BANANA RACHIS CHARCOAL TO REMOVE CHROMIUM FROM TANNERY WASTEWATER

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ABSTRACT

In this study, banana rachis waste, a carbonaceous material, was used to remove chromium from a real chrome tanning wastewater. The process was carried out using this banana rachis waste as an adsorbent. The waste solid banana rachis was cut, dried, and then burnt to produce charcoal. In the batch experiment, the ground charcoal was used for the treatment process: at optimized conditions, 3g charcoal was mixed with 75 mL chromium-containing wastewater, stirred for 15 min, settled, and then chromium content in the filtrate was measured by the titrimetric method. Chromium content in the raw wastewater and filtrate was been 3373.5 mg/L and 12.1 mg/L respectively. The chromium removal efficiency was 99.8% at pH 6.7. The reduction efficiencies for biological biochemical oxygen demand, chemical oxygen demand and chloride were 97%, 93%, and 60% respectively. The effectiveness of charcoal for the chromium removal efficiency was studied against different parameters, e.g., charcoal dose, contact time, and relative pH. This study revealed banana rachis waste as an efficient adsorbent for the remediation of chrome tanning wastewater.

Keywords: *Tannery wastewater, Chromium, Banana Rachis, Environment*

1. INTRODUCTION

Heavy metals contamination is now one of the most familiar and growing issues affecting biodiversity throughout the world (Khamis, Jumean & Abdo, 2009). Due to rapid industrialization, direct and indirect discharges of heavy metals to the environment through wastewater have tremendously been increased (Khamis, Jumean & Abdo, 2009). Among other heavy metals chromium, lead, arsenic, nickel, zinc are the most common and harmful heavy metals.

Tanning is the process of converting putrescible raw hide/skin into leather. During this process, the desired qualities are achieved by a series of chemical and mechanical operations. Currently more than 90% of the global leather production of 18 billion sq. ft ~~is~~ are tanned through chrome tanning process (Sundar, Rao & Muralidharan, 2002). Averagely, 60-70% of total chromium salts react with the hide protein and the rest of 30-40% of the chromium remains in the solid and liquid phases (especially as spent tanning liquor) (Ismailia, Mesdaghania & Vasirinejad, 2005). These remaining chromium pollutants, originating from the tannery wastewater possess a great hazard to human, animals, and plants through their incorporation in the food chain and the bioaccumulation effect (Khamis, Jumean & Abdo, 2009).

Chromium has several oxidation states among them trivalent and hexavalent chromium forms are common (Occupational Safety and Health Administration, 2003). High concentrations chromium is toxic, mutagenic, carcinogenic and teratogenic (Altaf, Masood & Malik, 2008). International Agency for Research on Cancer (IARC) has classified chromium (VI) in Group 1 (carcinogenic to humans) and metallic chromium and chromium (III) in Group 3 (not classifiable as to their carcinogenicity to humans (International Agency for Research on Cancer, 1994).

Concerns regarding the presence of chromium in the environment focus on the potential adverse health effects of Cr contaminated soils, groundwater, and surface water. According to Environmental Conservation Rules, 1997 the standard values of chromium (VI) discharge limit from industrial waste to inland surface water, public sewerage, irrigated land are 0.1, 1.0, 1.0 mg/L respectively (Environmental Conservation Rules, 1997).

Thus, chromium removal from the tannery wastewater is an important issue. Till today, numerous methods have been developed to remove chromium from the tannery wastewater. Chemical precipitation and electrochemical precipitation are widely used for the removal of heavy metals. But these techniques have a significant problem in terms of disposal of the precipitated wastes (Ozdemir, Karatas, Dursun, Argun & Dogan, 2005; Meunier, Drogui, Montane, Hausler, Mercier & Blais, 2006). The sedimentation (Song, Williams & Edyvean, 2000), electrochemical processes (Oda & Nakagawa, 2003), biological operations (Kapoora, Viraraghavana & Cullimoreb, 1999), cementation (Filibeli, Buyukkamaci & Senol, 2000), coagulation/flocculation (Song, Williams & Edyvean, 2004), filtration and membrane processes (Hafez, El-Manharawy & Khedr, 2002), chemical precipitation and solvent extraction (Macchi, Pagano, Pettine, Santrori & Tiravanti, 1991) are also used. Some of the low cost, non-conventional adsorbents include anaerobic sludge (Ulmanu, Marañón, Fernández, Castrillón, Anger & Dumitriu, 2003), apple residue (Lee, Jung, Chung, Lee & Yang, 1998), sawdust (Shukla, 2005), rice Polish (Singh, Rastogi & Hasan, 2005), clay (Farrah, & Pickering, 1977), zeolite (El-Kamash, Zaki & El Geleel, 2005), fly ash (Al-Qodah, 2006), chitosan (Jha, Iyengar & Rao, 1988), waste tea (Orhan & Büyükgüngör, 1993; Ahluwalia & Goyal, 2005), seaweeds (Da Costa & De França, 1996), polyaniline coated on sawdust (Mansour, Ossman & Farag, 2011), and *Carica papaya* plant (Sheikh, Apon & Hashem, 2017) which have been used for the purpose, but all these attempts have become inefficient because of the less available nature of adsorbent.

