INVESTIGATION OF DYE ADSORPTION ON THERMALLY ACTIVATED ADSORBENT DERIVED FROM *TAMARINDUS INDICA* LEAVES

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ABSTRACT

In leather processing, dyeing is an essential operation in leather manufacturing to make the final leather attractive. The resulting dyeing effluent poses a significant threat to both human health and the aquatic ecosystem. This study examines the feasibility of using thermally activated adsorbent derived from the *Tamarindus indica* leaves to remove the dye from dyeing effluent. The collected Tamarindus indica leaves were subjected to thermally activated at 350°C for two hours. Before and after use the adsorbent was characterized through Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FT-IR) spectroscopy. Batch experiments were conducted to evaluate the dye adsorption capacity of the activated adsorbent from a tannery. For maximum dye removal efficacy, several factors- adsorbent dose, pH, stirring time, and setting time are optimized. The results showed that the highest dye removal efficiency was achieved by the thermally activated *Tamarindus indica* leaves adsorbent 97.09% with an adsorbent of 0.75 g/25 mL wastewater, pH 4.8, stirring time 30 minutes, coagulant dose 0.3-g/25 mL wastewater, and 20 hours settling time. Moreover, the study was able to reduce turbidity, Biochemical Oxygen Demand (BOD), and Chemical Oxygen Demand (COD) levels by 99.62%, 80.38%, and 43.70%, respectively. The research findings suggest that *Tamarindus indica* leaves-based activated adsorbent is promising for dye removal from tannery wastewater.

Keywords: *Adsorption, Tannery wastewater, Isotherm, Tamarindus indica, Environment*

1. INTRODUCTION

Leather manufacturing is a process of producing finished leather, which was established at least 5000 years ago (Covington, 2016). It is one of the oldest industries in Bangladesh. It has become the country's second-highest source of foreign exchange after ready-made garments (RMG) by exporting almost 10% of the global demand for leather. The entire leather manufacturing is divided into different subsectors e.g. beamhouse, tanning, and finishing. During leather processing, a significant amount of waste is generated in the form of solid, liquid, and gaseous. The generated waste from the process includes raw trimmings, trimmed leather, sludge, dye, chemicals, and water that have been used. A method used in the wet finishing stage is dyeing. While producing crust leather the leather is dyed with various dyestuffs to make it attractive, and adaptable for fashion styling. Fat/oil, synthetic or natural re-tanning agents, and dyes themselves are a few examples of the chemicals that cause the production of relatively harmful and intricate effluents (Piccin et al. 2016).

The wastewater emitted from dyeing affects photosynthesis (Ferreira et al. 2014) and is known to cause various health effects to human beings e.g. skin diseases, breathing difficulties, eye burn, vomiting, nausea, etc. (Rafatullah et al. 2010; Crini, 2006). Moreover, many dyes are toxic and even carcinogenic, thus, affecting the aquatic biota and human health (Kyzas and Kostoglou, 2014; Yagub et al. 2014). Nowadays, the necessity for cost-effective and sustainable solutions for wastewater treatment is more critical than ever before. One of the physicochemical treatment methods is adsorption utilizing solid adsorbent, which is effective and affordable (Hassani et al. 2015). Activated carbon was the most commonly used adsorbent despite this, but its use has been restricted because of its expensive initial and ongoing expenses (Attia et al. 2006). The conventional adsorbent, activated carbon, though effective, has remained encumbered by exorbitant upfront and operational expenses, rendering it inaccessible for many sectors and communities grappling with wastewater pollution. Consequently, there exists an increasing demand for inventive materials that can proficiently capture and remove organic dyes from effluent streams, particularly in regions where water contamination poses a grave concern.

