Research Article

Removal of methylene blue and other pollutants from tannery wastewater using chemically modified tannery solid waste

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ABSTRACT

The adsorption of methylene blue (MB) was investigated using the prepared activated carbon (AC); obtained by the chemical activation of chrome shaving dust (CSD). Results represented that the increase of particle size and impregnation ratio of AC possessed a proportional effect on the adsorption of MB. AC produced by H3PO4, impregnation ratio of 1:6, and mesh size of 40 showed the highest adsorption performance. The removal of other organic and inorganic pollutants from different tannery effluent was found satisfactory like pH, conductivity, turbidity, BOD5, COD, and Cl- values are reduced to 5.5-8.48, 73-93%, 76-92%, 80-96%, 71-87% and 84-94%, respectively which are nearly closed to the WHO’s standards for industrial effluent to the environment. The microscopic analysis confirmed the smooth and porous surface characteristics of the adsorbent. Hence, CSDAC can be expected to become an effective, low-cost, and suitable adsorbent for both dye and pollutants removal from industrial wastewater.

Introduction

For the last few decades, water pollution has become a global phenomenon that results in the scarcity of fresh water for drinking and carrying out our daily activities smoothly. UNO assumes that by the year 2050, approximately 40% of the world population will face a drinking water shortage if this scenario continues (de Aquim et al., 2010). Hence, the water resource management authorities should give more attention to water conservation and the sustainability of the human race on earth. Rapid industrialization and extensive use of mechanized and chemical appliances in agricultural and household activities have been categorized as the major causes of water pollution. Among industries, paper, pulp, thermal, metal extraction, paints and pigments, textile, and leather generate a significant quantity of color and toxic metal wastes with wastewater that are responsible for both aesthetical and toxicological problems (Anandkumar and Mandal, 2009). The discharged color effluents release a substantial amount of dissolved and suspended solids with a high degree of biochemical and chemical oxygen demand when mixed with groundwater (Etezad and Sadeghi-Kiakhani, 2021). Moreover, these compounds act as interference in water that blocks sunlight penetration, hampers photosynthesis, and show toxicity in some microbial species and carcinogenic effects in the human body (Kasmaei et al., 2020). Therefore, the remediation of dyes from effluents is essential before discharging them into water resources to reduce water pollution. MB is a well-known dye that has extensive applications in several industries. It was first synthesized by Caro and has a wide range of applications in textile coloration, calico-printing, and titration indicators (Dutta, 1990).

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It is a dark green-coloured cationic dye and highly soluble in aqueous and alcoholic media. Despite its benefits to industries, MB shows negative symptoms in the human body, such as inhaled respiratory problems, nausea, vomiting, burning sensation, mental confusion, etc., upon swallowing (Wijaya et al., 2020). As a result, the quantity of MB in industrial wastewater should be kept within the permissible limit.

Some wastewater treatment methods have recently been developed to reduce water pollution [viz. Reverse Osmosis (RO), adsorption, ion exchange, chemical coagulation, membrane filtration, etc.]. These techniques are also used to mitigate pollutants from industrial effluents (Thilagavathy and Santhi, 2013). However, adsorption is becoming more popular than all other treatment methods. It is highly efficacious due to the easy removal of various chemicals using activated carbon, nano-magnetic materials, and zeolites (Ebrahimi et al., 2013; Khalid et al., 2018). These materials require high preparation costs and possess less recyclability. Thus, developing low-cost, recyclable, and locally available adsorbents is a prime need for the redemption of different types of toxins from wastewaters.

In the history of human civilization, the leather processing industry is the most ancient and important. Its worldwide importance is due to meet the global market demand for leather. But a huge amount of solid wastes and effluents are produced during the hide/skin processing. According to literature, approximately 750-850 kg of solid wastes in both tanned and un-tanned is generated per ton of hides/skins processing, and the global rate of tannery solid waste generation is 6 million tons per annum (Paul et al., 2013; Andrioli and Gutterres, 2015; Abajihad, 2012; Sundar et al., 2011). These solid wastes have limited applications but can cause many adverse effects on environmental and human health if they are not properly treated. Therefore, valorization of tannery solid waste is important rather than its disposal in landfilling or incineration, and effluent treatment should be monitored properly (Tahiri and de la Guardia, 2009, Hashem and Nur-A-Tomal, 2018, Madhavi et al., 2011; Li et al., 2019).