In this study, adsorbents prepared from waste banana rachis were used to remove chromium content from tannery wastewater. The estimated amount of banana rachis waste in Costa Rica (one of the biggest banana producers in the world) is 797,000 metric ton per year (Sibaja, Alvarado, Pereira & Moya, 1997). The banana rachis is usually unutilized and when disposed to water, it biologically degrades raising the oxygen demand of water body.

The main advantage of adsorption is that it gives the significant amount of energy saving from a more efficient wastewater treatment system operating for fewer hours; it is economically attractive because waste biomass is inexpensive and widely available.

In the present study, an attempt was made to remove chromium from tannery wastewater using low-cost charcoal prepared from banana rachis. The aims of the study are: **i**) remediation of chromium contaminated tannery effluent, **ii**) solid waste management of the unutilized banana rachis and **iii**) introduction of a convenient method to achieve a greater chrome removal efficiency than the previous studies using handy raw materials. The effectiveness of chromium removal was determined to investigate different parameters e.g. charcoal dose, contact time, and pH effect.

2. MATERIALS AND METHODS

2.1 Collection of Banana Rachis

Banana rachis waste was collected from a nearby banana market at Khulna, Bangladesh and was burnt to prepare charcoal for wastewater treatment.

2.2 Charcoal Preparation

After collection of banana rachis waste, it was washed and then cut into small pieces and was sun-dried. Then the dried pieces of banana rachis were burnt in aerobic condition, cooled and ground to make a powder using a mortar. The ground charcoal was sieved and preserved for the experiment.
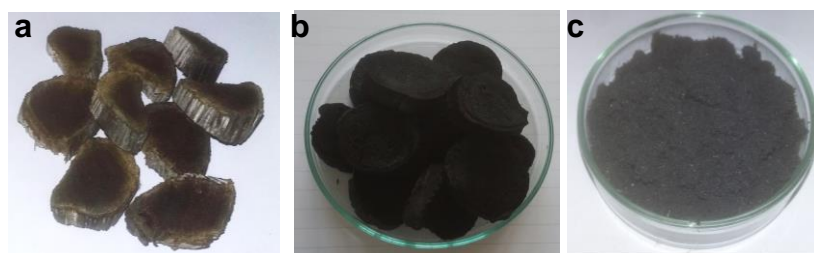

Figure 1: Dried waste banana rachis a) Burnt waste banana rachis and c) ground banana rachis charcoal

2.3 Wastewater Collection

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

2.4 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.

2.5 Characterization of Tanning Wastewater

Physicochemical properties of wastewater were measured in terms of chromium, pH, total dissolved solids (TDS), electrical conductivity (EC), salinity, dissolved oxygen (DO), biochemical oxygen demand for 5 days (BOD_5), and chemical oxygen demand (COD).

2.5.1 Determination of pH

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

2.5.2 Determination of TS, TSS, TDS, and EC

TS, TSS, and TDS of the spent chrome liquor and treated liquor were determined by APHA-2540 D method. A well-mixed sample was filtered through a weighed standard filter paper and the residue retained on the filter was dried to a constant weight at 103-105°C. The increase in weight of the filter represents the total suspended solids. To obtain an estimate of total suspended solids, the difference between total dissolved solids and total solids was calculated. Electrical conductivity (EC) was measured by using the conductivity meter (CT-676, BOECO, Germany).

2.5.3 Biochemical Oxygen Demand

Biochemical oxygen demand of the spent chrome liquor and treated liquor were determined by APHA-5210 B method. The sample was filled in an airtight bottle and was incubated at a specific temperature for 5 days. The dissolved oxygen (DO) content was determined before

and after five days of incubation at 20°C and the BOD were calculated from the difference between initial and final DO.

2.5.4 Chemical Oxygen Demand

Chemical oxygen demand of the spent chrome liquor and the treated liquor were determined by APHA-5220 C method. The organic matter present in sample gets oxidized completely by potassium dichromate ($K_2Cr_2O_7$) in the presence of sulphuric acid (H_2SO_4), silver sulfate (Ag_2SO_4) and mercury sulfate ($HgSO_4$) to produce CO_2 and H_2O. The sample was refluxed with a known amount of potassium dichromate ($K_2Cr_2O_7$) in the sulfuric acid medium and the excess potassium dichromate ($K_2Cr_2O_7$) was determined by titration against ferrous ammonium sulfate, using ferroin as an indicator. The dichromate consumed by the sample is equivalent to the amount of O_2 required to oxidize the organic matter.

