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Development of Adsorbent from Sugarcane Bagasse for the Removal of Pollutants from Chrome Tanning Effluents

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ABSTRACT
The leather sector is the second-largest export earning sector in Bangladesh which contributes to huge employment generation and economic development. However, the current situation of this sector is not good enough for its lack of cleaner technologies and waste management systems. Tanneries are using an ample amount of harmful chemicals that may impose a huge negative impact on human health and the environment. Therefore, it is an emerging requirement for the removal of pollutants from effluents before discharging them to the environment. For this, the development of an adsorbent from agricultural waste is significant for removing pollutants from the tanning effluent and greening the environment. In this study, a low-cost adsorbent is developed and used to remove pollutants from the chrome tanning effluent. The developed adsorbent is prepared from sugarcane bagasse and activated by using NaOH. The study was performed at pH 4, with an adsorption time of 1 hour, and the adsorbent doses of 2.5 g/L. The findings revealed that a considerable amount of pollution was mitigated with the reduction in BOD (42.17%), COD (75.00%), Cr₂O₃ (41.91%), TSS (81.85%), and TDS (84.24%).

KEYWORDS
Bagasse, Pyrolysis, Pollutant, Adsorbents, Effluent

INTRODUCTION
Tannery effluents are harmful to human health as well as to the natural environment. They have a long term impact on ground water and the environment. In the tannery, raw hides/skins undergo several chemical and mechanical operations, among which tanning is the most important process [1]. Tanning agents are considered as the paramount chemicals in the leather manufacturing. Among all tanning agents, basic chromium sulfate is the most popular as it provides unique properties and good hydrothermal stability to tanned leather [2]. About 90% of the tanneries use basic chromium sulfate (BCS) during tanning [3]. Every year, about 15,000 tonnes of chromium salt (basic chromium sulphate) is used for the production of 18 billion sq. ft. of tanned leather worldwide [4,5]. The previous studies reported that only 60-70% of used chromium is consumed by the pelt in the traditional chrome tanning process and the rest is discharged into the chrome tanning effluent, causing a great waste of chrome and severe environmental pollution [6,7]. Effluent comes from tannery operations, containing huge amounts of pollutants and heavy metals [8]. These pollutants may cause serious environmental pollution and may be considered as one of the biggest challenges for the sustainability of the leather industry [9-11]. However, most of the developing countries do not
have the proper technology to treat tannery effluents before discharging it in the natural environment [12]. The leather industries in Bangladesh have relocated to Saver for the betterment of the environment, introducing the Central Effluent Treatment Plant (CETP) [13]. Unfortunately, this CETP is not working properly. It is very crucial to make CETP functional for the treatment of tannery effluents as it contains sulphonated oils, phenolic compounds, chromium, etc. [14]. The main pollutants in tanneries are suspended solids, BOD, COD, and heavy metals [15-17]. Currently, tanneries are releasing toxic chemicals to the natural environment and damaging plants and biotics in the water bodies as they do not have a proper disposal system of the tanning waste.

The researchers have developed many methods i.e. filtration [18], distillation [19], precipitation, electrolysis [20], oxidation [21] and evaporation, reverse osmosis [22], coagulation [23], flotation, etc. for the treatment of tannery wastewater. Consequently, the development of low-cost adsorbents from natural sources to solve environmental problems has received special attention among researchers [24-26]. Adsorption is widely used for removing pollutants from tannery effluents. It is proven that adsorption can act as a multiple sequestration method of solute separation. Adsorbents may be developed from activated charcoals, wood dusts, agricultural wastes, etc.

In this study, sugarcane bagasse adsorbent was developed from natural agricultural wastes, like sugarcane bagasse, to investigate its efficiency in removing pollutants from chrome tanning effluents. The effort was given to investigate the removal efficiency of BOD$_5$, COD, Cr$_2$O$_7$ , TSS and TDS from tanning effluents.

EXPERIMENTAL

Materials

Sugarcane bagasse was collected from a local market in Dhaka, Bangladesh. Further, it was washed with deionized water in order to remove the dust, and then dried completely. Dried sugarcane bagasse was converted into an adsorbent via several processes.

