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Dye removal from tannery wastewater by adsorption-coagulation using *Moringa oleifera* bark charcoal

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ABSTRACT
In the tannery, dyeing is an essential post-tanning operation where coloring substances are applied to make the leather attractive and adaptable for fashion styles. The dyestuffs used in leather processing vary depending on the product range required along with the states of the emerging market. Mostly, acid dye is used in the leather industry. After dye fixation, a good fraction of dye remains unfixed that has to be rinsed out to prevent dye transfer from the leather. The released dyeing wastewater into the environment makes the effluent highly colored, increases biochemical oxygen demand (BOD), and chemical oxygen demand (COD), impairs photosynthesis and inhibits plant growth. Conventional techniques of effluent treatment have failed to provide effective results because of the higher cost and less efficiency. Even biological treatment may not be efficient in dye removal, especially in tannery wastewater because of higher dye concentration. In this investigation, an approach was made to eradicate dye from the tannery wastewater of composite dye with the *Moringa oleifera* bark charcoal adsorbent. The *Moringa oleifera* bark was burned in the furnace at 500°C and then batch-wise dye removal from the wastewater was conducted through the adsorption-coagulation process. The charcoal effectiveness for dye removal was analyzed by investigating relative pH, charcoal dose, contact time, dilution factor, isotherm model, and adsorption kinetics. Before and after use, Fourier Transform Infrared (FT-IR) spectroscopy was performed to differentiate the active components of the surface of the charcoal. The FT-IR spectrum indicated the shifting in bonds of the functional groups because of the dye adsorption. At optimal conditions, the dye removal efficiency was obtained at 81.9%. The use of native *Moringa oleifera* bark charcoal adsorbent could be a choice to remove dye from industrial tannery wastewater.

Keywords: Tannery, Dyeing wastewater, Environment, Adsorbent, *Moringa oleifera* bark

1. Introduction

Dyeing is one of the most frequent operations of the leather industry needed to provide the final appearance of a product. Dyes for leather coloration have been one of the most primitive uses to produce the product aesthetic and engage its user. Most of the dyes are synthetic dyes [1]. The unfixed dyes are released into the environment as wastewater that contains a huge amount of complicated ions. A great aquatic environmental issue with dyes is the absorption and reflection of sunlight in the water. Dyes are highly toxic and may even be carcinogenic to microbial pollution and mammalian biology. As a result, dyestuffs get into the alimentary chain and reach human beings [2]. Hence these are the most urgent to remove from industrial effluent discharge before running into water bodies.

In environmental pollution and protection, adsorption is relevant concerning water and wastewater treatment. In recent years, researchers investigated various techniques for dye removal from wastewater using activated carbon adsorption, electrochemical, ultrasonic technique, membrane technique, and reverse osmosis [3]. Indian sawdust was used to remove methylene blue from the solution [4]. Zeolite was used as an adsorbent to remove ionic dye from the aqueous dye solution. Reusing sludge is also being used as an active coagulating agent in textile dye removal. At present, tertiary treatments like nanofiltration or ozonation are also conducted after the coagulation-flocculation or adsorption process to remove almost 100% of the dye from wastewater [5]. But all the specified methods are too expensive and technology investment operation.

Many researchers have used adsorbents to remove dyes like banana peel [6], lemon peel [7] orange peel [8], rice husk [9], wood apple shell [10], etc. Agricultural byproducts were used in the removal of dye [11]. Coagulation/flocculation/adsorption/ozonation techniques were used to this extent [12]. Coagulation chemical methods were also used to remove dye from wastewater [13].

In this study, an investigation was made to adsorb dye from tannery wastewater with the *Moringa oleifera* (also known as 'moringa' or 'drumstick tree') bark as adsorbent. This treatment was conducted following the adsorption-coagulation process. This process is very simple and easy for any worker to proceed with or without creating any harm to the environment. Moreover, the adsorbent (*Moringa oleifera* bark) is available in Bangladesh and most foreign countries.

