Chromium adsorption on coir pith charcoal from tannery wastewater

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Abstract

Emission of high chrome tanning wastewater is catastrophic for the environment. In this work, the effectiveness of coir pith charcoal is stated for the removal of chromium from tannery wastewater. The charcoal yield from the coir pith was 2.4%. The prepared charcoal was characterized by Fourier transform infrared spectroscopy (FT-IR). The efficiency of coir pith charcoal for chromium removal was assessed experimenting with various parameters e.g., charcoal dose, contact time, and relative pH. The content of chromium in the raw wastewater and after treatment at filtrate was 3439.2 mg/L and 14.9 mg/L, individually. In the batch experiment at optimized condition, for 75 mL chrome wastewater at 4 g charcoal dose with 15 min contact time, the chromium removal efficiency was attained 99.6%. The level of chloride (Cl⁻), chemical oxygen demand (COD), and biochemical oxygen demand (BOD) were significantly reduced by 65.7%, 93.7%, and 95.6%, respectively. The use of coir pith charcoal could be an alternative source for the removal of chromium from chrome containing wastewater.

Keywords: Chromium; Coir pith; Charcoal; Adsorption; Tannery wastewater

Introduction

Chromium (Cr) is considered as one of the most toxic metals mainly originated from the tanneries through chrome tanning. Chrome tanning is used in leather processing for getting the highest thermal stability, even dyeing, and comfortable feel properties, which is still irreplaceable by any other tanning agents (Covington, 2009). In general, 60-70% of the total provided Cr is taken up during the conventional tanning process and about 30-40% endures in the waste effluent (Zhang et al., 2018). The concentration of Cr during ejection varies in the range between 2656-5420 mg/L with an acidic pH range of 2.4-3.0 (Hashem et al., 2015). The reduction of Cr content in the wastewater below the specified values is only possible through sustainable wastewater treatment.

Usually, the trivalent state of chromium, Cr(III) remaining in the waste effluent that can be converted into a hexavalent state, Cr(VI) by the exposure of heat (Burton et al., 2019). Both Cr(III) and Cr(VI) can adversely affect the human food chain. It is reported that Cr(VI) has carcinogenicity, mutagenicity, and 500 times more toxicity than Cr(III) (Xu et al., 2019). Because of high solubility in water, Cr(VI) has permeability through biological membranes. Furthermore, Cr(VI) can successively interact with intracellular proteins and nucleic acid of biological membranes (Samrithi and Usha 2012). Cr(III) is allergenic and sensitization can occur with high concentrations (Baruthio, 1992). Accumulation of Cr mainly occurs in the liver, kidneys, spleen, and bone marrow (Chaudhary et al., 2017). The discharged level of Cr in the waste effluent is 2 mg/L according to the environmental conservation rules (ECR, 1997). Unfortunately, maximum tanneries do not follow this discharge level. The high cost of wastewater treatment is the main cause of making the tanners apathetic. A few of them are concern about the environment.

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by considering the additional cost required for the recovery of the environment. Reduction or removal of Cr from the chromium containing wastewater is one of the ways to maintain the discharge level.

Numerous methods such as adsorption (Ha et al., 2018), chemical precipitation (Borra et al., 2017), ion-exchange (Cavaco et al., 2007), coagulation/flocculation (Mella et al., 2015), and membrane separation (Bao et al., 2015) have already been applied for the removal of Cr from the wastewater. Among these methods, adsorption is considered as one of the cheapest methods. It is a sludge-free process with low set up investment. The cost of adsorption is low compared to other treatment processes.

The commercial charcoal does not pose adequate heavy metal removal efficiency (Xu et al., 2015). Low-cost charcoal preparation mainly depends on two medium i) based on availability, and ii) nature (Grassi et al., 2012). Low-cost charcoal prepared from clay (Gier and Johns 2000), natural zeolite (Biskup and Subotic 2004), and agricultural byproduct (O’Connell et al., 2008) has already been applied for Cr removal from the industrial wastewater. But the less available nature of these materials makes these attempts unworthy. However, charcoal preparation from the coir pith may be a source that is the byproduct of the coconut oil industry. Charcoal preparation is economical from coir pith through only thermal alteration due to the abundance and low cost. The main advantage of applying this charcoal is cost-effective and attainable.