Regarding these circumstances, we attempted to valorize solid leather shaving waste by converting it into AC through pyrolysis and applying it for MB adsorption and other pollutants removal from tannery effluent. The other objectives included- (1) the study of the effect of impregnation ratio of various chemicals with prepared AC during chemical activation, (2) the study of the nature of chemically modified AC by spectral and microscopic analyses, and (3) the study of the removal capacity of the prepared adsorbent.

**Materials and Methods**

**Preparation of synthetic sample**

Analytical grade MB (Fig. 1) was purchased from Sigma-Aldrich, USA, to prepare a standard synthetic solution for batch experiments and a calibration curve for measuring dye removal amount. Stock MB solution (1000 mg/L) was made by dissolving the dye powder into deionized water in a 1000 mL Erlenmeyer flask using a magnetic stirrer at room temperature. Later, a desired intermediate standard solution (i.e., a solution in which the dye concentration was ranged from 50-200 mg/L) was prepared by mixing deionized water properly with the stock solution (methylene blue).

![Fig. 1. Chemical structure of methylene blue](image_url)

**Sample collection and characterization**

In an airtight polyethylene bag, chrome shaving dust (CSD) was collected from Samina tannery Ltd., at Hemayetpur, Savar, Dhaka. The collected CSD was immediately brought to the laboratory, thoroughly...
washed with tap water to remove impurities and sun-dried for a week. The dried CSD was crushed, and then divided into various mesh sizes: 20, 30, and 40 through a sieving machine (Retsch D-42459 HAAN, Germany). Proximate analysis of physical characteristics of CSD was tested by following standard testing methods (FAAS methods equipped with Zeeman background), and the result was shown in Table 1. Finally, the dried CSD powder was stored in the dark at room temperature for further experiment.

Table 1. The characters of analyzed chrome shaving dust (CSD)

| Parameter                        | Value (%) |
|----------------------------------|-----------|
| **Proximate analysis (weight, %)** |           |
| Water/Moisture content           | 13.29     |
| Volatile Matter                  | 53.40     |
| Fixed carbon                     | 24.53     |
| Ash                              | 9.56      |
| **Ultimate analysis (dry basis weight, %)** |         |
| Carbon (C)                       | 54.8      |
| Nitrogen (N)                     | 6.33      |
| Hydrogen (H)                     | 6.54      |
| Cl (Chlorine)                    | 4.32      |
| S (Sulfur)                       | 1.30      |
| Cr (Chromium)                    | 2.76      |
| Si (Silicon)                     | 2.74      |

**Carbonization**

The thermal activation of chemically impregnated raw material was conducted at 600°C for an hour in a pyrolyzer with having 500 mm long quartz tube with a 20 mm internal diameter under an inert atmosphere of nitrogen gas (99.99%) at a rate of 150 cm³/minute. The temperature was elevated to the desired temperature at a rate of 5°C/minute, and the temperature was kept constant for a certain time to complete the pyrolysis. After pyrolysis, a certain quantity of char was cooled at room temperature with nitrogen flow and then washed with deionized (DI) water to remove surplus chemicals. Finally, the sample was taken in a beaker, stirred with 250 ml HCl solution for an hour, and thoroughly washed with hot deionized (DI) water until it reached 6-7 pH (neutral).

**Batch studies**

The adsorption process of MB was carried out in batch mode. 100 ml solution of 200 ppm MB solution was taken on a 250 ml conical flask, treated with 1 gm of AC (various impregnation ratios with different chemical activation), and constantly shaken at a speed of 200 rpm (mechanically) for the desired time at ambient temperature. After the desired time, the mixture was
centrifuged at 5000 rpm for 10 minutes to separate the solid phase. The amount of MB in the solution was determined by a double-beamed Ultra-violet spectrophotometer (Shimadzu, Japan) at 668 nm with respect to the previously prepared calibration curve for minimal error. The calibration curve was reproducible and linear over the concentration range during analysis. Equations 1 and 2 were used to calculate the % removal of MB and adsorbed quantity, respectively.

\[
\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100 
\]

\[
\text{Amount absorbed (} q_e \text{)} = \frac{(C_i - C_f) \times V}{m} 
\]

Here, \( C_i \) and \( C_f \) were the initial concentration of dye solution before treatment and the final concentration of dye solution after treatment. \( V \) = volume of the dye solution (mL), and \( m \) = mass of AC used as adsorbent (mg/L). Each of the experiment series was further carried out by using the blank solution as control, and the average values of these experiments obtained from duplicate runs were further analyzed and compared.