2.5.5 Chloride Content

50 mL of the sample in a beaker with 5 drops (about 1mL) of potassium chromate indicator was titrated by standard (0.0141 N) silver nitrate solution from a burette, with constant stirring until the first permanent reddish color appeared. Chloride content was determined from the required amount of silver nitrate comparing with distilled water for blank following APHA-4500B method. If more than 7-8 mL of silver nitrate solution is required, the entire procedure should be repeated using a smaller sample diluted to 50 mL of distilled water.

2.5.6 Determination of Chromium

Chromium content in the untreated spent liquor and after treatment in the filtrate was measured by the titrimetric method by following the official methods of analysis of Society of Leather Technologist and Chemists (1996) official method of analysis SLC 208 (SLT6/4). A 50 mL sample was taken in 500 mL conical flask. 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; 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 as an indicator. The end color was indicated by a color change from the violet to green.

2.6 Treatment of Chromium Containing Wastewater

Batch-wise chromium removal examination was performed with the prepared charcoal. Firstly, physicochemical parameters of the untreated chromium-containing wastewater were analyzed and filtered through 0.45 µm pore size filter. Secondly, 75 mL filtrate wastewater was mixed the prepared charcoal. The charcoal mixed wastewater was stirred over a fixed period of time and the mixture was then allowed for settling for a fixed time. After settling, the mixture was filtered through 0.45 µm pore size filter again chromium content measurement was performed the same procedure as described in section 2.5.6.

3. RESULT AND DISCUSSION

3.1 Process Optimization

The removal efficiency of the experiment was optimized by carrying out different chromium removal parameters: charcoal dose, contact time, stirring time. The optimized conditions were established by investigating the removal efficiency of chromium of the wastewater based on the above parameters.

3.2 Effect of Adsorbent Dosage

The charcoal dose is the most important parameters that have a significant effect on the chromium removal. Chromium removal efficiency on charcoal dose and relative pH changes are shown in Fig. 2. The initial concentration of chromium (3373.5 mg/L) in the real chrome tanning wastewater, the number of adsorbent doses (1 g to 5 g for every 75 mL wastewater) and contact time (10 min) were kept constant.
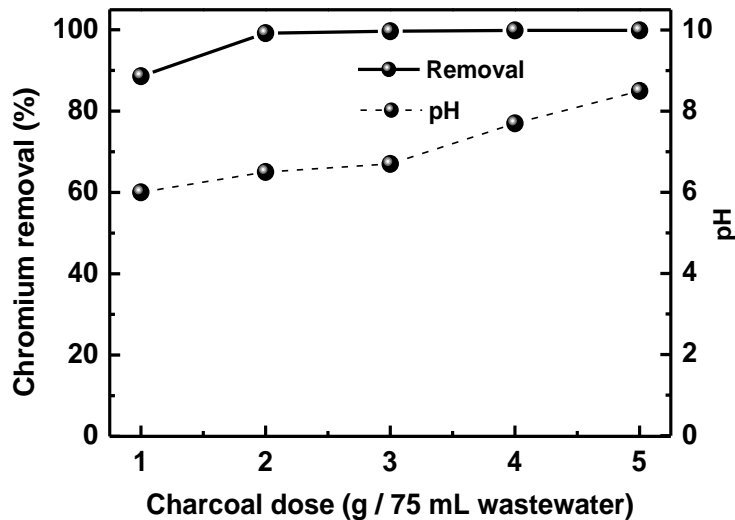

Figure 2: Batch wise chromium removal efficiency on different charcoal doses: 1 g, 2 g, 3 g, 4 g, and 5 g. In each batch 75 mL wastewater with fixed 10 min contact time was used.

It is clear from the Fig. 2 that the increase of charcoal dose results in the increase of pH. pH is an important parameter in adsorption because it is responsible for the protonation of metal (chromium) binding site. At lower pH (2 and 3), the low chromium removal may be attributed to: (i) the elevated concentration of protons that will compete with chromium cations on the surface sorbent active sites and hence reduce their adsorption; (ii) the dissolution of CaCO3, the principal constituent of the two adsorbents which lowers the adsorption. At higher pH (4 and 5), the important removal of chromium in the range can be attributed to: (i) the competitive effect (H^+ vs. Cr^{3+}) which becomes weaker, increasing the adsorption of Cr(III) (Chojnacka, 2005); (ii) the adsorption of hydrolysis products and precipitation of the metal as colloidal insoluble hydroxides, $Cr(OH)_3$.

