed period of time, settled, and filtered through 0.45 µm pore size. Chromium content in the raw sample and filtrate was measured by the titrimetric method. Chromium content in the raw wastewater and filtrate was 3190.1 mg/L and 5.2 mg/L, respectively. The chromium removal efficiency was obtained 99.8%. The use of low-cost indigenous charcoal could be an option for the chromium removal from tannery wastewater.

Keywords: Tannery wastewater; Chromium; Heavy metal; Environment; Charcoal.

1. Introduction

Leather industry plays a vital rule in economic development for the country. Leather processing are required essential steps of chemical and mechanical operations and each of these operations produce large amount of waste, which directly or indirectly hamper the ecosystem as well as the environment. In processing of one ton of wet salted hides/skins into leather required 452-ton chemicals or other necessary ingredients besides this 84% of used chemicals are discharged as waste in the environment [1].

Tanning is the subsequent operation of pickling where 90% tanneries use basic chromium sulfate as tanning agent to obtain better quality leather [2]. On average, only 60% of the chromium is up taken by the pickled pelt and 40% of chromium remains in the solid/liquid wastes, especially as spent chrome liquor [3]. Suresh et al. [4] reported that chromium contains in the conventional chrome tanning wastewater 1500-3000 mg/L. Therefore, the level of chromium in the spent chrome liquor is strictly regulated in many countries. Removal of chromium from the various industrial wastewaters, especially tannery wastewater is an important issue.

Chromium is discharged into the aquatic systems from the various anthropogenic activities. Contamination of water, soil or sediment by the chromium is a significant concern for the environment. Many works have been studied on the toxicological effects of chromium presence into various food items on the human health [5, 6]. Chromium has several oxidation states among them, the trivalent and hexavalent state of chromium can mainly exist in the aquatic environment [7]. Although chromium (III) is considered as an essential trace element for some metabolic function in the human body [8], a long-term exposure to Cr (III) is recognized to cause allergic skin reactions and cancer [9]. On the other hand, chromium (VI) can be toxic and carcinogenic [10].

Lots of research for chrome liquor treatment have already exist using different technique as eggshell and powdered marble [11], charcoal of bone [12], *Onopordom Heteracanthom* charcoal [13], marl [14], brown seaweed biomass [15], nanocarbonate-hydroxylapatite [16]; most of these techniques are developed for homogenous tannery waste water treatment. On the other hand chemical precipitation and electrochemical precipitation for heavy metal removal is complicated techniques [17, 18]. Ion exchange technique is economical for heavy metal removal [19].

In this study, an approach was made to investigate the effectiveness of *Artocarpus heterophyllus* bark charcoal to remove chromium from the tannery wastewater and recovery of chromium from the adsorbed charcoal as a green technology.

2. MATERIALS AND METHODS

Sample collection

The chrome tanning wastewater was collected from the tannery at Jessore, Bangladesh into polyethylene container that was pre-washed with diluted nitric acid, and immediately transported to the laboratory for experimentation. The *Artocarpus heterophyllus* bark was collected from the local sawmills Khulna, Bangladesh.

Reagents

The reagents perchloric acid (Merck, India), sulphuric acid (Merck KGaA, Germany), nitric acid (Merck KGaA, Germany), ammonium ferrous sulphate (Merck, India), *N*-phenylanthranilic (Loba Chemie, India), glass bed (Loba Chemie, India), and filter paper (Whatman No. 1) were purchased from a local scientific store, Khulna, Bangladesh.

Charcoal preparation

The collected *Artocarpus heterophyllus* bark was cut into small pieces and sun-dried. Then, the sun-dried bark was burnt at 450–550°C, cooled and grinded with mortar. The grinded charcoal was sieved on 80-mesh and preserved for the experiment.

Characterization of charcoal

The Fourier transform infrared spectroscopy (FT-IR) studies were carried out to obtain adsorption spectrum of pure and chromium-loaded charcoal. The FT-IR spectra were recorded using Fourier transform infrared spectrometer (FT-IR 1600, Perkin-Elmer) between 400 and 4000 cm^{-1}.