**Results and Discussion**

**Methylene blue (MB) adsorption**

In this experiment, chemical activation of three types of AC categorized in three dissimilar mesh sizes (20, 30, and 40) was done by two different chemicals (\( \text{H}_3\text{PO}_4 \) and \( \text{ZnCl}_2 \)) at various impregnation ratios (chrome shaving dust: \( \text{ZnCl}_2/\text{H}_3\text{PO}_4 = 1:2, 1:4, \) and \( 1:6 \)) to evaluate the superior adsorbent for the adsorption of MB from industrial wastewater among them. It was noted that the adsorption of MB was gradually increased with the increase of mesh number of the AC samples (Fig. 2). At the same time, the activation capacity of AC molecules was increased with the increasing quantity of applied chemicals because of the increasing percentage of chemical penetration inside the raw materials. The adsorption capacity of MB was found to increase with the gradual increase of the amount of activating chemicals. The excess contact time of impregnation chemicals char materials played a vital role in such phenomenon. Besides, the adsorption capacity of \( \text{H}_3\text{PO}_4 \) impregnated char was 1.27-1.36 times higher than that of \( \text{ZnCl}_2 \). It indicated that \( \text{H}_3\text{PO}_4 \) impregnated char was superior to \( \text{ZnCl}_2 \) impregnated char for MB adsorption. However, the difference was insignificant, and the chemical activation value was found to be closed as described in the literature (Pereira et al., 2014).

**Pollutant reduction**

Different types of tannery effluents discharged from different chemical operations of various leather-manufacturing stages were treated with the prepared AC to reduce the amount of both forms of pollutants (i.e., organic and inorganic) for the reduction of water pollution. In situ data analysis of the physicochemical parameters, e.g., pH, conductivity, turbidity, COD, BOD\(_5\), and Cl\(_1\), etc., of the collected wastewater samples, both initial and before treatment, were represented in a tabular form (Table 2).
From some literature, it was found that the values of pH, COD, BOD, Cl\textsuperscript{-}, and conductivity in surface water should be 5.5–9, 40 mg/L, 5 mg/L, 250 ppm, 1000 µS/cm, respectively (Thurston et al., 1981; Patil et al., 2012; Environment, 2008; Naubi et al., 2016). From the test results, it was observed that the pH values of each wastewater sample exceeded the threshold limit except for de-liming and bating wastewater before treatment. These values revealed that these wastewaters could bring about adverse effects on both aquatic life and the aquatic environment if they are discharged into the environment without any further treatment. However, the pH values of the wastewater sample were found within the tolerable limit (5.5–8.48).

Table 2. The physical properties of raw tannery outflow (before and after treatment)

| Effluent    | Before treatment | After treatment |
|-------------|------------------|-----------------|
|             | pH   | BOD\textsubscript{5} mg/L | COD mg/L | Conductivity µS/cm | Turbidity NTU | Chloride mg/l | pH   | BOD\textsubscript{5} mg/L | COD mg/l | Conductivity µS/cm | Turbidity NTU | Chloride mg/l |
| Soaking     | 8.1   | 2100 | 4350 | 1237 | 990 | 35.75 | 6.95 | 274.05 | 904 | 289 | 215 | 2 |
| Liming      | 13.2  | 5500 | 9523 | 1191 | 550 | 24.23 | 7.48 | 678.15 | 2136 | 215 | 57 | 4.3 |
| Deliming    | 7.77  | 2500 | 5563 | 2016 | 840 | 22.75 | 6.97 | 349.00 | 1245 | 385 | 170 | 3.5 |
| Bating      | 7.49  | 3000 | 6250 | 3160 | 660 | 78.88 | 7.4  | 450.00 | 1200 | 5  | 60 | 8  |
| Pickling    | 2.5   | 1100 | 2600 | 1515 | 1020 | 16.58 | 7.06 | 50.05  | 321  | 17.15 | 253 | 1.5 |
| Chrome Tanning | 2.4 | 1950 | 3650 | 425  | 1050 | 12  | 7.5  | 112.13 | 727  | 6.15  | 160 | 0.69 |
| Re-tanning  | 3.9   | 2100 | 4700 | 415  | 990  | 11.58 | 7.4  | 405.09 | 1255 | 10.9 | 153 | 0.5 |
| Fat liquoring | 3.62 | 4100 | 9500 | 750  | 1000 | 68.5 | 5.50 | 734.31 | 2700 | 11.17 | 107 | 10 |
| Dyeing      | 4.9   | 2700 | 7770 | 650  | 900  | 28.3 | 6.76 | 404.19 | 1542 | 15.15 | 228 | 4.5 |

