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Research Article

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

Mohammad Nazmul Hossain[1], Md Didarul Islam[2], Ashiqur Rahaman[3], Mahadi Hasan[4], Meem Muhtasim Mahdi[3], Md. Arafat Hossain[3], Nazma Khatun* and Md. Abdul Matin[1]

Atomic Energy Centre, Chattogram, Bangladesh Atomic Energy Commission, Chattogram, Bangladesh

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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 H_3PO_3, 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, BOD_5, 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).

*Corresponding author: <nazmabaec@gmail.com>

[1]Department of Glass and Ceramic Engineering, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh
[2]Department of Applied Chemistry and Chemical Engineering, University of Dhaka, Dhaka, Bangladesh
[3]Institute of Leather Engineering and Technology, University of Dhaka, Dhaka, Bangladesh
[4]Faculty of Environmental Science and Engineering, Babes-Bolyai University, Cluj-Napoca, Romania

It is a dark green-colored 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).

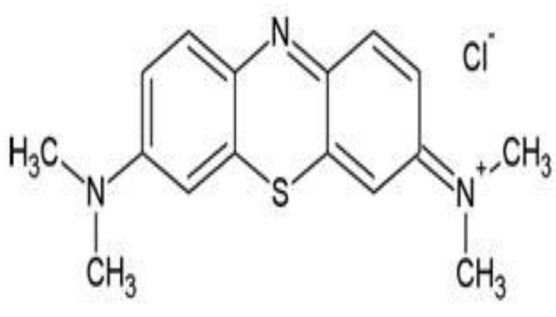


Fig. 1. Chemical structure of methylene blue

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

Wastewater collection

A sufficient amount of wastewater from different chemical operations of leather processing was obtained from Ruma tannery Ltd., at Hemayetpur, Savar, Dhaka by following Pearson et al. method (Pearson et al., 1987). The spent liquors were collected in labeled, airtight plastic bottles from the discharge point that led to the sewage line. The bottles were previously disinfected by soaking them overnight in 10% HNO_3 solution, washed thoroughly with deionized water to remove the surplus acid, and oven-dried at 80ºC for two (2) hours to avoid any contamination during sample collection. The collected wastewater sample was stored at 3-5ºC in the laboratory upon filtration to prevent further oxidation/hydrolysis.

Adsorbent preparation

Chemical impregnation

The dried CSD sample was chemically impregnated for its surface modification before pyrolysis. CSD of various particle sizes was placed in 250 mL beakers and mixed with standard solutions of H_3PO_3 and $ZnCl_2$ at different ratios. Chemical impregnation was done in an oven at 110ºC for 6 hours. After impregnation, the chemically impregnated leather wastes were transferred into a horizontal tube furnace after loading them inside a ceramic tube for pyrolysis.

Carbonization

The thermal activation of chemically impregnated raw material was conducted at 600ºC 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 cm^3/minute. The temperature was elevated to the desired temperature at a rate of 5ºC/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.

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

$$\text{Amount absorbed } (q_e) = \frac{(C_i - C_f) \times V}{m} \quad (2)$$

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.

Analysis of physicochemical properties of wastewater

Several physicochemical parameters like pH, conductivity, turbidity, TDS, BOD_5 and COD values of the wastewater sample were tested by using calibrated machinery as per their standard operating procedure. pH was measured by a digital pH meter, conductivity was estimated by following the electrometric method, turbidity was determined by a turbidity meter and a digitalized potentiometer was used to measure the amount of total dissolved solids in wastewater. BOD and COD were assessed by following the five-day BOD test and open reflux method suggested by Kopp (1979). Each of the physicochemical parameters was tested before and after treatment to evaluate the adsorption efficiency of the developed AC (i.e., generated by activation with H_3PO_4 1:6 impregnated ratio and mesh size 40).

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 (H_3PO_3 and $ZnCl_2$) at various impregnation ratios (chrome shaving dust: $ZnCl_2/H_3PO_4$= 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 H_3PO_3 impregnated char was 1.27-1.36 times higher than that of $ZnCl_2$. It indicated that H_3PO_3 impregnated char was superior to $ZnCl_2$ 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^-, etc., of the collected wastewater samples, both initial and before treatment, were represented in a tabular form (Table 2).