Treatment of wastewater

Batch-wise chromium removal test was performed. The scheme for the treatment of chrome tanning wastewater is shown in Fig. 1.

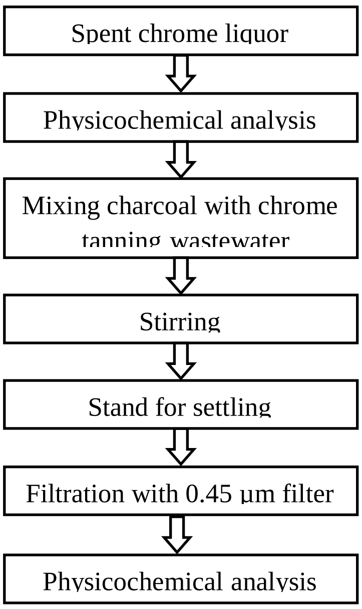

Fig. 1. Schematic flow chart for the chromium removal treatment process.

Physicochemical parameters of the untreated chrome tanning wastewater were analyzed and filtrate through 0.45 µm pore size filter. Then, 75 mL filtrate wastewater was mixed with the prepared charcoal and mixture was stirred over a fixed period of time. After settling for a fixed time of period, the mixture was filtered through 0.45 µm pore size filter. Chromium and physicochemical parameters of the supernatant were analyzed.

Determination of pH

pH was measured by the digital pH instrument (UPH-314, UNILAB, USA). Before measuring pH, the instrument was calibrated in the two points with standard solutions of pH 4.01 and pH 7.00, respectively.

Chromium determination

Chromium content in the untreated chrome tanning wastewater and after treatment in the filtrate was performed by the titrimetric method following the official methods of analysis of Society of Leather Technologist and Chemists [20] official method of analysis (SLC 208). A 50 mL sample volume was taken in 500 mL conical flask then 20 mL concentrated nitric acid was added followed by 20 mL perchloric acid/sulphuric acid mixture. The flask containing mixture was gently heated and boiled until the mixture had become a pure orange-red color 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 swirling in cold-water bath. Carefully, a 100 mL-distilled water was added with a few glass beads and boiled for 10 minutes removing 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 ferrous ammonium sulfate solution with six drops of *N*-phenyl anthranilic acid as an indicator. The end color was indicated by a color change from the violet to green.

Process optimization

Batch-wise examinations were carried out to optimize the chromium removal parameters: charcoal dose, contact time and relative pH. The optimized conditions were established investigating the chromium removal efficiency of the wastewater.

3. RESULTS AND DISCUSSION

Characteristic of charcoal

The FT-IR spectrum of the charcoal before and after the adsorption of chromium is shown in Fig. 2. The figure shows a shift in the peak intensity. The FT-IR was determined to understand the changes of frequency in the functional groups of the charcoal due to adsorption of chromium. This indicates that various functional groups, which were responsible for the removal of chromium by the charcoal.

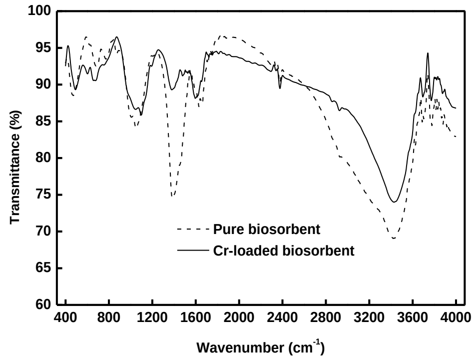

Fig. 2. FT-IR spectrum of the prepared *Artocarpus heterophyllus* bark pure and chromium-loaded charcoal

Optimal charcoal dose

The dose of charcoal is the most important parameter that has a significant effect on the chromium removal. Chromium removal efficiency on adsorbent dose and relative pH changes are depicted in Fig. 3. It is clear from the figure that chromium removal efficiency was increased with the increasing of adsorbent dose.