2. Materials and methodology

The *Moringa oleifera* bark was collected and prepared adsorbent to apply for dye removal from industrial wastewater.

2.1 Materials collection

The moringa bark (Fig.1) was collected from the roadside of the Jashore-Khulna highway. Analytical-grade chemicals were purchased from a local scientific store. The dye wastewater shown in Fig.2 was collected from SAF Leather Industry, Jahsore. The dye wastewater contains 2.5% Brown MFR, 0.5% Yellow-G, 1.5%

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Orange OR, 0.5% SF Havana, and 0.5% Beige- E dyes into it. Further information about the dyes is charted in Table 1.

Table 1 Characteristics of the dyes used in this study.

Dye	Comm. Name	Chemical formula	MW	Source
Brown MFA	Fat Brown R	$RC_{16}H_1$	262.4	Adorn
Yellow-G	Acridine Yellow G	$C_{15}H_{15}N_3 \cdot HCl$	273.8	Merck
Orange OR	Disperse Orange	$3O_2NC_6H_4N=NC_6H_4NH_2$	242.2	Merck
SF Havana	Havana	$C_6H_4(NH_2)_2$	106	S.F

Comm. Name=Commercial name,
MW= Molecular weight in g/mol

Fig.1 *Moringa oleifera* bark after sun drying

Fig.2 Raw dying wastewater

2.2 Adsorbent preparation

Firstly, the collected moringa bark was chopped and then sun-dried for 15 days. After that, the bark was kept in an oven for 24 hours at 105ºC due to moisture control and then kept in a desiccator for 24 hours.

Fig.3 Prepared adsorbent

Later, the bark was burned on a furnace for 3 hours at 500°C. When the burner cooled down then the adsorbent was taken off and ground and sieved. About 100 g of adsorbents were made from moringa bark represented in Fig.3.

2.3 Reagents

The reagents that are used in experimental work are:

Lime was used to adjust different doses of pH. Aluminum sulfate was used as a coagulant agent, sodium thiosulfate, sulfuric acid, alkaline azide solution, and manganese sulfate solution, and the starch indicator was used for dissolved oxygen (DO) determination. Potassium dichromate, sulfuric acid, ferrous ammonium sulfate, and ferroin indicators were used for chemical oxygen demand (COD) determination.

2.4 Experimental system for dye removal

Adsorbent and coagulant both were used to remove dye from the tannery wastewater. At first, the dye wastewater was treated with lime for pH adjustment to 7.5. Then, the sample solution was made by diluting the raw dye wastewater. The adsorbent was mixed with the wastewater and stirred at 250 rpm for a few minutes then settled down. After that $Al_2(SO_4)_3$ was added as a coagulant to the mix and again stirred at the same rpm and settled down. The dye and other particles were adsorbed and coagulated and sedimentation occurred thus the dye was removed from the wastewater.

2.5 Application process

Following the experimental process, absorbance, pH, electrical conductivity (EC), salinity, and total dissolved solids (TDS) was checked. DO and COD of the raw dye wastewater and the optimized sample were determined. For each sample, the data has been taken three times and the mean value has been calculated.

2.6 Determination of absorbance

The absorbance was measured by a 4802 UV/ Vis double-beam spectrophotometer (4802, UNICO, Germany). At first, the machine was warmed up for 15 minutes and after that, the peak wavelength of the wastewater was determined. The peak wavelength was 600 nm. Then the wavelength was selected and set up. Then two tubes were filled with distilled water and blanking has to done. After that in one tube, the sample has to be taken and the absorbance was measured.

2.7 Determination of pH

The pH of raw dye wastewater and treated liquor was measured by calibrated pH mater (UPH-314, UNILAB, USA).

2.8 Determination of TDS, EC & Salinity

After calibrating the conductivity meter (CT-676, BOECO, Germany) with a standard solution TDS, EC and salinity were measured.

