

Chemical Science and Biomolecular Engineering

Effective Technique of Tannery Effluent Purification

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Abstract

This study had been conducted using low-cost agricultural waste to remove chromium and other parameters from tannery effluents. Orange peel and tea waste were used as bioadsorbent for this study; the findings were then compared with that of commercially activated carbon. The nature of these Bio-adsorbent was examined using Fourier-transform infrared spectrometer (FTIR) technique. The maximum adsorption capacity for tea waste and orange peel were 11.25 mg/g and for 10.83 mg/g. Characterization of the effluents was done both before and after treatments. The result represents the maximum removal percentage of TDS 97.13, Turbidity 99.7, conductivity 97.5 and chromium 97.63. The order of adsorption activated carbon > tea waste > orange peel. Tea waste has better removal ability to remove chromium than orange peel, although in the case of conductivity and Total dissolved solid (TDS) orange peel is better. The aim of this research involves implementation of low cost agricultural waste for the purpose of tannery effluent treatment.

Keywords

Adsorbent; Tannery effluents; Chromium

Introduction

Chromium is the 7th most abundant metal on the earth, which is present in the environment, mainly in two oxidation states Cr³⁺ and Cr⁶⁺ having average concentration 100 mg/kg. Chromium is commonly used in electroplating, leather tanning, metal finishing, wood treatment [1,2]. About 10⁷ tons of chromium is produced annually and 60-70% is used in alloys containing stainless steel and 15% in chemical manufacturing practices, mainly leather tanning and pigment [3,4]. Nowadays about 80-90% of international leather production is tanned using trivalent chromium known as basic chromium sulfate [5]. One of the major concerns of tannin industry is to dispose of chrome-containing effluent that is produced as a by-product of chrome tanning [6]. The removal of chromium from tannery waste water is important as most of the cases it poses a threat to the human being as well as environment due to their non-degradability and toxic effect on the aquatic organism. Retention of hexavalent chromium can cause skin disease, inhalation and damage of internal organs [7,8]. In Bangladesh, less than 2 mg/l chromium concentration in the effluent is allowed to discharge into drains [9]. Several physical and chemical processes like chemical precipitation, reverse osmosis; ultrafiltration, ion exchange, electrochemical and adsorption are available for the removal of chromium from tannery waste water. But these processes are costly, generate poisonous sludge result in partial metal removal. As a result, adsorption has become one of the alternative processes in recent years. Several studies have been completed using bio-adsorbents like garlic peel [10], olives tone [11], Carica papaya seed [12], Anabaena and vetiveria [13], rice husk [14], green alga [15], maple sawdust [16], sugar industry waste [17], red mud [18], duolite [19], sugarcane [20] oriental beech sawdust [21] cotton seed hulls [22,23] mustard seed cane [24] coconut waste [25] to remove chromium and other heavy metal from waste water [26,27]. In this study, we used tea waste and orange peel to remove chromium from the tannery waste water. Tea is a very common and popular drink in Bangladesh as well as orange is also a popular fruit. So tea waste and orange peel are available in Bangladesh with low economic value. The aim of this study is to investigate the possible use of tea waste and orange peel in the adsorption of chromium from the tannery waste water.

Materials and Methods

Chemical and instrumental analysis

Tea waste and orange peel both were modified by using only NaOH. An AAS flame technique at $\lambda=357.9$ nm was used for measuring chrome concentration with flame atomization model AA-7000. The functional group in bio adsorbents was identified

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by transforming infrared spectrophotometer (FTIR Shimadzu Corporation, model- IR prestige 21, serial no-A21004501831). Parameter such as DO, conductivity, total dissolved solid (TDS) and turbidity were measured by HACH and digital direct reading meter.

Sample collection and preparation of bio-Adsorbents

The bio-adsorbent materials orange peel and tea waste both were collected 11 February 2016 from the local market of Dhaka. After cleaning with distilled water both samples were dried at 60°C until constant mass. Then the samples were crushed into small particle of approximately sieve size $\leq 60 \mu\text{m}$. Deionized water was used to wash the powder then oven dried at 60°C until constant mass is acquired. These final samples were preserved in an air tight bottle for further use.

Chemical modification of bio-Adsorbents.

In this study, 50 gm of each bio-adsorbents were treated with 500 ml (0.1 M) NaOH for 24 hours shaking at 120 rpm. After treatment, the modified bio-adsorbents were washed with deionized water until the pH of this solution became neutral.

Effluent samples collection

The chrome tannin and retannin effluents were collected 3rd march 2016 from the Ruma tannery at Hazaribagh. Ndimele and Kumolu-Johnson (2012) procedure was followed for water sampling of the river. 5 L of plastic bottle was used to collect water. Before sampling, 10% HNO_3 was used to clean plastic bottle and rinsed well with distilled water. To abate of metals adsorption onto the wall of the plastic bottle 2 to 3 drops of HNO_3 was added to the sample. In tannin industry, Basic chromium sulfate was used in tannin and retannin operation.