The activated charcoal, or activated carbon, is like the unsung hero of filtration and purification. It may look like regular charcoal, but its unique structure and properties make it a superstar when it comes to adsorption. Picture it as a microscopic sponge with countless nooks and crannies that trap impurities like a magnet. It's incredibly porous, providing an immense surface area for grabbing onto all sorts of substances. This makes it a go-to choice for cleansing air and water of contaminants, toxins, and even unwanted odours. Its utilization has been limited due to high initial and operating costs. As a consequence, there is an evolving need for ingenious materials that are developed for adsorbing organic dyes from waste effluent. *Tamarindus indica* is a non-endangered semi-evergreen fast-growing species distributed throughout the tropical American region and also the African and Asian countries. It can be used as a potential adsorbent for the removal of dye from the wastewater. It is one of the affordable biological waste products due to its vast cultivation and they are easily accessible. Research into the adsorption capacity of activation made from Tamarind leaves may lead to the development of cost-effective and sustainable technologies for treating dye-contaminated industrial effluents. Tamarind leaves unique chemical composition and surface reactivity make them a promising candidate for various wastewater treatment applications beyond dye removal.

In this study, thermally activated *Tamarindus indica* leaves adsorbent is used to adsorb dye from the tannery dyeing wastewater. The equipped adsorbent was characterized through Fourier Transform Infrared (FT-IR) spectroscopy, Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray (EDX) spectroscopy. The physicochemical parameters of treated wastewater were compared to the standard discharged level.

2. METHODOLOGY

2.1 Sample collection

The *Tamarindus indica* leaves were collected on the university campus of Khulna University of Engineering & Technology, Khulna, Bangladesh. Various analytical grade reagents-sodium hydroxide, aluminium sulfate, and sulfuric acid were obtained from the scientific store in Khulna, Bangladesh. The dyeing wastewater was acquired from SAF Leather Ltd., Jashore, Bangladesh.

2.2 Adsorbent preparation

Collected *Tamarindus indica* leaves were thoroughly washed by using distilled water to remove any contaminants. Then, it was sun-dried and dried in an oven at 105°C for 24 h. The oven-dried leaves were subject to thermally activated in a muffle furnace at 350°C for 2 h. After cooling, the thermally activated adsorbent was ground by using a laboratory pulverizer with a sieving 0.5 mm mesh size. Figure 1 depicts the prepared adsorbent.

Figure 1: Prepared thermally activated *Tamarindus indica* leaves adsorbent

2.3 Batch test for dye adsorption

A batch-wise dye removal test of the dyeing wastewater was conducted with the prepared adsorbent. Initially, the physiochemical parameters-pH, Electrical Conductivity (EC), salinity, Total Dissolved Solids (TDS), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and turbidity of the dyeing wastewater were monitored. At first, the dyeing wastewater was treated with alum as a coagulant to remove the Dissolved Solids (DS). The alum-treated filtrate was treated with the thermally activated adsorbent for dye removal. The prepared adsorbent was combined with 25 mL of alum-treated dyeing wastewater, stirred, and settled over a predetermined period. The filtrate was assessed for absorbance using UV-visible spectroscopy at the wavelength of 475 nm and dye removal efficacy was calculated. For optimum dye removal various parameters e.g. alum dose, adsorbent dose, contact time, and settling time were optimized. After dye removal at optimized conditions, the physicochemical parameters of the treated wastewater were compared to the standard limit.

2.3.1 Process optimization

For determining the optimum coagulant (alum) dose, various doses 0.025, 0.075, 0.125, 0.20, 0.25, 0.30, 0.40, 0.50, 0.70, and 0.85 g were added to dyeing wastewater of 25 mL (each batch). The coagulant mixed dyeing wastewater was stirred on a magnetic stirrer for 10 min and kept settling for 2 h. The absorbance of the filtrate was measured and the optimum coagulant dose was defined for optimization of other parameters. Different doses of adsorbent 0.25, 0.50, 0.75, 1.00, 1.25, and 1.50 g were used for each batch (25 mL) while other parameters were kept unchanged. Afterwards, stirred, settled, and filtered; the absorbance of the filtrate was measured via a UV-visible spectrophotometer (UNICO, Germany) and dye removal efficacy was calculated. For the optimization of stirring time, an interval of 15, 20, 25, 30, 45, and 60 min was predefined with optimized adsorbent dose (0.75 g) while other parameters were kept untouched. To adjust the settling time, a period of 4, 6, 8, 12, 16, 20, 24, and 30 h was predefined while the optimized dose (0.75 g) and stirring time (30 min) were maintained.