2.9 Determination of dissolved oxygen (DO)

The test was performed according to APHA standard method 5210B [14], diluted sample was prepared and placed in the biochemical oxygen demand (BOD) bottle of 300 mL. Phosphate buffer, magnesium sulfate, and calcium chloride & ferric chloride were added. Then pH was adjusted by acid or alkali solution and 100 mL solution was taken in a conical flask and 2-3 drops of the indicator were given and titrated against sodium thiosulfate. Thus, the initial and the treated DO were measured.

2.10 Determination of chemical oxygen demand (COD)

The test was performed according to APHA standard method 5220 C [14], diluted raw effluent of 2.5 mL was taken in a culture tube and 1 mL of potassium dichromate, 3.5 mL of concentrated H_2SO_4 was poured into it. Then it was set in the digester for 2 hours at 150°C. After that, it was cooled and taken in a conical flask. 1-2 drops of ferroin indicator were given and titrated against 0.1 N ferrous ammonium sulfate solutions. Then, COD (mg/L) is measured following Eq. (1):

$$\mathrm{COD} = \frac{\{(\mathrm{Blank} - \mathrm{Sample}) \times 0.1 \times 1000\}}{\mathrm{Volume\ of\ sample}} \qquad (1)$$

3. Results and discussion

The optimum removal condition was analyzed through the effect of pH, dose, contact time, and dilution factor. The wastewater characterization showed BOD, COD, salinity removal efficiency of 81.29%, 83.44%, and 28.91%, respectively. The EC and TDS increased after adsorption possibly due to the inclusion of dissolved matter from the adsorbent. Moreover, the isotherm and kinetics of the study were also investigated.

3.1. Effect of pH

The effect of pH on dye adsorption onto moringa bark is presented in Fig.4.

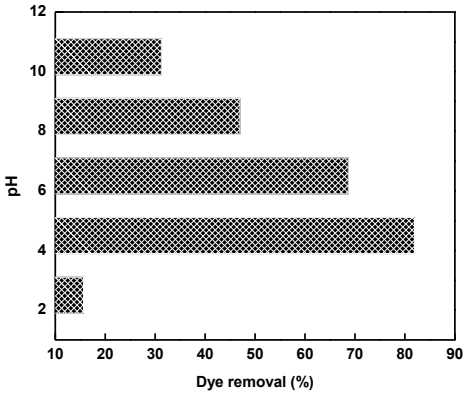

Fig.4 Effect of pH on the removal of dye

The maximum adsorption capacity (81.92%) was obtained at pH 4.5. After pH 4.5, the adsorption capacity was reduced sharply. It could be seen that the pH of the solution has a certain influence on the adsorption of composite dye removal from wastewater. Adsorption efficiency depends on the pH because of its changing power of the degree of melting properties [15]. The activity of the charcoal and the adsorption capability depends on the zero electric charge point [16].

A comparison with the previous study is shown in Table 2. It can be seen that this study provides a better removal efficiency at a lower pH. Adak et al. 2005 [17] and Kumar et al. 2005 [18] explained that a higher pH was required to remove the dye particles from the wastewater. Thus, in this case, additional pH adjustment was required to change the pH of the raw wastewater. However, in this investigation, better removal efficiency was achieved without any pH modification of the wastewater.

Table 2 Comparison with the previous study.

Reference	pH	Dye removal (%)
Adak et al. 2005 [17]	10.8	80
Kumar et al. 2005 [18]	8.0	45
This study	4.5	81.92

3.2. Optimal contact time

The dye removal efficiency was optimized by observing at a regular time interval which is shown in Fig.5. It indicates that the dye removal for 5 min, 10 min, 15 min, 20 min, and 25 min was 14.63%, 36.58%, 80.73%, 60.24%, and 33.73%, respectively. It can be seen that at first up to 15 minutes the removal efficiency of the dye was raised with the increase in contact time. But after that, it decreases with the increase of the contact time. Thus, it was decided that 15 minutes was the optimal time for maximum removal efficiency of dye.