The purpose of this investigation is to introduce coir pith charcoal an alternative source for Cr removal from the chrome tanning wastewater. The efficacy of Cr removal efficiency was determined in terms of charcoal dose, contact time, and relative pH.

Materials and methods

Sampling

Wastewater containing chromium was collected from a tannery in Khulna, Bangladesh. The sample was collected in a plastic bottle for laboratory investigation. Before experimenting, wastewater was filtered through a 0.45 μm pore size filter to avoid the unwanted suspended solids.

Preparation of charcoal

The coir pith was collected from Khulna city, Bangladesh. The collected coir pith was sun-dried then oven-dried at 105°C and burnt at 540-550°C in the muffle furnace. The burnt coir pith was ground with mortar. The ground charcoal was sieved on 80-mesh and reserved for further experiment. Fig. 1 depicts the raw coir pith and prepared coir pith charcoal.

Fig. 1. a) Raw coir pith b) prepared coir pith charcoal

Chemicals

All chemicals used in this experiment were analytical grade. The reagents concentrated nitric acid, HNO₃ (Merck KGaA, Germany), sulfuric acid, H₂SO₄ (Merck KGaA, Germany), perchloric acid, HClO₄ (Merck, India), ammonium iron sulfate hexahydrate (Merck, India), and N-phenyl anthranilic acid (Merck, India) were used in this study. The glass beads (Loba Chemie, India) were used as anti-bumping agents. For determining chloride (Cl⁻), biochemical oxygen demand (BOD), and chemical oxygen demand (COD) analytical grade chemicals were used. All the reagents/chemicals were procured from the local scientific store, Khulna, Bangladesh.

Batch-wise adsorption experiment

The batch-wise Cr adsorption experiment was performed at ambient temperature using a given mass of charcoal.
Different doses of coir pith charcoal (1, 2, 3, 4, 5, and 6 g) were applied in a batch-wise experiment into a series of Erlenmeyer flasks containing 75 ml of chrome containing wastewater. After that, charcoal mixed wastewater was stirred on a magnetic stirrer for a predefined time and allowed to settle for a time. At last, the mixture was filtered through the filter paper (Whatman No. 1). An illustration of the flow chart for the treatment of wastewater depicts in Fig. 2.

Raw and treated effluent characterization

The main characteristics of raw effluent and treated effluent were tested in terms of Cr, pH, total dissolved solids (TDS), total suspended solids (TSS), salinity, chloride (Cl⁻), BOD, and COD. All the measurements were conducted in triplicate and results were calculated as average with standard deviation (Avg. ± STDEV).

Determination of Cr content

Cr content was determined in both raw wastewater and treated effluent. For Cr content determination, the titrimetric method SLC 208 (SLT6/4) of SLTC (1996) was followed. A 25 ml of filtrate was taken in a 250 ml Erlenmeyer flask. Then, 10 ml concentrated HNO₃ and 10 ml admixture (H₂SO₄ and HClO₄) was added. The mixture was gradually warmed and boiled until converting into pure orange-red color. After getting an orange-red color, boiling was continued for about 1 min. After removing the flask from the heating source, it was cooled in a water bath. Then, 50 ml distilled water with few glass beads was added and boiled for 10 min to remove free chlorine. Afterward, 5 ml of 30% H₂SO₄ was added and kept for cooling to ambient room temperature. Titration was performed with freshly prepared 0.1N ammonium iron sulfate hexahydrate solution by several drops of 0.1% solution of N-phenyl anthranilic acid as an indicator. The endpoint was determined by a color conversion from the violet to green.

pH determination

A digital pH meter (BT-675, BOECO, Germany) was used to monitor the pH. Calibration of the pH meter was performed before measuring pH with standard solutions.