Equipment

In this study, locally made Pyrolyser (temperature control from 50 to 600 °C) was used for pyrolysis. The pH of the solution was investigated by using a pH meter (HANNA Instruments). Grinding was carried out by an electric grinding machine. All required shaking was performed by a shaking machine (SK-L330-Pro, DLAB). A scanning electron microscope (JEOL, JSM-6490) was used to investigate the surface morphology of the sugarcane bagasse adsorbent. A Fourier Transform InfraRed spectrometer (IRPrestige-21, Shimadzu Corporation, Kyoto, Japan) was utilized to analyse the functional groups on the surface of the adsorbent.

Experimental work methodology

Adsorption experiments were conducted in a beaker at a constant temperature. The adsorbent was well mixed with the collected sample in the shaking machine and filtered through a Whatman No.1 filter paper. The residual concentration of pollutants in the filtrate was analysed.
The adsorption percentages of the pollutants were calculated as follows [27,28]:

$$Removal\ rate\ (%) = \frac{C_o - C_t}{C_o} \times 100$$  \hspace{1cm} (1)

where $C_o$ and $C_t$ are the concentration of pollutants in the sample solution at the beginning and after the adsorption time $t$, respectively.

**Preparation of adsorbents**

**Pyrolysis of raw sugarcane bagasse**

Pyrolysis is the carbonatization and charring process which converts the sugarcane bagasse fibres to charcoal by decomposition through heating in the absence of oxygen [29]. In this study, sugarcane bagasse was pyrolyzed at 500 °C ± 10 °C for 2 hours.

In the pyrolysis process, 70% of the mass is discharged into the atmosphere and the remaining 30% is converted to charcoal. It is noticed that during the carbonization process, water vapor, CO$_2$, methane, and various types of organic vapours are released [30-34]. Figure 1(a) shows the raw sugarcane bagasse used in this study and 1(b) shows the sugarcane bagasse charcoal which was produced through pyrolysis process.

![Figure 1. (a) raw sugarcane bagasse; (b) sugarcane bagasse charcoal](image)

**Development of sugarcane bagasse charcoal by chemical activation**

In this study, the sugarcane bagasse charcoal was activated by chemical treatment. 50 g of sugarcane bagasse charcoal have been taken in a clean beaker filled with 250 ml of water and 10%-sodium hydroxide of analytical grade (5 g) was added to activate and increase the adsorption capacity of the charcoal.

The process of chemical activation for the preparation of adsorbent from raw sugarcane bagasse is summarized in the following Figure 2.
After developing the sugarcane bagasse charcoal by chemical activation, the collected effluent was treated as follows: BOD₅ was measured by the OXITOP measurement system; COD was investigated using the standard method (ASTM D1252-06); Cr₂O₃ was measured using SLC 8 (IUC 8; BS 1309:8) standard method; TDS and TSS were measured consequently using SLC 115 (SLT 2/3c) and SLC 114 (SLT 2/3b) standard procedures.
RESULTS AND DISCUSSION

SEM analysis

Surface morphologies of the NaOH-activated sugarcane bagasse were explored through SEM (Figure 4). It is expressed that NaOH-activated sugarcane bagasse has lamellar feature, irregular and heterogeneous structure and cavities which favour the adsorption process in aqueous solutions [35].

![Figure 4](image_url)

The SEM images (Figure 4) show the morphological structures of the NaOH-activated sugarcane bagasse. It is clearly observed that there is a change in surface morphology before and after the adsorption. The structure of the adsorbent is found to have irregular porosities in the image taken before the adsorption, whereas their porous surface became less visible after the adsorption.

Fourier Transform Infrared Spectroscopy (FT-IR)