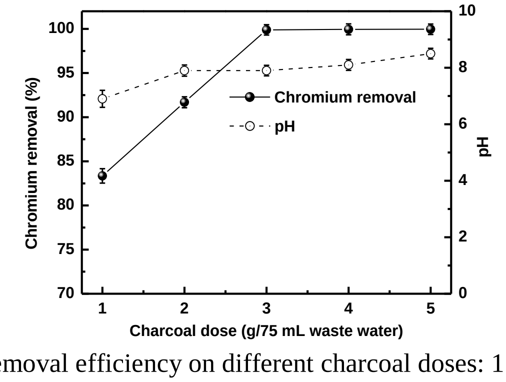

Fig. 3. Batch wise chromium removal efficiency on different charcoal doses: 1 g, 2 g, 3 g, 4 g, and 5 g; in each batch 75 mL wastewater with fixed 10 min contact time was used

The chromium removal efficiencies for the charcoal doses 1 g, 2 g and 3 g were 83.4%, 91.7% and 99.8%, respectively. It was also perceived that with increasing the adsorbent doses increasing the mixture pH; gradual increase the pH simultaneously increases the chromium removal efficiency. When charcoal dose was 4 g or 5 g for each 75 mL wastewater, the chromium removal efficiencies were same as 3 g/75 mL wastewater. Therefore, it was estimated that the maximum removal of chromium occurred with 3 g charcoal dose for every 75 mL wastewater where pH was 7.9.

Optimal contact time

Contact is one of the important for the removal of chromium in the spent chrome liquor. In Fig. 4 shows the chromium efficiency on contact time.

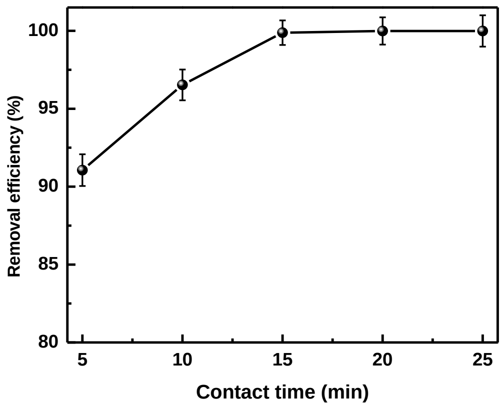

Fig. 4. Batch wise chromium removal efficiency on different contact time: 5, 10, 15, 20, and 25 min; in each batch 75 mL wastewater with fixed 3 g charcoal was used

It is clear from the above figure that chromium removal efficiency was gradually increased with increasing the contact time. The chromium removal efficiency for 5 min, 10 min, and 15 min was 91.1%, 96.5%, and 99.9%, respectively and after that removal efficiency was unchanged. Thus, it was assumed that extreme removal of chromium happened at 15 min contact time.

Efficiency of treatment process

The results of the treatment process with optimum conditions are represented in Table 1. The physicochemical parameters were obtained after all stages of treatments were: chromium 5.2 mg/L, pH 7.9, TDS 48.7 mg/L, EC 80.3 mS, and salinity 50.0 ppt. The highest percentage of chromium removal of chromium was 99.8%. It seems that after treatment pH was within the discharged level although other parameters e.g., TDS, EC, and salinity were slightly increased. In batch-wise experiment higher percentage of chromium was removed from the tannery wastewater using *Artocarpus heterophyllus* bark charcoal as adsorbent.

Table 1. Data comparison with Bangladesh standard [21]

Parameters	Raw sample	Treated sample	Bangladesh Standard
Cr (mg/L)	3190.1±1.7	5.2 ±0.31	2.0
pH	3.6±0.3	7.9±0.4	6–9
TDS (mg/L)	45.1±0.3	48.7±1.2	2100
EC (mS)	74.6±0.7	80.3±0.8	1.20
Salinity (ppt)	45.1±0.5	50.0±0.5	–

4. Conclusions

Batch-wise chromium removal treatment was performed from chromium containing wastewater. The removal efficiency of chromium at optimized conditions was obtained 99.8% although others parameters were slightly increased. The investigation indicates that it was an effective technique to reduce toxic substances that will minimize pollution load from the spent chrome liquor. The study could be helpful to design the treatment of spent chrome liquor in the house prior to discharge and the adsorbed chromium could be recovered by desorption.

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