2.3.2 Characterization of adsorbent

Before and after using the thermally activated adsorbent, it was characterized in terms of Fourier Transform Infrared (FTIR) spectroscopy (Spectrum 100, Perkin Elmer, USA), Energy-dispersive X-ray Spectroscopy (EDX) (Sigma HV, Carl Zeiss Microscopy Ltd.), and SEM (JEOL JSM-6490, USA) techniques were applied to investigate the adsorbent characteristics. The Scanning Electron Microscope (SEM, (S3400, Hitachi, Japan) image was captured of the pure adsorbent and dye-loaded adsorbent at 25.00KX magnification.

2.3.3 Wastewater characterization

pH of the raw dyeing wastewater and the treated wastewater were monitored using a calibrated pH meter (UPH-314, UNILAB, USA). The conductivity meter (CT-676, BOECO, Germany) was used for the monitoring of TDS, EC, and salinity. For the determination of BOD and COD, the standard APHA methods of APHA-5220 C (2012) and APHA 5210-B (2012) were followed.

3. RESULTS AND DISCUSSION

3.1 Coagulant dose

Figure 2 represents the optimization of alum dose for the removal of dye from the dyeing wastewater. For the coagulant dose of 0.03-g/25 mL wastewater, dye removal was only 9.47%. It seems that by increasing the coagulant dose, the dye removal efficiency was gradually increased. In the case of coagulant dose 0.20-g/25 mL wastewater, dye removal was 67.76% and later on with increasing the coagulant dose, dye removal was not significantly increased. The maximum dye removal achieved was 72.50% for a coagulant dose of 0.30 g/25 mL wastewater. Afterwards, the dye removal was gradually decreased although the coagulant dose was increased. Therefore, a coagulant dose of 0.30-g/25 mL wastewater was selected as an optimum dose. The relative solution pH was gradually decreased with increased coagulant dose. For the coagulant dose from 0.03-g/25 mL to 0.25-g/25 mL, pH was linearly (R^2=0.9754) decreased. From the coagulant dose of 0.30-g/25 mL wastewater, pH changes or decreases were very insignificant. It is obvious that at acidic pH dye removal was the maximum.

