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Efficacy of Acid-treated Sawdust in Decolourization of Tanning Wastewater

M. Alhassan^{1*} M. Suleiman¹ A. A. Isah² A. G. Abdulrashid¹ Y. Nasiru¹ A. Bello¹

1. Department of Chemistry, Sokoto State University, Sokoto, Nigeria

2. Department of Chemistry, Usmanu Danfodiyo University, Sokoto, Nigeria

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ABSTRACT

Colour removal from dye-bearing effluent is a serious challenge due to the difficulty in treating such wastewater by conventional treatment methods. The present investigation explores the decolourization of contaminated wastewater using acid-activated sawdust as an adsorbent. The physicochemical properties of wastewater samples labelled A, B, and C viz average temperature; pH; electrical conductivity; and total dissolved solids were determined using standard methods to be 302.63; 6.1; 284.47 $\mu\text{S}/\text{cm}$; 35116.66 mg/L respectively. Colour removal efficiency of the adsorbent was studied under variable conditions (contact time, rate of agitation, loading). Experimental results demonstrated that the sawdust adsorbent has a significant capacity for colour removal from tannery effluent. There was significant variation in the absorbance of the treated samples. Adsorbent dose, stirring rate, and contact time were found to be directly proportional to colour removal while pH variation of the samples show that the effluents became less alkaline (slightly acidic) after decolourization.

1. Introduction

Diverse environmental and anthropogenic pollution have been posed by Chemical industries producing waste effluents for over a decade. These effluents are a major threat to the environment as they appreciably affect green industrial activities and are unquestionably one of the most important problems of industrialization^[1].

Tanning, the chemical process that converts animal hides and skin into leather and related products, is usually achieved employing tanning agents and the process generates highly turbid, colored, and foul-smelling wastewater. The major components of the effluents include large quantities of solid waste, sulfides, volatile organic compounds, suspended solids like animal hair, etc^[2].

The uncontrolled release of tannery effluents (containing high COD, BOD levels, trivalent chromium, sulfides, sodium chloride, calcium, magnesium, organics, and other toxic ingredients) to the natural water bodies affect the plant and animals, the ecosystem and increases the health risk of human beings^[3,4].

Development of profitable and economically feasible way of curtailing the effects of tannery effluents cannot be overemphasized especially using local waste materials as precursors. Literature by^[5-7], reported an estimated production capacity of 1.8 billion metric tons of leather yearly, with a larger part of the product processed in Africa and Asia, factored by the high labour intensity involved in the manufacture and treatment of leather.

**Corresponding Author:*

M. Alhassan,

Department of Chemistry, Sokoto State University, Sokoto, Nigeria;

Email: mansuralhassan@gmail.com

According to reports of^[8,9], colour removal in wastewater is one of the most difficult challenges to be addressed by textile finishing, tanning, dye manufacturing, pulp, and paper industries, among others.

Over the last few years, adsorption has gained importance as a separation, purification, and or detoxification process on an industrial scale. It has been used to purify^[2], decolorize^[6-8], detoxify^[12], deodorize^[2], separate^[4], concentrate^[5], and recover the harmful products from liquid solutions and gas mixtures^[9].

Aerobic digestion is based on consumption of organic matter and its degradation to produce single cell protein, CO₂ and water. Anaerobic digestion (AD) incorporates a series of interdependent biochemical reactions through the metabolic pathways of anaerobic microorganisms in the absence of air (oxygen). It is used as a pre-treatment step to improve efficiency and valorize organic mill waste (OMW) to achieve up to 80-85% COD, 59-87% reduction in toxicity, 65-95% removal of total phenols etc. Accordingly, Sungur and Özkan^[10], considered adsorption processes one of the best choices compared to other methods due to its convenience, ease of operation, simplicity of design, high efficiency, and wider applicability in water pollution control.

2. Experimental

2.1 Sample Collection and Treatment

The sawdust was collected from a local sawmill in Sokoto State. It was carefully screened, washed several times with distilled water to remove dirt (sand dust), colour and other surface adhering particles, filtered, dried in a thermostatic oven at 105 °C^[26].