Fig. 2. MB adsorption of different sizes AC impregnated by H\textsubscript{3}PO\textsubscript{4} and ZnCl\textsubscript{2} at various impregnation ratio
The values of both COD and BOD5 of every untreated effluent were beyond the acceptable limit prescribed by WHO. Those effluents were not suitable for any specific reuse, especially in irrigation or agricultural applications. At the same time, those effluents seemed very threatening to the aquatic living beings if they were discharged into the rivers. Besides, the BOD5 (80-96%), and COD (71-87%) values of these respective wastewater samples were significantly reduced after treatment (Fig. 3) which

Conductivity and turbidity are two critical parameters describing water’s aesthetic quality. Conductivity narrates the total amount of dissolved matter, and turbidity is an essential indicator in determining the suspended sediment quantity in water. These two parameters were also examined for the collected wastewater samples before and after treatment with activated carbon. It was observed from the analysis (Fig. 3) that a substantial amount of reduction in the values of conductivity (73-93%) and

![Graphs showing the decrease in COD, BOD, COD, Conductivity, Turbidity, and Chloride](image-url)

**Fig. 3.** Decrease all physical parameters of wastewater by using activated carbon where S, L, D, B, P, C, R, F, and D indicate Soaking, Liming, Deliming, Bating, Pickling, Chrome tanning, Re-tanning, Fat liquoring, and Dyeing respectively.
turbidity (76-92%) was obtained in the treated effluents. Most of the values were found closed to the acceptable level recommended by WHO for wastewater released into the environment. Additionally, Cl\(^{-}\) concentration was also remarkably decreased (84-94%) from the effluents.

**Microscopic analysis**

SEM micrographs of AC samples after MB adsorption are shown in Fig. 4. The micrographs demonstrated AC’s smooth surface and porous structure that occurred due to surface modification by phosphoric acid before pyrolysis. The high temperature of pyrolysis causes the reaction of the organic compounds present in CSD with H\(_3\)PO\(_4\) and finally, the release of the organic compounds causes pores in the structure. These pores enhance adsorption by offering increased surface area.

**Conclusion**

This research was conducted to evaluate the adsorption effectiveness of prepared AC from leather shaving dust that was mainly attempted to create value addition of solid leather waste along with pollution control. Leather wastes were chemically impregnated using different chemicals at different impregnation ratios before pyrolysis for surface modification to improve their adsorption capacity. Finally, the produced char was used for MB adsorption from an aqueous solution. It has been observed that the chemically impregnated char with phosphoric acid (similar impregnation ratio and similar mesh size) was the superior adsorbent. The adsorption capacity was in a proportional relationship with the impregnation ratio of chemicals and particle size of shaving dust as well. The tested water quality parameters viz. pH, electrical conductivity, turbidity, TDS, chloride, BOD, and COD of the collected effluent samples discharged from each chemical operation during leather manufacturing were also studied. After treatment with AC activated by phosphoric acid, significant amount of pH (5.5-8.48), conductivity (73-93%), turbidity (76-92%), BOD\(_5\) (80-96 %), COD (71-87 %), Cl\(^{-}\) (84-94%) were decreased. From the above outcomes, it can be summarized that AC produced from chrome shaving dust can be a very fruitful adsorbent that can be used for wastewater treatment and a suitable example of a waste recycling system.

**Statements and Declarations**

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![Fig. 4. SEM analysis of adsorbent (a) raw CSD (b) CSDAC activated by H\(_3\)PO\(_4\) (c) MB adsorbed CSDAC](image-url)
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**Availability of Data and Material**

The data in this study are available from the corresponding author on reasonable request.

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