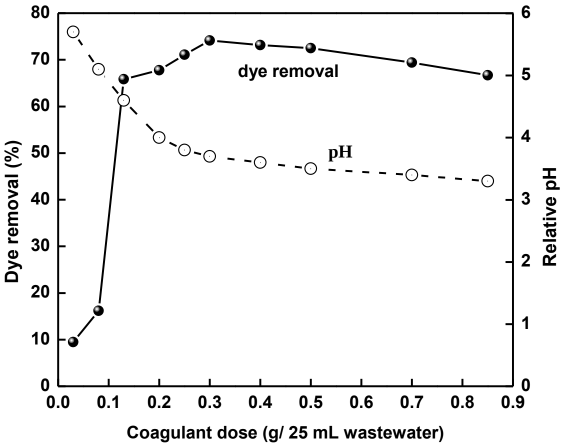


Figure 2: Effect of alum dosages on dye removal efficiency from wastewater

3.2 Effect of adsorbent dose

The adsorbent quantity is the crucial factor in determining the adsorbent capacity under specific operating conditions. Figure 3 depicts the relationship between removal efficiency and adsorbent doses. For adsorbent doses of 0.25, 0.50, 0.75, 1.00, 1.25, and 1.50 g, the corresponding dye removal efficiencies were 87.31%, 91.26%, 96.54%, 96.27%, 96.08%, and 95.39%, respectively. Notably, it's evident that up to a dose of 0.75 g, the dye removal efficiency was increased very steeply (R^2=0.9913). This trend typically occurs due to the greater availability of adsorption sites on the surface as the dose increases. This emphasizes the economic viability and importance of understanding the impact of adsorbent material dose in the adsorption process (Salleh et al. 2011). Then, a decrease in the efficiency with the increase in dose may be due to pore blocking, aggregation, and competitive adsorption. Hence, the optimal dose for the maximum removal efficiency would be 0.75-g/25 mL wastewater. The relative pH of the solution was steadily increased up to an adsorbent dose of 1.25-g/25 mL wastewater. For an adsorbent dose of 1.5-g/25 mL wastewater, pH was a little higher trend compared to dose increases. However, increasing the adsorbent dose into the wastewater, pH was increased. It might be the reason that adsorbents contain alkali earth metal e.g. calcium (Ca).

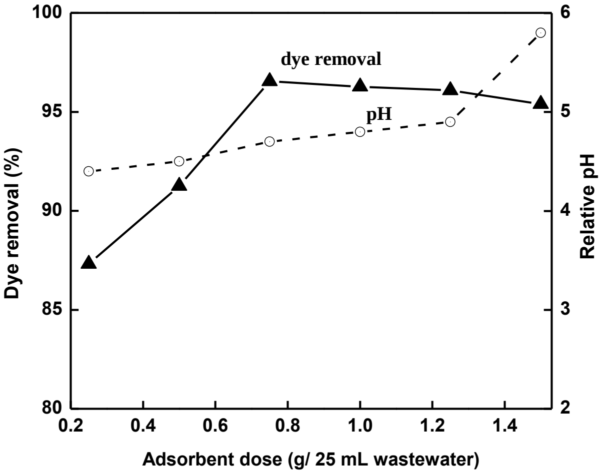


Figure 3: Effect of adsorbent dosages on dye removal efficiency from wastewater

3.3 Effect of stirring time

Figure 4 represents the dye removal efficiency at a specific stirring interval. For stirring times of 15, 20, 25, 30, 45, and 60 minutes, the percentage of dye removal was achieved at 96.27%, 96.42%, 96.90%, 97.09%, 96.60%, and 95.84%, respectively. Initially, extending the contact time up to 30 min, the dye removal efficiency was enhanced.

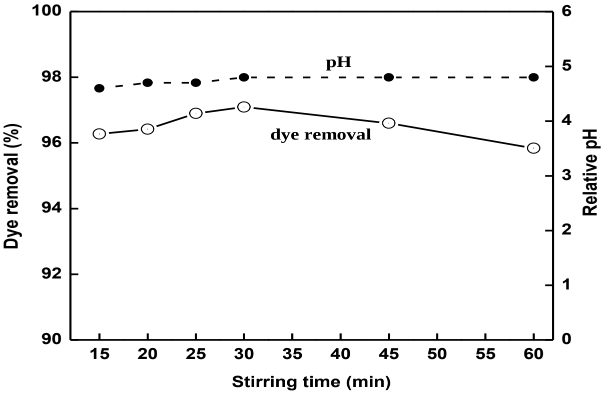


Figure 4: Effect of stirring time on dye removal efficiency from wastewater

However, beyond this point, the dye removal efficiency slowly declined. This drop could be attributed to bond breakage or formation during dye-adsorbent interactions and the disintegration of flocks facilitating dye removal. Another factor affecting decreased adsorption during prolonged stirring could be the formation of air pockets within the adsorbent bed, limiting surface area and contact time. Consequently, the optimal stirring time for maximal dye removal efficiency was found to be 30 minutes (97.09%). The relative pH of the solution concerning stirring time was almost the same.

3.4 Effect of settling time

Figure 5 depicts the dye removal efficacy at a specific settling time. Dye elimination percentages at 4, 6, 8, 12, 16, 20, 24, and 30 h were 81.45%, 86.00%, 89.62%, 93.08%, 93.17%, 95.05%, 94.51%, and 93.53%, respectively. It is seen that with extending the settling time, dye removal efficiency was gradually increased up to 12 h, then dye removal efficiency increases was very slow. The dye removal at 20 h was obtained at 95.05%. Afterwards, the dye removal efficiency was slowly decreased. This decline may be due to the redistribution of inadequately physically adsorbed dye molecules on the adsorbent surface and the interaction of other chemicals in the supernatant, leading to the solution cloudiness. Hence, the optimal settling time for the maximum dye removal efficiency was determined to be 20 h. The solution's relative pH was not significantly changed. For settling times 4 and 30 h, the pH difference was only 0.2.