The dried sample was ground to smaller particles size with a mechanical blender and used for the preparation of the adsorbent. The tannery wastewater that was used was collected from a local tannery located at Tudun Wada and Bauchi Road areas of Sokoto State. The method of collection was by direct dipping of a 2 L plastic bottle into different depths of the effluent. The bottle was removed, covered, and brought to the laboratory for analysis. Adopting the method reported by^[27] the temperature, pH, total dissolved solids and conductivity were determined as soon as the samples were brought to the laboratory. The samples were used as obtained without any treatment.

2.2 Preparation of Adsorbent

The method reported elsewhere^[2] was adopted for preparing the adsorbent. Powdered sawdust (150 g) was accurately weighed using an analytical balance and transferred into an empty 1000 cm³ beaker where 500

cm³ of 5 % sulfuric acid (H₂SO₄) solution was added. The mixture was placed on a magnetic stirrer/heating mantle for continuous stirring and heating at 32 °C for 24 h until a thick slurry was obtained. The slurry (acidified sawdust) was washed (continuously) with distilled water until a weakly acidic pH of more than 5. The acid-treated sawdust was dried in a thermostatic oven at 50 °C overnight and then stored in a glass container before further investigations.

2.3 Decolourization

Tannery wastewater was used to evaluate the effectiveness of the acid-modified sawdust for decolourization. The temperature, pH, conductivity, total dissolved solids, and colour of the tannery effluents were determined before and after the adsorption process. The physical properties of the effluent viz temperature, pH, and conductivity were analyzed using a mercury thermometer, digital pH meter (Model KL-031), and a conductivity meter respectively. Total Dissolved Solid was tested as per APHA standards. The adsorption studies were carried out at variable contact time (seconds), adsorbent dosage (g), and agitation speeds (revolutions per minute, rpm). Decolourization of the wastewater was carried out using the batch method as described elsewhere^[28].

2.4 Adsorption Experiments

Effect of Variable Adsorbent Dosage

Wastewater sample (100 cm³ each) was accurately measured and transferred into 3 containers (500 cm³ beakers) labelled A, B, and C. Adsorbent dosage of 5 g, 10 g, and 15 g at a constant agitation speed of 120 rpm and contact time of 300 seconds were added to A, B, and C respectively. The mixtures were filtered and the filtrate was analyzed for the extent of decolourization.

Effect of Agitation Speed /Stirring Rate

To a similar set of beakers labelled A, B, and C, having 100 cm³ each of wastewater maintained for 300 seconds, containing 10g of adsorbent each, the stirring rate was varied to 100 rpm, 120 rpm, and 140 rpm in A, B and C respectively. The mixture was filtered and the filtrates were analyzed for the extent of decolourization.

Effect of Contact Time

Wastewater samples (100 cm³) placed in beakers labelled A, B, and C containing 10 g each of the adsorbent stirred at 120rpm were maintained for 10, 20, and 30 minutes respectively.

The absorbance of the tannery wastewater was obtained

using a UV-VIS spectrophotometer (Spectrum lab 23A) at a pre-optimized λ_{max} (wavelength corresponding to maximum absorption) as described by [1]. After equilibration and filtering of the adsorbent, the adsorbate solutions were examined for the extent of decolourization through the differences in absorbance.

3. Results

3.1 Result of Physicochemical Parameters

The result of physicochemical parameters of the tannery wastewater before and (after) decolourization is presented in Table 1.

Table 1. Physicochemical Parameters of Tannery wastewater

Parameter	Samples			SPL (WHO, 2002)
	A	B	C	
Temperature (K)	302.5 (296.7)	302.8 (299.5)	302.6 (296)	N/A
pH	5.2 (5.78)	5.3 (5.96)	7.8 (8.77)	6.5 - 9.5
Electrical Conductivity ($\mu\text{S/cm}$)	15.62 (25.89)	15.98 (32.76)	821.83 (850.01)	1200
Total Dissolved Solids (mg/L)	53470 (5005)	23230 (5235)	28650 (5306)	2100
Colour	Brown (Cloudy)	Brown (Cloudy)	Brown (Cloudy)	Light Permeable

SPL: Standard Permissible Limit [1]; values before and (after) adsorption.

3.2 Results of Predetermined λ_{max} /Absorbance

Table 2 presents the absorbance of samples at a predetermined wavelength (630 nm).

