Paper ID: AB-250

Chromium Removal from the Tannery Wastewater Using Coir Pith Charcoal

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Abstract

Tanning industries discharge huge amount of chromium containing wastewater. In this work, chromium removal efficiency of the equipped charcoal from the coir pith charcoal is stated. After storing, coir pith bark was sun-dried, burnt at 450–550°C, grinded and sieved on 80-mesh. The prepared charcoal was characterized by Fourier transform infrared spectroscopy (FT-IR). The effectiveness of charcoal for the chromium removal efficiency was examined investigating different parameters e.g., charcoal dose, contact time, and relative pH. In batch wise treatment process at optimized conditions, 75 mL chromium containing wastewater was mixed with 5 g charcoal, stirred for 15 min, settled, and chromium content was measured by the titrimetric method. Chromium content in the raw wastewater and filtrate was 3439.2 mg/L and 14.9 mg/L, respectively. The chromium removal efficiency was obtained 99.6%. The use of low-cost indigenous charcoal could be an option for the chromium removal from tannery wastewater.

Keywords: Tannery wastewater, Chromium, Environment, Charcoal

1. Introduction

In tanning process, 90% tanning industry use basic chromium sulfate as tanning agent [1] where 60% chromium is taken up by the pickle pelt and the remaining 40% chromium remained as the solid and liquid wastes especially in spent chrome liquor [2]. Anthropogenic activities e.g., tanning industries, electroplating, metal finishing, textile industries, and chromate preparation helps to enter chromium into the environment. Contamination of water, soil or sediment by the chromium is a significant concern for the environment. It can enter into human food chain from the water, soil or sediment. Although chromium (III) is considered as an essential trace element for some metabolic function in the human body [3] but a long-term exposure to Cr (III) is recognized to cause allergic skin reactions and cancer [4]. On the other hand, chromium (VI) can be toxic and carcinogenic [5, 6].

Mostly, in the spent chrome liquor contain high concentration of chromium. It is reported that chromium content in the wet blue spent chrome liquor ranges from 2656-5420 mg/L [7]. In the many countries, level of chromium in the spent chrome liquor is strictly regulated. Several attempts have been carried out to remove chromium from industrial wastewater with low-cost adsorbents e.g., wood materials [8], agricultural by-product [9], natural zeolite [10], clay [11], and eggshell and powered marble [12], unfortunately all these attempts have become unworthy because of the less available nature of adsorbent.

In this study coir pith charcoal was used to remove chromium from the chrome tanned waste water. The effectiveness of chromium removal was determined investigating different parameters e.g., charcoal dose, contact time, and relative pH.

2. Material and Methods

Sample Collection

Chromium containing wastewater was collected from the tannery at Khulna, Bangladesh. The wastewater containing chromium sample was collected in a plastic container, pre-washed with diluted nitric acid, and immediately transported to the laboratory for experimentation.

Charcoal preparation

The coir pith was collected from the local area at Khulna, Bangladesh. Then it was sun-dried, burnt at 450-

550°C in the present of air, grinded with mortar to make powder. The grinded charcoal was sieved on 80-mesh and preserved for the experiment.

Reagents

The reagents: nitric acid (Merck KGaA, Germany), sulphuric acid (Merck KGaA, Germany), perchloric acid (Merck, India), N-phenyl anthranilic acid (Merck, India), ferrous ammonium sulphate (Merck, India) and glass beads (Loba Chemie, India) were purchased from a local scientific store, Khulna, Bangladesh.

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 chromium-containing wastewater

Batch-wise chromium removal examination was performed. The schematic flow chart for the treatment of wastewater is shown in Fig. 1.

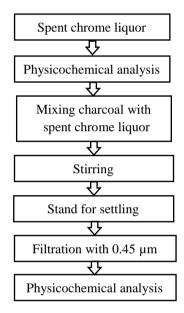


Fig. 1. Schematic flow chart for the chromium removal treatment process

Firstly, physicochemical parameters of the untreated chromium-containing wastewater were analyzed and filtered through 0.45 µm pore size filter. Secondly, 75 mL wastewater was mixed with the prepared charcoal. The charcoal mixed wastewater was stirred over a fixed period of time and the mixture was allowed settling for a fixed period of time. After settling, the mixture was filtrate through 0.45 µm pore size filter. The chromium content and physicochemical parameters of the filtrate were analyzed. Total dissolved solids (TDS) were determined gravimetrically following the standard methods of APHA [13].