Adsorption Experiments

Procedure

At first, 20 gm of adsorbent was added to 200 ml of tannery effluent in a beaker. The solution was then stirred with magnetic for one hour and kept overnight. The solution filtered using Whatman 11 cm filter paper onto volumetric flask. After preparing all of these samples were kept at room temperature until analysis.

Adsorption studies

The percentage of adsorption was determined by the following equation.

$$(\%) = \frac{C_o - C_e}{C_o} \times 100\% \quad \text{..... (1)}$$

Where, C_o and C_e represent the initial concentration of the solution and the concentration of the solution after adsorption respectively. In this study, the concentration of chromium was higher in chrome tannin effluent than re-tannin. The effect of chromium concentration on adsorption was calculated using the equation below

$$q_e = \frac{C_o - C_e}{m} \times V \quad \text{..... (2)}$$

Here, C_o and C_e are the concentration of chromium at initial and equilibrium respectively, m is the weight of adsorbents in g, V is the volume of effluent in L.

Results and Discussion

Characterization of chrome tannin and re-tannin

Table 1 represents the characterization of the chrome tannin and re-tannin. It was determined as described in *Materials and Methods* section.

Fourier transform infrared (FTIR) analysis

The FTIR spectrum for raw and treated orange peel is illustrated in Figure 1. In raw orange peel adsorption band, 3764.91 cm^{-1} may represent alkenes or alkynes. Adsorption band 3500 cm^{-1} to 2900 cm^{-1} indicates the presence of -OH and -NH groups. The peaks of

Parameter	Tannin	Re-tannin
Cr concentration (mg/L)	1526	1056
Turbidity (NTU)	247	177
Conductivity (mS/sec)	97.1	53.3
TDS (g/L)	54.3	27.3
Dissolved oxygen (mg/L)	1.67	2.63

Table 1: Characterization of chrome tannin and re-tannin effluents

2920 cm^{-1} to 2390 cm^{-1} may be due to C-H and CH_2 group present in the lignin structure. The peak of 767.67 cm^{-1} to 632.65 cm^{-1} in the raw orange peel may represent the C-H group which was removed by treating with NaOH. An unknown peak of 518.85 was also shown in raw orange, but it was slightly shifted to 528.50 cm^{-1} during treated with NaOH which may represent the aromatic compound of the C-H bond. Band 1064.71 cm^{-1} in the raw orange peel may be stretching of C-OH of alcohols and carboxylic acid, which also shifted to 1033.85 cm^{-1} due to treatment with NaOH. Band at 1735.93 cm^{-1} to 1616.35 cm^{-1} may due to the asymmetric and symmetric vibration of the carboxylic groups. Furthermore, peaks at 1421.54 cm^{-1} may convert into 1377.17 cm^{-1} for treating with NaOH because of stretching of the C=O group into -COOH group. Ester groups and bending N-H group from 1521.84 cm^{-1} to 1265.30 cm^{-1} was present in the treated orange peel. Figure 2 shows the FTIR spectrum of raw tea waste and treated tea waste. The adsorption band around 3439.08 to 2854.65 ensured the presence of carboxylic acid and -OH group present in the raw and treated tea waste. The adsorption peak at 1639.49 cm^{-1} in indicating the amide and -COOH, which shifted into 1631.78 cm^{-1} due alkali treatment by NaOH. Moreover, the carboxylic and ester group also present in the 1531.48 cm^{-1} to 1240.23 cm^{-1} band.

Adsorption studies

In the study, it was found that tea waste was the better adsorbent than orange peel. Tea waste had better-absorbed percentages also the rate of chromium ion absorbed per gram of biomass. In chrome tannin effluent the concentration of chromium is more than re-chroming. The adsorption percentages and chromium ion absorbed per gram of biomass are better in the case of re-tannin (Table 2).

Effect of Adsorption

Reduction of chromium: The removal of chromium from tannin and re-tannin operation is represented in Figure 3. In both cases, the adsorption of activated carbon is better than tea waste and orange peel. The order of adsorption is Activated Carbon>Tea Waste>Orange Peel, respectively.

Reduction of turbidity, conductivity and TDS: Reduction of TDS, turbidity, conductivity in tannin and re-tannin are represented in Figure 4 and Figure 5, respectively. Activated carbon shows the better percentage of removal for TDS, turbidity, and conductivity. Tea waste shows better results between the bio-adsorbents.

Effect on dissolve oxygen

Figure 6 illustrates the results of DO before and after treatment of chrome tannin and Retannin effluents. Effluents which treated

	Orange peel		Tea waste	
	Chrome tannin	Re-taining	Chrome tannin	Re-taining
Percentage removal	70	69	73.7	82.67
Adsorption capacity of adsorbent (mg/g)	10.83	8.35	11.25	8.73