Table 2. Sample Absorbance at Predetermined Wavelength

Sample	λ_{max} (nm)	Absorbance
A	490 (204)	2.232 (0.929)
B	410 (186)	2.146 (0.973)
C	490 (201)	0.094 (0.038)

Values before and (after) decolourization.

3.3 Result Variable of Adsorbent Dosage

Table 3 shows the absorbance (at 490 nm) of the various wastewater samples after treatment.

Table 3. Absorbance of Samples with Variable Adsorbent Dosage

Adsorbent Dosage (g)	Absorbance		
	A	B	C
5	1.873	1.913	0.04
10	1.635	1.649	ND
15	1.216	1.107	ND

ND= Not Detected

3.4 Result of Variable Agitation

Table 4 presents the absorbance of the wastewater samples after treatment, at variable agitation speed.

Table 4. Absorbance of Samples at Variable Agitation Speed

Agitation Speed (rpm)	Absorbance		
	A	B	C
100	1.220	1.121	ND
120	1.209	1.101	ND
140	1.188	1.098	ND

ND= Not Detected

3.5 Result of Variable Contact Time

The absorbance (at 490 nm) of the various wastewater samples after treatment, by varying the contact time at an agitation speed of 120 rpm and constant adsorbent dosage of 10 g is presented in Table 5.

Table 5. Effect of Contact time at 120 rpm and Adsorbent Dosage of 10 g

Contact Time (min)	Absorbance		
	A	B	C
10	1.162	1.083	ND
20	1.137	1.049	ND
30	1.121	1.037	ND

ND=Not Detected

4. Discussion

The physicochemical characteristics of the tannery wastewater were reported in Table 1. The average recorded temperatures (K) before and after are 302.63 and 297.4 K respectively. This informs that clarity obtained leads to a decrease in suspended solids which makes the samples colder (lower temperature). The temperature obtained for samples A, B, and C in this study is higher compared to 296.9 K reported by [29]. The slight temperature difference showed a gradual appreciable pattern of decrease. In this study, average pH of 6.1 and 6.83 was recorded for the

samples before and after decolourization. However, [30] reported a pH value of 10.5, which is greater than the values recorded for the studied samples. The average pH value of 6.8 close to 7.8 recorded for sample C was also reported by [31]. This shows that the degree of acidity or alkalinity of tannery wastewater can vary greatly depending on the concentration of chemicals. The slight decrease in acidity in the pH values shows that the effluents became less alkaline (slightly acidic) after use. This confirms that they can be used for shaving hairs from the skins of animals. The pH values recorded for the wastewater in this study are within the standard discharge limit of 6.5 - 9.5 as shown in the standard permissible limit (SPL) by the World Health Organization (WHO).

The electrical conductivity (EC) recorded in $\mu\text{S}/\text{cm}$ for the samples are 15.62, 15.98, and 821.83 accordingly while 25.89, 32.76, and 850.01 for treated samples respectively. The values for electrical conductivity (EC) in samples A (25.89) and B (32.76) are lower compared to 850.01 recorded in sample C. However, the three samples recorded an EC value that is within the standard of 1200 $\mu\text{S}/\text{cm}$ stipulated for the discharge of wastewater into the environment. These values are low compared to 1348 $\mu\text{S}/\text{cm}$ recorded by [1]. The variation in the total electrical conductivity may be dependent on the different kinds of chemicals used in the different stages of the tannery processes. The amount of total dissolved solids (TDS) recorded for samples A, B and C are in the order 53470, 23230, and 28650 mg/L respectively. Reports by [2] and [31] presented lower TDS values of 14020mg/L and 1318 mg/L respectively. Compared to the values of 2100 mg/L reported as the standard discharge limit for wastewater, values in this finding are much higher, which means that the tannery wastewater samples were quite polluted; samples A B and C are brownish in colour but became cloudy after decolourization.

Table 2 presents the results of the predetermined wavelength (630 nm) of maximum absorption (λ_{max}) and their corresponding absorbance values. The extent of colour removal was assessed based on the difference in absorbance of the sampled wastewater. Distilled deionized water was used as blank while the different wastewater samples were analyzed at 630 nm. The observed λ_{max} for the respective samples may be due to the various absorbing molecules contained in the sample solution. Samples A and C recorded absorbance of 490 nm each, before adsorption and 204 and 201 nm respectively after adsorption. By this similarity in absorbance, samples A and C likely contain similar absorbing molecules (though at different concentrations) than sample B whose absorbance is 410

nm. The best condition for the colour removal of the wastewater samples is thus established from the initial absorbance obtained for the untreated tannery wastewater. This means that reduction in the absorbance obtained for the untreated wastewater samples was regarded as an indication of colour removal capability of the prepared adsorbent.