The functional groups present in the NaOH-activated sugarcane bagasse were characterized using the FTIR. The infrared spectra are taken at a range of 700-4000 cm\(^{-1}\). Previous study shows many functional groups shifted to different frequency levels or disappeared after the adsorption, indicating the possible involvement of functional groups in the uptake of metal cations [36]. Figure 5 shows the FTIR of the NaOH-activated sugarcane bagasse (a) before and (b) after the Cr(III) adsorption. Characteristic frequencies in the range from 3200 cm\(^{-1}\) to 3650 cm\(^{-1}\) may be mainly associated with the stretching vibrations of the hydroxyl group (\(-\text{OH}\) bond). The possible stretching vibrations of \(-\text{OH}\) bond for sugarcane bagasse were found at 3603 cm\(^{-1}\) before and at 3597 cm\(^{-1}\) after the Cr(III) adsorption. The frequencies in the range from 1680 cm\(^{-1}\) to 1750 cm\(^{-1}\) were mainly associated with the stretching vibrations of the carbonyl groups (C=O bond). Figure 5 showed peaks at 1689 cm\(^{-1}\) and 1685 cm\(^{-1}\) of (a) and (b) which specify that there may be stretching vibrations of the carbonyl groups. Moreover, the \(-\text{CH}\) stretching bond was found at 2891 cm\(^{-1}\) for sugarcane bagasse before the Cr(III) adsorption and 1533 cm\(^{-1}\) frequencies were found for both (a) and (b) due to the C=C bond.
The developed adsorbent was utilized for the treatment of the chrome tanning effluent collected from the Tannery Industrial Estate, Dhaka (TIED). The chrome tanning effluent is mainly contaminated with a large amount of Cr(III) along with other pollutants. Here, some pollutants were reduced in the tanning industry wastewater by using the developed adsorbent.

**Physico-chemical parameters of the collected chrome tanning effluent**

The effluent was analysed in the laboratory. The physico-chemical characteristics of the samples are shown in the following Table 1.
Table 1. Characteristics of the chrome tanning effluent collected from the Tannery Industrial Estate, Dhaka (TIED)

| Sl. No. | Parameters  | Details       |
|--------|-------------|---------------|
| 1      | pH          | 4             |
| 2      | Temperature | 28.4°C        |
| 3      | Colour      | blackish blue |
| 4      | Cr₂O₃       | 504.88044 mg/L|
| 5      | BOD₅        | 3320          |
| 6      | COD         | 19200         |
| 7      | Chloride content | 0.55692 g |
| 8      | TDS         | 10.2198 g     |
| 9      | TSS         | 0.339 g       |

In this study, the temperature was measured by the direct reading of the thermometer. Colour/odour was measured by visual observation and the pH was measured by a pH meter.

Adsorption Experiments

The collected chrome tanning effluent was tested considering the following different parameters: the volume of the effluent (500 mL), the sugarcane bagasse dose (2.5 g/L), the shaking time (1 hour) for the removal of some pollutants, such as BOD₅, COD, Cr₂O₃ content, TSS and TDS. The BOD₅, COD, Cr₂O₃, TSS, and TDS values of the collected sample before and after the adsorption are presented in Figures 6, 7, 8, 9 and 10 respectively.
Finally, the removal rate of the pollutants by using the NaOH-activated sugarcane bagasse charcoal is presented in Figure 11.
CONCLUSION

The investigations proved that the adsorption technique is one of the efficient modes of physico-chemical treatment of the tannery wastewater. In this study, the level of pollutants i.e., $\text{BOD}_5$, COD, $\text{Cr}_2\text{O}_3$, TSS and TDS were investigated. The findings of the study revealed that $\text{BOD}_5$ value was reduced to 42%. It is also noticed that, after the adsorption, the COD value, the $\text{Cr}_2\text{O}_3$ content, TSS and TDS were reduced to 75%, 41.91%, 81.85% and 84.24% respectively. Therefore, it is stated that sugarcane bagasse can be used as an effective adsorbent for the treatment of the chrome tanning effluent. In the future, this study can be extended by taking various samples from multiple tanneries. Furthermore, sugarcane bagasse can be activated by using various chemicals to investigate its efficiency.

Author Contribution

Conceptualization – Razia Sultana, Sobur Ahmed and Fatema-Tuj-ZOHRA; methodology – Razia Sultana; formal analysis – Razia Sultana, Fatema-Tuj-ZOHRA; investigation – Razia Sultana, Fatema-Tuj-ZOHRA; resources – Fatema-Tuj-ZOHRA and Sobur Ahmed; writing, original draft preparation – Razia Sultana; writing, review and editing – Fatema-Tuj-ZOHRA and Sobur Ahmed; visualization – Fatema-Tuj-ZOHRA; supervision – Fatema-Tuj-ZOHRA. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

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