Determination of TS, TSS, TDS, EC, salinity, and turbidity

APHA-2540-D method was used for determining TS, TSS, and TDS of the waste chrome liquor. At first, filtration was performed using a weighted standard (Whatman No. 1) filter paper. The residue on the filter paper was dried at 103-105°C in a oven until to obtain constant weight. The increasing weight of the filter paper shows the value of TSS. The calculation of the difference between TDS and TS was performed to obtain an estimation of TSS. The measurement of EC and salinity was performed with ion meter (CT-676, BOECO, Germany).

Determination of Cl⁻

A 50 ml sample was taken in an Erlenmeyer flask and 4-5 drops of the freshly prepared starch indicator were added in it. Then, titration was performed with standard silver nitrate solution (0.0141 N) using a burette with continual stirring until appearing the initial permanent reddish color. The Cl⁻ content was determined from the required amount of silver nitrate comparing with distilled water for blank following the Mohr method.

BOD determination

BOD measurement was performed using the standard method of APHA 5210-B (APHA, 2012). At first, by placing a fixed volume of diluted water in a BOD bottle and phosphate buffer, magnesium sulfate, calcium chloride, and ferric chloride solutions were added. pH was adjusted at the range of 6.5 to 7.5 by using an H₂SO₄/caustic soda solution. Then, the BOD bottle was filled with 300 ml of sample volume with readied diluted water solution so that the removal of air as well as leaving of all bubbles could be performed after insertion of the stopper. After that, a blank sample solution was prepared with only diluted water after checking on the purity of the diluted water sample and the cleanliness of the incubated BOD bottle. The initial DO measurement was performed using the DO meter (DO-580, BOECO, Germany). The incubation of the BOD bottle was performed at 20±1°C for 5 days. Then, the final DO was determined after 5 days of incubation and calculated BOD₅.

COD determination

For COD measurement was performed using the standard method of APHA-5220 C (APHA, 2012). Wastewater diluted with distilled water was kept in a prewashed (20% H₂SO₄ and potassium dichromate solution) culture tube. Proper care was taken at the time of adding H₂SO₄ into the culture tube so that the formation of an acid layer could occur at the solution layer during sample digestion. After tightly capping the culture tube, the solution was mixed properly. The inversion of the culture tube was performed several times to mix up the solution completely. For preheating at 150°C, the tube was kept in block digester and refluxed using a protective shield maintaining for 2 h. After cooling at ambient temperature, the
culture tube was kept in the test tube holder. Capping out the tube, 1-2 drops of ferroin indicator was added in it. To get ready for titration with continual stirring, a little tetrafluoroethylene (TFE) covered magnetic stirrer bar was used. Then, titration was performed using ferrous ammonium sulfate (0.10 M) solution with continuous stirring. The turning point was marked by the conversion of reddish-brown from blue-green color whereas the reappearance of blue-green occurred within a minute. Finally, a blank test was performed using distilled water as a previous determination.

Charcoal characterization
The characterization of charcoal before and after treatment was performed using FT-IR. The data were taken between the adsorption spectrum of 400 and 4000 cm⁻¹ employing Fourier transform infrared spectroscopy (FT-IR 1600, Perkin-Elmer).

Process optimization
For batch experimentation, different parameters like the dosage of charcoal, contact time, and relative pH were investigated. The investigation of Cr removal efficiency was determined by establishing these conditions.

Optimization of charcoal dose
In process optimization, different dosages 1, 2, 3, 4, 5, and 6 g of coir pith charcoal were applied with constant contact time. For optimization of charcoal dose, the constant contact time (15 min), as well as other factors, was left unchanged.