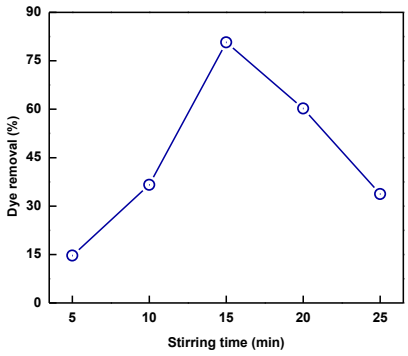

Fig.5 Effect of contact time on the removal of dye

3.3 Optimal dose

The amount of adsorbent required is an important parameter for determining the adsorbent capacity for a given amount of adsorbent in an operating condition. Fig.6 explains the removal efficiency with the adsorbent dose. It represents the removal efficiency for the dose of 0.3 g, 0.5 g, 0.7 g, 0.9 g, and 1.1 g were 10.12%, 60.97%, 32.92%, 24.39%, and 13.47% respectively.

Here we observed that up to 0.5 g of dose the removal efficiency was increased with the increase of dose and then the efficiency decreased. The optimal dose for the maximum removal efficiency was taken to be 0.5 g.

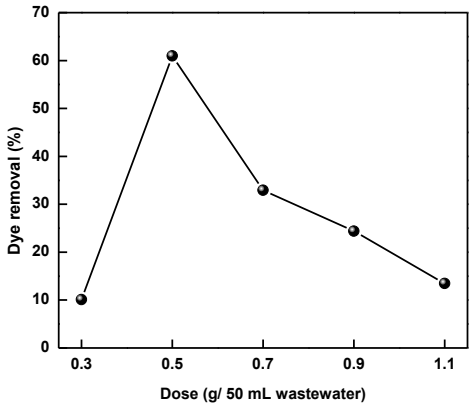

Fig.6 Effect of adsorbent dose on dye removal efficiency

3.4 Optimal dilution factor

Fig.7 represents that the removal efficiency for dilution of 10 times, 20 times, 30 times, 40 times, 50 times, and 60 times were 48%, 25%, 54%, 60%, 83%, and 10% respectively. Initially, the adsorbate was greater than the adsorbent required, and gradually with the increasing of the dilution factor balanced with the adsorbent. At 50 times dilution, the activity of the adsorbent was maximum.

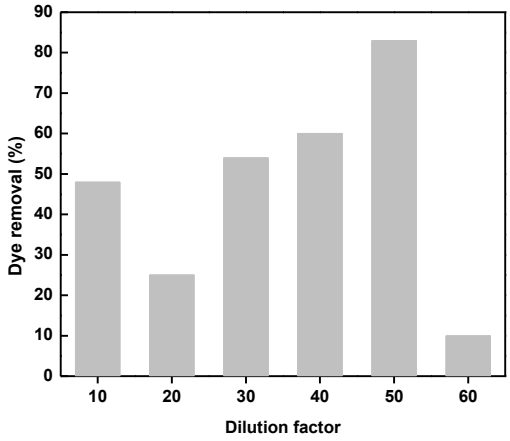

Fig.7 Effect of dilution factor on removal efficiency of dye from wastewater

3.5 Adsorption isotherm

Langmuir and Freundlich's isotherm models have described the adsorption mechanism and the maximum adsorption capacity at equilibrium conditions. The linear form of Langmuir isotherm is expressed as the following Eq. (2) and (3):

$$\frac{C_e}{Q_e} = \frac{1}{Q_m \times b} + \frac{C_e}{Q_m} \qquad (2)$$

$$R_L = \frac{1}{(1 + C_m b)} \qquad (3)$$

Here, q_e= amount of adsorbed dye per unit mass of adsorbent (mg/g), C_e= equilibrium dye concentration (mg/L), q_m= adsorption capacity (mg/g), b= Langmuir constant (L/mg), R_L= separation factor. The value of R^2, and (R_L) were found at 0.887, and 0.0123 for the linear Langmuir isotherm model shown in Fig.8.