Determination of pH

The pH of the spent chrome liquor was measured by using the pH (UPH-314, UNILAB, USA) meter. Before measuring, the meter was calibrated with the standard buffer solutions.

Determination of chromium

Chromium content in the untreated spent chrome liquor and after treatment in the filtrate was performed by the titrimetric method by following the official methods of analysis of Society of Leather Technologist and Chemists [14] official method of analysis (SLC 208). A 50 mL sample volume was taken in 500 mL conical flask. Twenty (20) mL concentrated nitric acid was added followed by 20 mL perchloric acid/sulphuric acid mixture; the flask 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. Then, rapidly the flask was cooled by swirling in cold water bath. Carefully, 100 mL 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 ferrous ammonium sulfate solution with six drops of *N*-phenyl anthranilic acid solution as an indicator. The end color was indicated by a color change from the violet to green.

Process optimization

In batch-wise examination, various parameters: charcoal dose, contact time and relative was optimized. The optimized conditions were established by investigating the chromium removal efficiency.

Effect of charcoal dose

To optimize the charcoal dose, varying doses were used for each batch 1, 2, 3, 4, 5 and 6 g where other parameters were left unchanged, for instance contact time (15 min) and initial pH (3.7).

Effect of contact time

Chromium removal percentage was increased with increasing the contact time. When the contact time of the chromium ions and binding sites was extended, the adsorption becomes more effective. To determine optimal contact time, varying stirring time were maintained for each batch 5, 10, 15, 20, 25, and 30 min respectively, while the other parameters remained constant.

3. Results and Discussion

Characteristic of charcoal

The FT-IR spectrum of the charcoal before and after the adsorption of chromium is depicted 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.

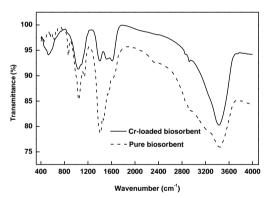


Fig. 2. FT-IR spectrum of the prepared coir pith pure charcoal and chromium-loaded charcoal

Optimal charcoal dose

The charcoal dose is the most important parameter in the treatment process. The effect of charcoal dose on the efficacy of chromium removal from the wastewater is depicted in Fig. 3.

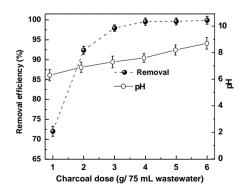


Fig. 3 Batch wise chromium removal efficiency on different charcoal doses: 1 g, 2 g, 3 g, 4 g, 5 g, and 6 g; in each batch 75 mL wastewater with fixed 10 min contact time was used

The chromium removal efficiencies for the charcoal doses 1 g, 2 g and 3 g were 72.0%, 92.4% and 97.9%, respectively. It is clear that with increasing the charcoal doses, the mixture pH also increased and simultaneously the chromium removal efficiency also increased. When charcoal dose was 4 g, 5 g or 6 g for each 75 mL wastewater, the chromium removal efficiencies were same as 4 g/75 mL wastewater. Therefore, it was estimated that the maximum removal of chromium occurred with 4 g charcoal dose for every 75 mL wastewater where pH was 7.6.

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.

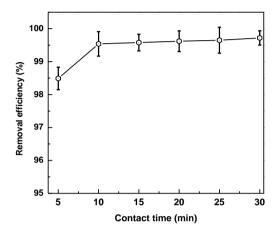


Fig. 4 Batch wise chromium removal efficiency on different contact time: 5, 10, 15, 20, 25, and 30 min; in each batch 75 mL wastewater with fixed 4 g charcoal was used

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 98.5%, 99.5%, and 99.6%, 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.

Table 1. Data comparison with Bangladesh standard (ECR, 1997)

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Parameters	Raw sample	Treated sample	[15]
Cr (mg/L)	3439.2±2.3	14.9±0.8	2.0
pН	3.7 ± 0.1	7.6 ± 0.7	6–9
TDS (mg/L)	49.7±1.2	51.1±0.7	2100
EC (mS)	73.4 ± 0.6	78.3 ± 1.3	1.20
Salinity (ppt)	44.1 ± 0.9	52.0 ± 0.7	_

The physicochemical parameters were obtained after all stages of treatments were: chromium 14.9 mg/L, pH 7.6±0.7, TDS 51.1±0.7 mg/L, EC 78.3±1.3 mS, and salinity 52.0±0.7 ppt. The highest percentage of chromium removal of chromium was 99.6%. It appears 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 by coir pith charcoal as adsorbent.