Optimization of contact time
Removal of Cr (%) is usually increased with increasing contact time. With increasing contact time, binding sites get extended and adsorption capacity is increased. For obtaining optimal contact time on adsorption of Cr, experimentation was performed with each batch 5, 10, 15, 20, 25, and 30 min, individually remaining dose unchanged.

Results and discussion
Charcoal characterization
Coir pith charcoal yield was 2.4%. The mechanism of the interaction of Cr with charcoal is of interest and was studied using Fourier-transform infrared spectroscopy (FT-IR). Fig. 3 depicts the FT-IR spectrum of the pure charcoal (before

![Fig. 3. FT-IR spectrum of prepared coir pith pure charcoal and Cr-loaded charcoal](image-url)
Cr-adsorption) before and after the Cr-loaded (after Cr adsorption). The FT-IR data imply the changes of frequency in the functional groups of the charcoal due to Cr-adsorption.

The shifting in the intensity is an indication of the changes in the functional group in the charcoal just after the adsorption process. The various functional groups e.g., C=O, C–H, O–H present in the pure coir pith charcoal were responsible for taking out of Cr during adsorption. The spectrum of the Cr-loaded charcoal confirmed the functional groups responsible for metal binding.

**Effect of charcoal dose**

In the adsorption process, the dose is one of the most important factors. The significance of charcoal dose in case of the Cr removal adsorption no coir pith charcoal was analyzed. The consequence of charcoal dose on adsorption of Cr is shown in Fig. 4. It is clear from the figure that with increasing the charcoal doses (1 to 6 g) Cr removal efficacy was increased. For example, Cr removal efficiencies for the charcoal doses of 1, 2, and 3 g were 72.0%, 92.4%, and 97.9%, respectively.

It seems that with increasing the charcoal doses, the pH of the suspension also increased; simultaneously the Cr removal efficiency also increased. The Cr removal (%) slightly increased with the charcoal dose 4, 5, and 6 g for each 75 mL wastewater, which was very little. Therefore, charcoal dose 4 g was preferred instead of 5 or 6 g considering both charcoal dose and percentage of Cr removal. The Cr removal efficiency was increased with the increase of the charcoal dose due to the availability of more surface area as well as the functional groups of the adsorbent for adsorption. The pH value of the suspension is an important controlling parameter in this removal process.

The pH of the suspension for the doses of 1, 2, 3, 4, 5, and 6 g was 6.3, 6.9, 7.3, 7.6, 8.2, and 8.7, respectively. It is noticeable from the figure that pH was found to be increased with increasing charcoal dose. A small variation in pH influences both the charcoal surface and ionic species of metal in solution. It seems that pH is responsible for metal binding on the charcoal surface. Hashem et al. (2020) observed that at elevated pH hydrolysis sorption happens where Cr is precipitated as insoluble colloidal chromium hydroxide, Cr(OH)₃. Therefore, it was anticipated that

![Graph showing chromium removal efficiency on different charcoal doses](image-url)

**Fig. 4.** Batch wise chromium removal efficiency on different charcoal doses: 1, 2, 3, 4, 5, and 6 g; in each batch 75 mL wastewater was mixed with fixed 15 min contact time
maximum Cr adsorption occurs with 4 g charcoal dose for every 75 mL wastewater where suspension pH is 7.6.

**Effect of contact time**

Contact time (interaction time) is another important parameter for the adsorption of Cr. Fig. 5 represents the significance of contact time for the Cr adsorption on the charcoal surface.

Fig. 5 depicts that gradually Cr removal efficiency was increased with expanding contact time. For two preselected contact time 5 and 10 min, Cr adsorption was steep as more Cr was allowed to adsorb on the binding sites with increases the contact time. The percentage of Cr removal for 5, 10, and 15 min was obtained by 92.5, 97.5, and 99.6%, individually. After 15 min (e.g. 20 and 25 min contact time), Cr removal (%) was slightly increased which is negligible. Based on Cr removal efficiency, 15 min was considered as optimum contact time.