Table 2: Percentage removal and Capacity of Bio-adsorbents

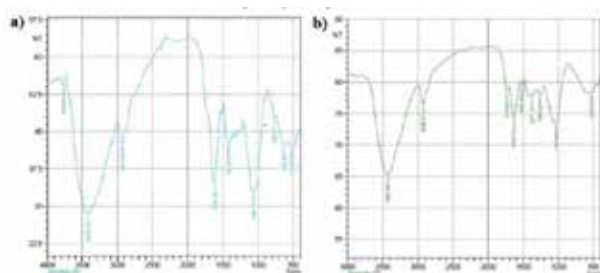


Figure 1: FTIR spectrum of a) raw and b) treated orange peel adsorbent

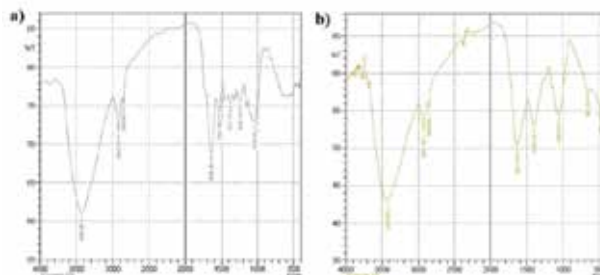


Figure 2: FTIR spectrum of a) raw and b) treated tea waste adsorbent

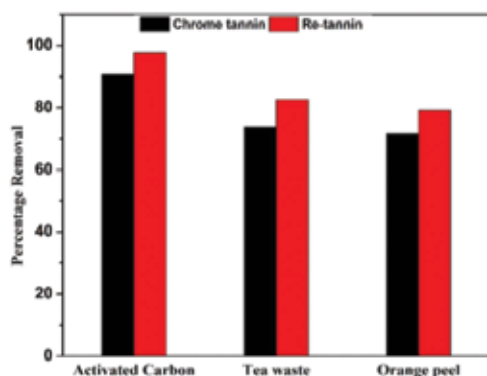


Figure 3: Removal percentage of chrome tannin and re-tannin with adsorbents

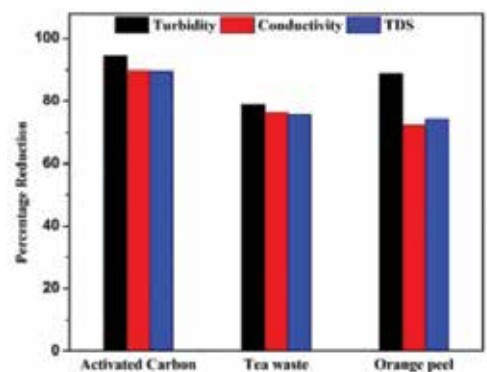


Figure 4: Reduction of different parameters in chrome tannin after treatment of adsorbents

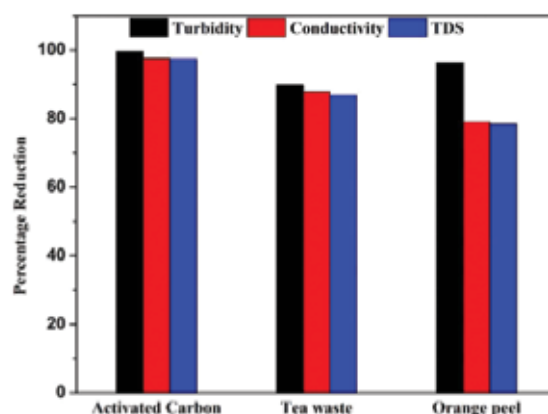


Figure 5: Reduction of different parameters in re-tannin after treatment of adsorbents

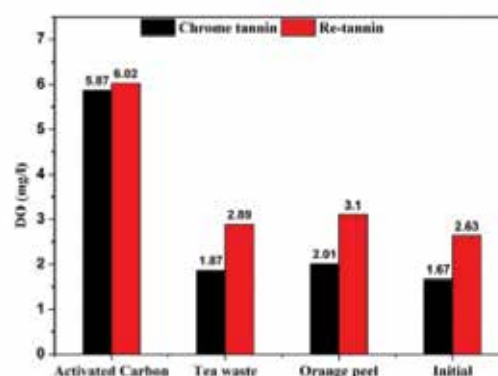


Figure 6: Effect of adsorption on DO quantity in chrome tannin and re-tannin

with activated carbon represent better results than others bio-adsorbents. This is due to the release of soluble organic compounds from Bioadsorbents which also to raise the BOD, COD, and TOC of the effluents. Therefore, bioadsorbent need to be treated with some acid or base. This research had been conducted by treating those bio adsorbents with NaOH.

Conclusion

In this study, tannery effluent was directly treated by bio-adsorbents which is the main difference from others studies. Orange peel and tea waste were modified by NaOH to enhance the ability to remove chromium and their ability was then compared with the activated carbon. The characterization of the bio-adsorbent indicated the presence of $-\text{COOH}$ groups which responsible for the removal of chromium from the tannery effluent. Though a significant amount of chromium removes from effluent, the quantity of effluent does not improve because of leaching out of lignin and other materials from bio-adsorbent. In this research, it has been found that activated carbon has better adsorption and removal tendency compared to other two adsorbents. But in compare to price of adsorbent it can be concluded that these low-cost wasted bio-adsorbents can be used for effluent treatment purpose. Further research work should be done in this respect to established this process for potential use in the industrial waste water treatment.

Author Contributions

First and second author contribute equally in this study.

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