4. Conclusion

Batch-wise spent chrome liquor was treated to remove chromium from chrome tanning wastewater. The removal efficiency of chromium at optimized condition was 99.6%. The investigation indicates that, it was an effective technique to reduce toxic substances, which 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.

References

- [1] R. Avindhan, B. Madhan, J. R. Rao, B.U. Nair, and T. Amasami, "Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse", *Environmental Science & Technology*, Vol. 38, pp. 300–306, 2004
- [2] C. Fabiani, F. Ruscio, M. Spadoni, and M. Pizzichini, "Chromium(III) salts recovery process from tannery wastewaters", *Desalination*, Vol. 108, pp. 183–191, 1997.
- [3] S. Kalidhasan, M. Ganesh, S. Sricharan, and N. Rajesh, "Extractive separation, determination of chromium in tannery effluents and electroplating waste water using tribenzylamine as the extractant", *Journal Hazardous Martials*, Vol. 165, pp. 886–892, 2009.
- [4] R. Eisler, Chromium Hazards to Fish, Wildlife, and Inverte-brates: A Synoptic Review; Biological Report 85 1.6; Contaminated Hazard Reviews Report 6; U.S. Department of the Interior, Fish and Wildlife Service: Laurel, MD, 1986.
- [5] G. D. Matos, B. Edmagno, E.B. Dos Reis, A.C.S. Costa, L.C. Sergio, and S. L. C. Ferreira, "Speciation of chromium in river water samples contaminated with leather effluents by flame atomic absorption spectrometry after separation/preconcentration by cloud point extraction", *Microchemical Journal*, Vol. 92, pp. 135–139, 2009.
- [6] S. Yalçin, and R. Apak, "Chromium (III, VI) speciation analysis with preconcentration on a maleic acid-functionalized XAD sorbent", *Analytica Chimica Acta*, Vol. 505, pp. 25–35, 2004.
- [7] M. A. Hashem, A. Islam, S. Mohsin, and M. S. Nur-A-Tomal, "Green environment suffers by discharging of high-chromiumcontaining wastewater from the tanneries at Hazaribagh, Bangladesh", *Sustainable Water Resources Management*, Vol. 1, pp. 343–347, 2015.
- [8] A. Shukla, Y. H. Zang, P. Dubey, J. L. Margrave, and S.S. Shukla, "The role of sawdust in the removal of unwanted materials from water", *Journal of Hazardous Materials*, Vol. 95, pp. 137–152, 2002.
- [9] T. G. Chuah, A. Jumasiah, I. Azni, S. Katayon, and S.Y. Thomas Choong, "Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview", *Desalination*. Vol. 175, 305–316, 2005.
- [10] E. Erdem, N. Karapinar, and R. Donat, "The removal of heavy metal cations by natural zeolites", *Journal of Colloid and Interface Science*, Vol. 280, pp. 309–314, 2004.
- [11] G. E. Marquez, M.J.P. Ribeiro, J. M. Ventura, and J. A. Labrincha, "Removal of nickel from aqueous solutions by clay-based beds", *Ceramics International*, Vol. 30, pp. 111–119, 2004.
- [12] S. Elabbas, L. Mandi, F. Berrekhis, M.N. Pons, J.P. Leclerc, and N. Ouazzani, "Removal of Cr(III) from chrome tanning wastewater by adsorption using two natural carbonaceous materials: Eggshell and powdered marble", *Journal of Environmental Management*, Vol. 166, pp. 589–595, 2016.
- [13] APHA, Standard Methods for the Examination of Water and Wastewater, twenty-second ed. American Public Health Association. American Water Works Association, Water Environment Federation, Washington DC, USA, 2012.
- [14] Society of Leather Technologist and Chemists, Official Methods of Analysis. Northampton, UK, 1996.
- [15] Environment Conservation Rules, Ministry of Environment & Forests (MoEF), Government of the People's Republic of Bangladesh, 1997.