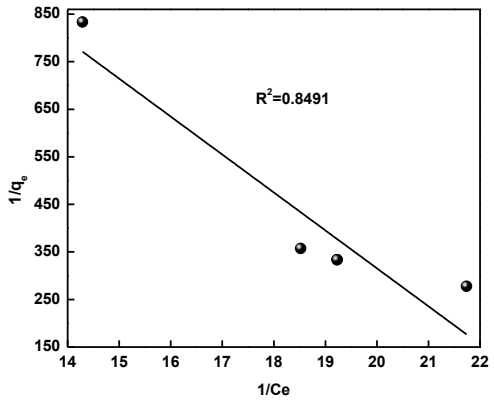

Fig.8 Langmuir isotherm model of dye adsorption

The Freundlich's isotherm model represents the adsorption of dye molecules on a heterogeneous surface by the multilayer adsorption process. The expression of this model is given below as Eq. (4):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (4)$$

Here, K_F=adsorption capacity, 1/n =adsorption intensity. The graphical representation of $\log q_e$ and $\log C_e$ showed that the plot was a straight line with an intercept of $\log K_F$ and a slope of 1/n (Fig.9).

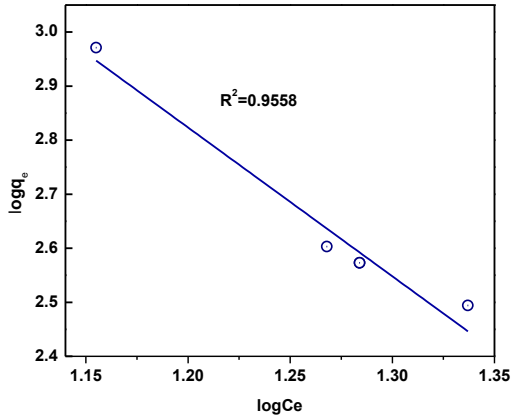

Fig.9 Freundlich isotherm model of dye adsorption

The value of the correlation coefficient, R^2 was found 0.966 revealing the heterogeneity of the moringa bark adsorbent surface and multilayer adsorption process. The Freundlich isotherm model best fitted the adsorption mechanism.

3.6 Adsorption kinetics

Pseudo-first order and pseudo-second reaction models are used to interpret dye adsorption onto adsorbent [19]. In many studies, adsorption kinetics was described by pseudo-first-order using the Lagergren Eq. (5):

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1 t}{2.303}\right) t \qquad (5)$$

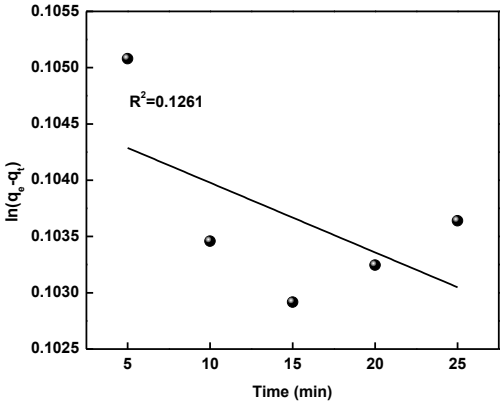

Fig.10 Pseudo-first order of *Moringa oleifera* bark for dye removal

Pseudo-second-order adsorption kinetics was explained using the following equation (6):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^{\,2}} + \left(\frac{1}{q_e}\right) t \qquad (6)$$

Here, q_e = amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q_t = amount of solute adsorbed at any time (mg/g), and K_1 = adsorption constant for the pseudo-first-order reaction, and K_2 = adsorption constant for the pseudo-second-order reaction.