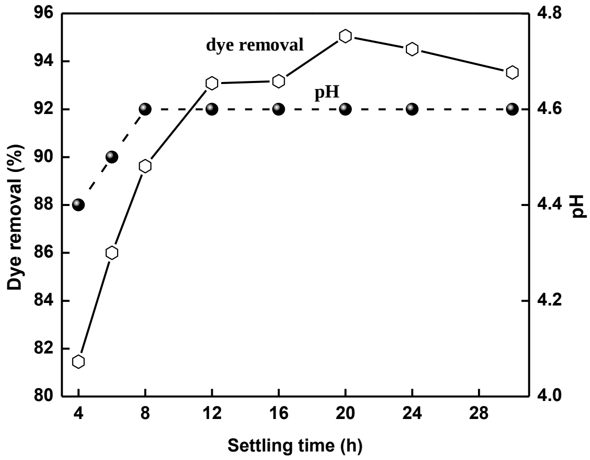


Figure 5: Effect of settling time on dye removal efficiency from wastewater

3.5 FTIR analysis

Figure 6 demonstrates the FT-IR spectrum of pure and dye-loaded thermally activated adsorbent. The FT-IR analysis of the thermally activated adsorbent, both pure and dye-loaded adsorbent revealed significant changes in functional groups.

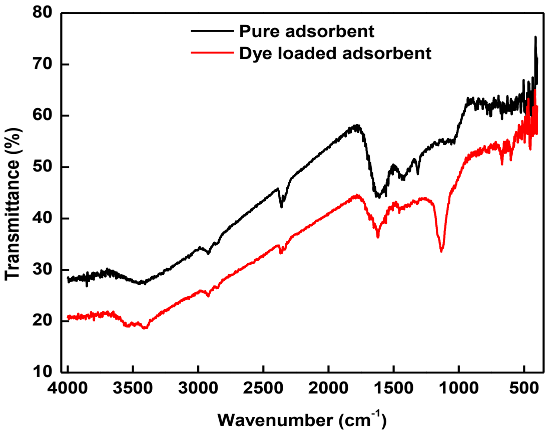


Figure 6: FT-IR spectrum of thermally activated pure adsorbent and dye-loaded adsorbent

Before treatment, absorption bands were observed at 571 cm^{-1}, 609 cm-1, 758 cm^{-1}, 872 cm^{-1},1315 cm^{-1}, 1559 cm^{-1}, 1639 cm^{-1}, and 3406cm^{-1}. After treatment, new absorption bands appeared at 548 cm^{-1}, 621 cm^{-1}, 669 cm^{-1}, 1068 cm^{-1}, 1135 cm^{-1}, 1171 cm^{-1}, 1210 cm^{-1}, 1622 cm^{-1},1790 cm^{-1}, and 3414 cm^{-1}. Notably, the peaks in the ranges of 550-850 cm^{-1} (R-X, alkyl halide), and 3200-3550 cm^{-1} (O-H, alcohol or phenol) remained unchanged. These shifts in absorption bands suggest alterations in functional groups, with new peaks corresponding to S=O, C-N, R-COO-R', R-O-R', -C=C-, and R-COOH. These changes are indicative of surface modifications facilitating adsorption. The adsorption process primarily involves hydrogen bonds, electrostatic bonds, and chemisorption. These findings affirm the adsorption capability of the thermally activated adsorbent for the treatment of dyeing wastewater.