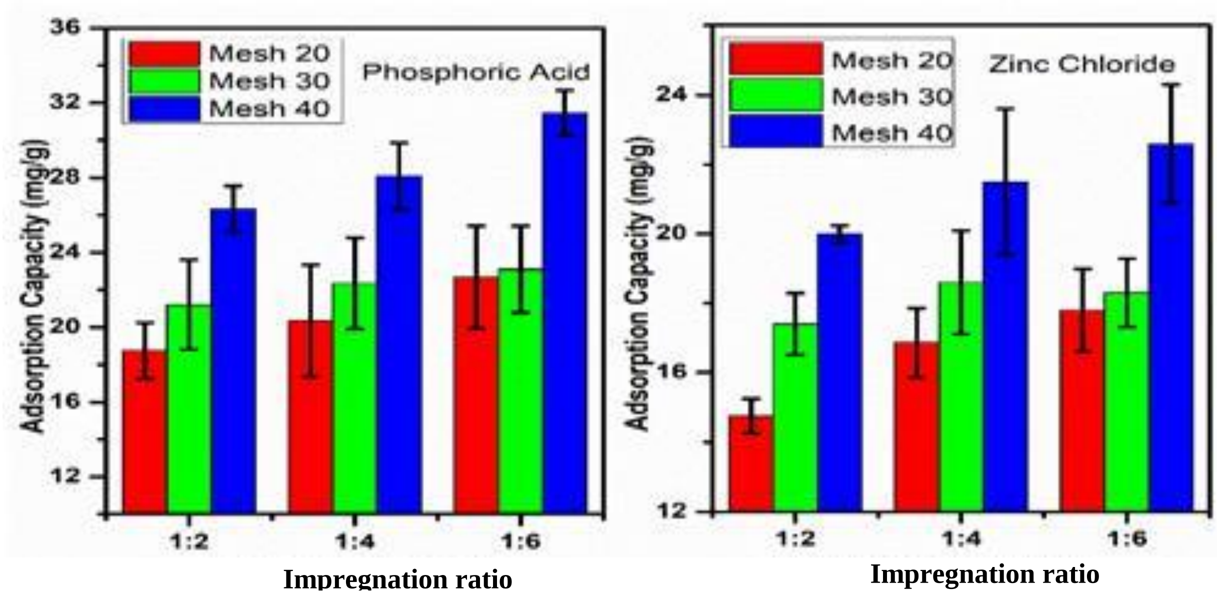


Fig. 2. MB adsorption of different sizes AC impregnated by H_3PO_3 and $ZnCl_2$ at various impregnation ratio

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

Effluent	Before treatment						After treatment					
Sample	pH	BOD_5 mg/l	COD mg/l	Conductivity μS/cm	Turbidity NTU	Chloride mg/l	pH	BOD_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

From some literature, it was found that the values of pH, COD, BOD, Cl^-, 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).

The values of both COD and BOD_5 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 BOD_5 (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