Table 3 displays the result of variable absorbance recorded for samples, A, B, and C, at stirring speed of 120 rpm for 5 min while the adsorbent dosages varied at 5, 10, and 15 g respectively. The colour removal efficacy of the prepared adsorbent was determined at a different dosage. It was observed that upon subjecting the samples to stated conditions and 5g of the adsorbent, the absorbance values obtained were 1.873, 1.913, and 0.04. When the adsorbent load was increased to 10 g, there was a decrease in the absorbance values for samples A and B to 1.635 and 1.649 while there was no absorbance detected for sample C. Further increase in the adsorbent loading resulted to a decrease in absorbance values while there was no absorbance for sample C. This shows that adsorbent dosage is a significant factor in the removal of colour from tannery wastewater.

A difference of 0.238 in absorbance is noticed when the dosage is increased from 5 g to 10 g and 0.419 from 10 g to 15 g for sample A respectively. For sample B, the difference in absorbance values is 0.264 and 0.542 respectively, when the load was increased from 5 g to 10 g and from 10 to 15 g.

The efficiency of the colour removal increased from 16.08 % to 45.52 % for sample A; from 10.86 % to 48.42 % while it increased from 57.45 % to 100 % for sample C with increasing adsorbent dosage from 5 to 15 g for all samples. According to Sharma and Uma [33], adsorption increased from 86.75 to 99.83 % with increasing adsorbent dose from 0.40 to 0.60 g. Accordingly, [34] also reported an increase in removal efficiency for MB dye with an increasing amount of adsorbent.

The effect of stirring speed on colour removal of the samples, A, B, and C was presented in Table 4. Different agitation rates of 100, 120 and 140 rpm at an adsorbent load of 10g for 300 seconds. 10 grams of adsorbent was used because it gave the best colour removal capability from the previous experiment. At the speed of 100 rpm, the absorbance values of 1.220 and 1.121 were recorded for samples A and B while sample C does not show any absorbance. When the stirring speed was increased to 120 rpm there was a slight decrease in the absorbance of the samples. A further increase in the stirring speed also resulted in a decrease in the values of the absorbance. Significant variation in absorbance values is attributed to

shooting up of the stirring rate from 100 rpm to 120 rpm and 120 rpm to 140 rpm.

Although the effects are not well pronounced as revealed by the present investigation, probably due to saturation and exhaustion of the binding sites on the adsorbents^[32-33].

Furthermore, the effect of contact time on colour adsorption by the prepared adsorbent was investigated. Table 5 shows the absorbance of samples A, B, and C, with an adsorbent load of 10 g at a stirring speed of 120 rpm for a period of 10 min, 20 min and 30 min respectively. For sample A, the absorbance dropped from 1.162 to 1.137 and further 1.121 at a contact time of 10 min and stirring speed of 120 rpm.

Sample B recorded a drop in value of absorbance from 1.083 to 1.049 and finally to 1.037 from 30 to 20 to 10 minutes respectively. Reduction in values of the absorbance is an indication of colour removal by the prepared adsorbent. The efficiency of removal is assessed by the level of reduction in the absorbance. It is obvious from Table 5 that time is an important parameter for the adsorption of colour on activated sawdust. The activated sawdust is also very effective in the removal of colour from sample C.

5. Conclusions

Based on the research findings, it can be seen that adsorbent dosage, stirring speed as well as contact time are all important factors in colour removal from wastewater. The adsorbing molecules of the constituent of coloured solution may also affect the efficiency of colour removal.

Adsorption of colour was influenced by various parameters such as adsorbent dosage, agitation speed, and contact time. Adsorption increased with increasing the quantity of adsorbent over an extended time and it was also observed that the efficiency of colour removal was concentration-dependent. The present investigation proved that adsorbents made from sawdust can be employed for the decolourization of tannery wastewater and will add to the existing technology of waste minimization. However, in order to establish its effectiveness, the current findings should be verified on an industrial (large) scale.

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