3.6 SEM and EDX analysis

Figure 7 illustrates the SEM images of pure adsorbent and dye-loaded adsorbent. There is a significant difference between the pur adsorbent and dye-loaded adsorbent. For the pure adsorbent Figure 7(a), the material exhibits a rough, irregular surface with visible pores and cracks, which can potentially serve as an adsorption site for dye molecules. However, after treatment in Figure 7(b), the thermally activated carbon presents a notably smoother and more uniform surface, suggesting effective dye molecule adsorption and an increased adsorption capacity.

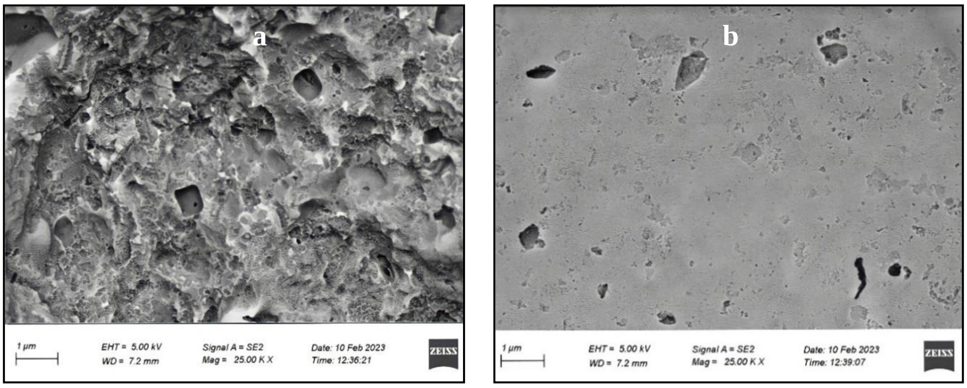
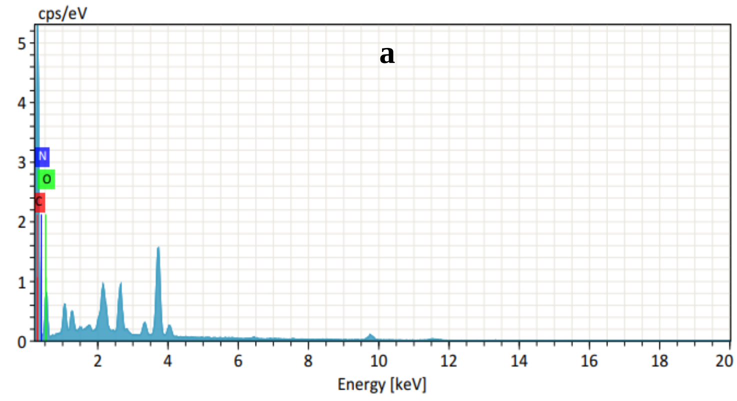
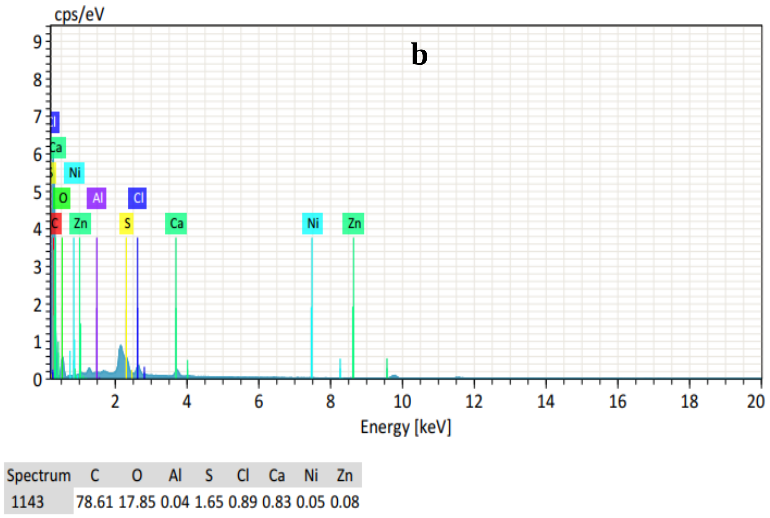