Thus chromium removal efficiency was increased with the increase of adsorbent dose. At adsorbent dose, 3 g per 75 mL wastewater, chromium removal efficiency was 99.6%. After that, there were no significant changes in chromium removal. Therefore, it was projected that the maximum chromium removal occurred with 3 g adsorbent dose for every 75 mL wastewater at pH 6.7.

3.3 Effect of Contact Time

Fig. 3 shows that chromium removal efficiency was increased with the increase of contact time. When the contact time of the chromium ions and binding sites was extended, the adsorption became more effective. The optimized removal efficiency was 99.8% at 15 min. For the first two batches, the adsorption rate increases more rapidly. After that, the reaction becomes lower when the remaining active sites are less available and the equilibrium phase was reached.
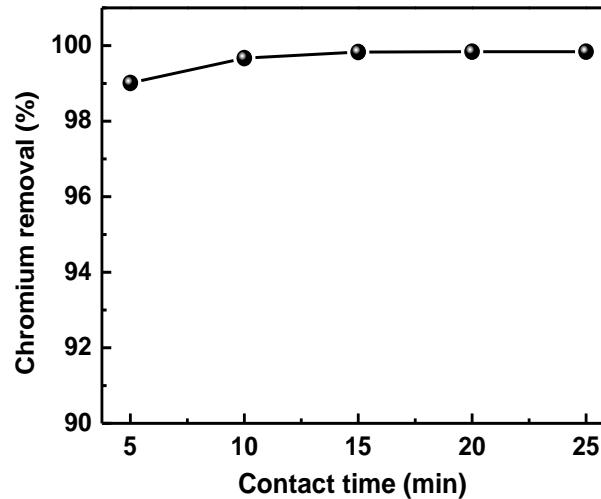
Figure 3: Batch wise chromium removal efficiency on different contact time: 1, 5, 10, 15, 20, and 25 min, each batch 75 mL wastewater with fixed 3 g charcoal was used.

Figure 3 shows that chromium removal percentage was increased with the increase of contact time. When the contact time of the chromium ions and binding sites was extended, the adsorption becomes more effective. So the removal efficiency increases with the increase of time. The optimized removal efficiency was 99.8% at 15 min. For the first two batches, the adsorption rate increases more rapidly. After that, the reaction becomes lower when the remaining active sites are less available and the equilibrium phase was reached.

3.4 Treatment Process Efficiency

Characteristics of wastewater are shown in Table 1. It seems that wastewater had heavy pollution loads because it contained higher quantities of pollutants e. g., high chromium content, total dissolved solids (TDS), high acidity (pH 3.9). Wastewater containing chromium is a threat to the environment, so it is very important to treat the chromium-containing wastewater before discharging it to the environment.

Table 1: Data comparison with Bangladesh standard (ECR 1997)

Parameters	Raw sample	Treated sample	(ECR 1997)
Cr (mg/L)	3373.5	12.1	2.0
pH	4.5	6.7	6–9
BOD (mg/L)	3197	107	250
COD (mg/L)	4297	293	400
TDS (g/L)	29.83	36.3	2.1
EC (mS)	66.9	81.2	1.20
Chloride (mg/L)	17021	6872	600

The results of the treatment process with optimum conditions are represented in Table 1. It shows that after treatment pH, BOD, COD was within the discharged level although other parameters e.g., TDS, EC, chloride (Cl⁻) were high from the discharge limit; but after treatment, they were reduced a noticeable level. During treatment banana rachis charcoal acts as adsorbent and the inorganic and organic pollutants are adsorbed on the charcoal surface. Thus, after filtration, the pollutants are removed with the adsorbent from the wastewater and reduce Cr, BOD, and COD.

Table 2: Data comparison with the previous works

Adsorbent	Chrome removal efficiency (%)	
	Previous studies	This study
Almond Shell (Pehlivan & Altun, 2008)	55.00	
Waste newspaper (Dehghani, Sanaei, Ali & Bhatnagar, 2016)	64.00	99.8
Walnut Shell (Pehlivan & Altun, 2008)	85.32	
Hazelnut Shell (Pehlivan & Altun, 2008)	88.46	

In Table 2 shows that chromium removal efficiency of this study was compared with the previous works. In this present study, the percentage of chromium removal efficiency was 99.8% whereas in the previous work chromium removal efficiency was maximum 88.46%. This study shows a noticeable increment of chromium removal efficiency.

4. CONCLUSIONS

In the batch-wise technique, chromium-containing wastewater was treated to remove chromium using banana rachis charcoal. The removal efficiency of chromium at optimized condition was 99.8%. The reduction of BOD, COD, and chloride were 97%, 93%, and 60%, respectively. The investigation indicates that it was an effective technique to reduce toxic substances, which will minimize pollution load from the spent chrome liquor as well as an efficient approach towards solid waste management. The study could be helpful to design the treatment of spent chrome liquor in the reservoir prior to discharge.

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