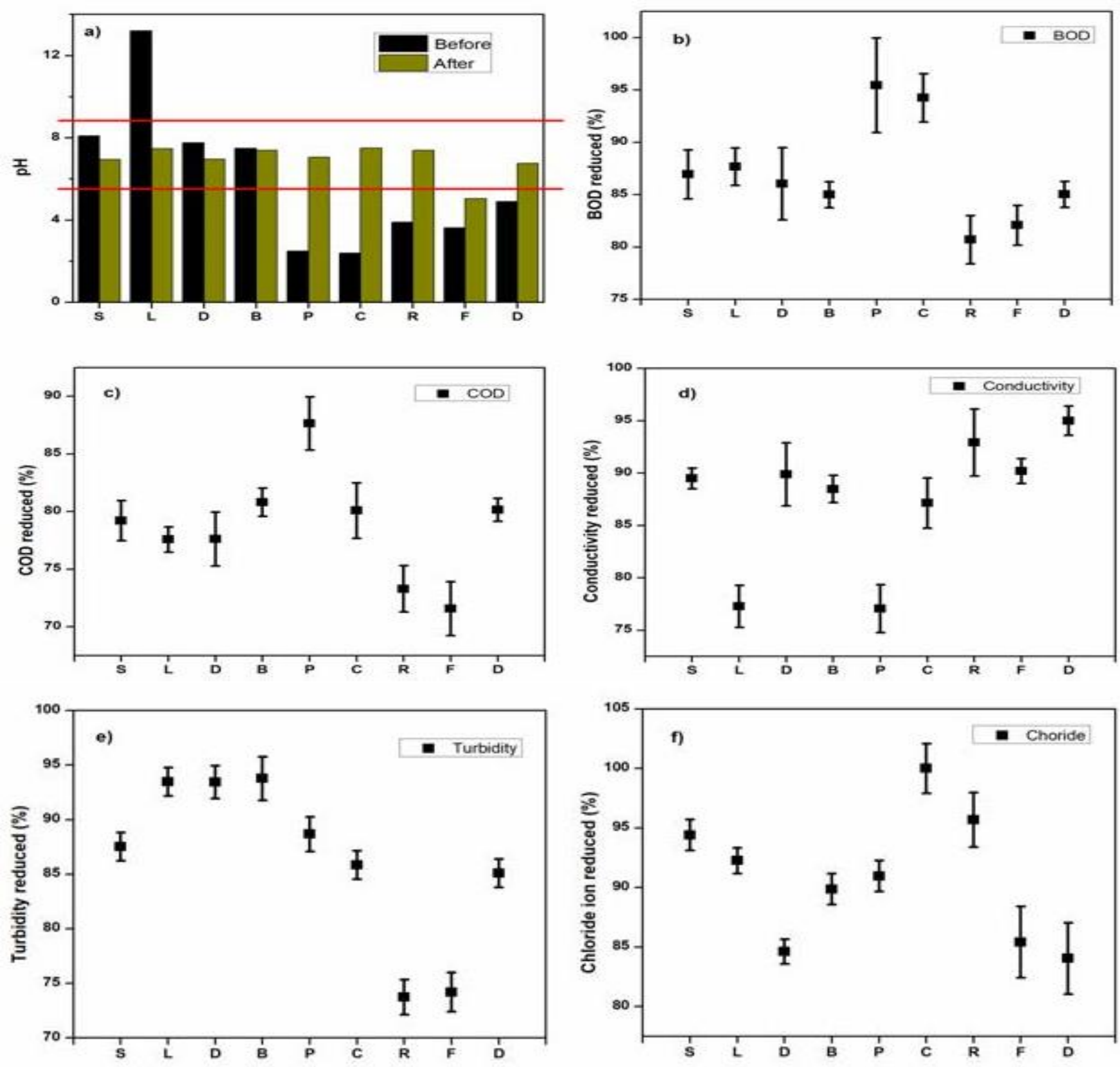
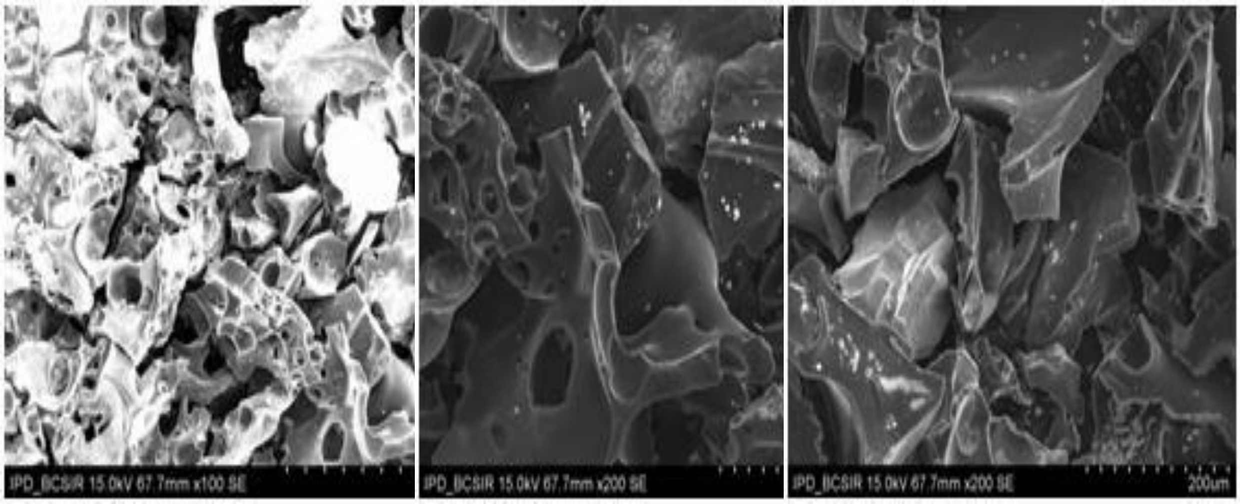


Fig. 3. Decrease all physical parameters of wastewater by using activated carbon where S, L, D, B, P, C, R, F, and D indicate Soaking, Liming, Deliming, Bating, Pickling, Chrome tanning, Re-tanning, Fat liquoring, and Dyeing respectively.

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^{-1} 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_3PO_3, and finally, the release of the organic compounds causes pores in the structure. These pores enhance adsorption by offering increased surface area.



(a) (b) (c)

Fig. 4. SEM analysis of adsorbent (a) raw CSD (b) CSDAC activated by H_3PO_3 (c) MB adsorbed CSDAC

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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Availability of Data and Material

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

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Conflict of Interest: The authors declare that they have no conflict of interest.

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