Figure 7: Pure adsorbent *Tamarindus indica* leaves adsorbent (a) dye load *Tamarindus indica* leaves adsorbent (b)

Figure 8 demonstrates EDX analysis of pure and dye-loaded adsorbent. Figure 8(a) represents the presence of carbon (C), nitrogen (N), and oxygen (O) in the pure adsorbent. The maximum percentage of adsorbent is C (55.86%). After dye adsorption in Figure 8(b), aluminium (Al), sulfur (S), chlorine (Cl), calcium (Ca), nickel (Ni), and zinc (Zn) are detected, further confirming the adsorption process. These findings are crucial for optimizing activated carbon applications in various fields, including air and water purification.



Spectrum	C	N	O
1142	55.86	21.16	22.98



Spectrum	C	O	Al	S	Cl	Ca	Ni	Zn
1143	78.61	17.85	0.04	1.65	0.89	0.83	0.05	0.08

Figure 8: EDX analysis pure adsorbent *Tamarindus indica* leaves adsorbent (a) dye load *Tamarindus indica* leaves adsorbent (b)

3.7 Characteristics of wastewater and comparison with standards

Table 2 shows the outcome of this study under optimal circumstances. The physicochemical parameters-pH, TDS, EC, salinity, turbidity, BOD, and COD of the raw dyeing wastewater were 3.9, 4278 mg/L, 8.87 mS/cm, 5.6 ppt, 2510 NTU, 2166 mg/L, and 38169 mg/L, respectively. After treatment at optimized conditions, the physicochemical parameters e.g. pH, TDS, EC, salinity, turbidity, BOD, and COD of the treated wastewater were 5.1, 6885 mg/L, 17.2 mS/cm, 8.4 ppt, 9.53 NTU, 425 mg/L, and 21490 mg/L, accordingly. During the adsorption process, the organic and inorganic contaminants were adsorbed on the thermally activated *Tamarindus indica* leaves adsorbent resulting in a reduction of turbidity, Biochemical Oxygen Demand (BOD), and Chemical Oxygen Demand (COD) achieved by 99.62%, 80.38%, and 43.70%, respectively. Although some of the parameters- EC, TDS, and salinity were increased. This might be the mineral from the adsorbent.

Table 1: Comparison of wastewater characteristics with standards

Parameters	**Raw dyeing wastewater**	**Treated dyeing wastewater**	**(ECR, 2023)**	**Unit**
pH	3.9±0.2	4.8±0.13	6-9	-
TDS	4278±9.5	6885±9.3	2100	mg/L
EC	8.87±2.3	17.2±3.5	1.2	mS/cm
Salinity	5.6±1.8	8.4±2.01	-	ppt
Turbidity	2510±6.4	9.53±3.4	50	NTU
BOD	2166±10.7	425±4.5	200	mg/L
COD	38169±16.8	21490±25.9	400	mg/L

4. CONCLUSION

This study has demonstrated the potential use of *Tamarindus indica* leaves adsorbent as a sustainable and cost-effective adsorbent for treating dyeing wastewater generated in the tannery. Except for chemical impregnation only thermally activated adsorbent has dye removal efficacy. Besides, the equipped *Tamarindus indica* leaves adsorbent and removes other pollutants from the wastewater. The dye removal adsorption was confirmed through SEM images, EDX, and FTIR analysis. The maximum dye removal efficiency was achieved at 97.09%. Additionally, the study reduced turbidity, $BOD_{5,}$ and COD levels by 99.62%, 80.38%, and 43.69% respectively. Overall, these findings suggest that *Tamarindus indica* leaves adsorbent can be an effective and eco-friendly bio-adsorbent for the treatment of dyeing wastewater emitted from the tannery. Further research in this area could explore the practical applications of this sustainable approach to mitigate the impact of tannery effluents on the environment.

ACKNOWLEDGEMENTS

The authors are grateful to the related personnel for providing facilities for conducting research work at the Department of Leather Engineering, Khulna University of Engineering & Technology (KUET), Khulna-9203, Bangladesh for granting the required laboratory and other resources.

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