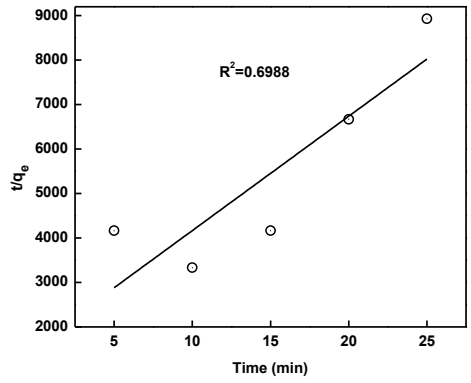

Fig.11 Pseudo-second order of *Moringa oleifera* bark for dye removal

Thus, the experimental data fitted well with the pseudo-second-order kinetic model (R^2 value 0.774) shown in Fig.11, rather than the pseudo-first-order showed in Fig.10. q_e and k_2 were established from the slope and intercept of the plot. The parameters related to both kinetic models were shown in Table 3.

Table 3 Summary adsorption kinetics and isotherm contents for composite dye adsorption

Adsorption kinetic		Adsorption isotherm	
Pseudo 1st order	Pseudo 2nd order	Langmuir isotherm	Freundlich isotherm
R^2 = 0.3152	R^2 = 0.7741	R^2 = 0.8871	R^2 = 0.9661
		R_L= 0.0123	R_L= 21.217

3.7 FT-IR spectroscopy analysis

The IR spectrum shown in Fig.12 of moringa bark showed peaks of the raw sample (dye wastewater) at 588.72 cm^{-1}, 829.95 cm^{-1}, 1025.11 cm^{-1}, 1260.74 cm^{-1}, 1751.12 cm^{-1}, and 3448.65 cm^{-1} that represented the existence of C-Br Stretching of alkyl halides, C-Cl Stretching of alkyl halide, Ethers=C-O-C= symmetric stretching, C-H waging of alkyl halides, esters of C=O stretching and alcohol and phenols of OH stretching.

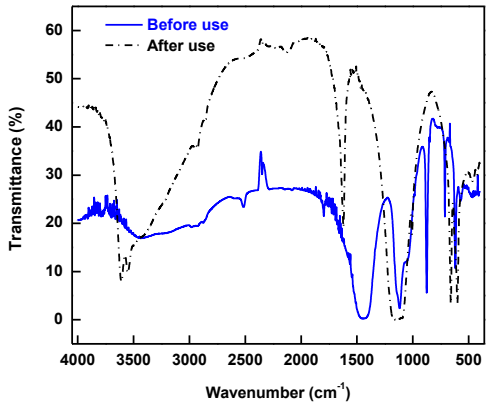

Fig.12 FT-IR spectrum of raw adsorbent and after dye adsorption

However, the addition of new peaks was found after adsorbent (moringa bark charcoal) activation at regions 680.95 cm^{-1}, 1511.76 $cm^{-1,}$ 1745.67 cm^{-1}, 3745.12 cm^{-1},2475.56 cm^{-1} that represents the functional groups C-S linkage, phenol ring, C=O stretching, OH groups of amide and R-COOH and many more groups are erased. Finally, the presence of the peak at 500.13 cm^{-1}, 650.86 cm^{-1}, 1446.02 cm^{-1}, 1511.76 cm^{-1}, 1745.67 cm^{-1}, 2475.56 $cm^{-1,}$ and 3745.12cm^{-1} confirmed the characteristic peaks of moringa bark after dye adsorption.

4. Conclusion

The most available *Moringa oleifera* bark can be used as an adsorbent for the treatment of composite dye wastewater released from tannery industry. The adsorption process was optimum at pH 4.5 with a dose of 10 g/L and 15 min contact time. Maximum 81.92% of dye removal was achieved at ambient temperature with BOD, COD, and salinity removal efficiency of

81.29%, 83.44%, and 28.91%, respectively maintaining the optimum parameters. Moreover, the isotherm and kinetics analysis indicate that the adsorption process follows multilayer second order reaction following Freundlich isotherm and Pseudo second order kinetics model. This study could be adopted to treat the dyeing wastewater from tannery industry at a lower cost.

5. References

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