![Graph showing Cr removal (%) vs. Contact time (min)](image)

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

**Process reliability**

The physicochemical properties of both raw chrome wastewater and treated effluent in comparison with Bangladesh standard (ECR, 1997) are shown in Table I.

| Parameters | Raw sample | Treated | (ECR, 1997) |
|------------|------------|---------|-------------|
| Cr (mg/l)  | 3439.2±2.3 | 14.9±0.8 | 2.0         |
| pH         | 3.7±0.1   | 7.6±0.7 | 6–9         |
| TDS (g/l)  | 49.7±1.2  | 51.1±0.7 | 2.1         |
| EC (mS)    | 73.4±0.6  | 78.3±1.3 | 1.20        |
| Salinity (ppt) | 44.1±0.9 | 52.0±0.7 | –           |
| Chloride (mg/l) | 17998±13.7 | 6179±5.1/65.7 | 600 |
| BOD (mg/l) | 3523±15.3 | 156±3.8/95.6 | 250         |
| COD (mg/l) | 5313±21.7 | 335±4.3/93.7 | 400         |

It is clear from Table I that after treatment there was a significant decrease in the values of Cr, Cl, BOD, and COD. After treatment, 99.6% Cr was removed from the wastewater and the pH of the treated effluent was found within the...
discharged limit (6-9). Other parameters e.g., TDS, EC, and salinity were found slightly increased. The soluble content from the coir pith might increase the TDS, EC, and salinity of the treated sample. It is assumed that the higher percentage of Cr removal is possible through a batch-wise experiment from the tannery wastewater by coir pith charcoal as adsorbent.

Comparison with previous studies

A comparison of Cr removal (%) following adsorption capacity is not often considered. Different parameters e.g., charcoal dose, contact time, pH of the treated effluent are important parameters for comparison of Cr removal (%). Comparative studies of the coir pith charcoal with other adsorbents are depicted in Table II.

Table II. Cr removal efficiency compared with the previous studies

| Adsorbent            | Removal (%) | Contact time | References               |
|----------------------|-------------|--------------|--------------------------|
| Sargassum wightii    | 83          | 6 h          | Aravindhan et al., 2004  |
| Bone charcoal        | 90          | 30 min       | Dahbi et al., 2002       |
| Eggshell             | 99          | 840 min      | Elabbas et al., 2016     |
| Powdered marble      | 99          | 30 min       | Elabbas et al., 2016     |
| Shrimp shells        | 90          | 2 h          | Fabbricino et al., 2013  |
| Coir pith charcoal   | 99.6        | 15 min       | This study               |

Table II implies that among these adsorbents, the coir pith charcoal offers higher Cr removal efficiency without any additional chemicals at least contact time (15 min). For Sargassum wightii, bone charcoal, eggshell, powdered marble, and shrimp shells where Cr removal efficiency was 83, 90, 99, 99, and 90%, respectively with contact time was 6 h, 30 min, 840 min, 30 min, and 2 h, respectively. Table 2 also implies that adsorbent representing greater than 90% Cr removal efficiency takes higher contact time. Elabbas et al. (2016) obtained 99% Cr removal efficiency for both eggshell and powdered marble but contact time was much higher. However, coir pith charcoal shows 99.6% Cr removal efficiency with short contact time (15 min). The adsorption capacity of charcoal depends on both removal efficiency and contact time. It seems that coir pith charcoal is more effective compared to other charcoal/adsorbent.

Conclusion

This study reveals the effectiveness of chromium adsorption on coir pith charcoal from the tannery wastewater. The chromium removal efficiency was obtained at optimized conditions by 99.6% while total dissolved solids, electrical conductivity, and salinity were somewhat increased. The chloride was significantly reduced by 65.7%. The pH, biochemical oxygen demand, and chemical oxygen demand values of the treated wastewater were within the discharge level. This study recommends using coir pith charcoal to reduce toxic chromium from tannery wastewater, which will abate the effluence burden caused by the tannery.

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