

COD Removal of Tannery Wastewater using Groundnut shell

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Abstract: *Water pollution by industrial effluent both organic and inorganic is of serious environmental concern all over the world. In India, Leather tanning consumes a huge amount of water and introduces serious water pollution to the environment. The present study deals with utilization of agricultural by-products (Groundnut shell) for the removal of Chemical Oxygen Demand (COD) from tannery wastewater. COD removal was studied by batch process with varying adsorbent dose, contact time and pH of the solution to find optimum conditions. The maximum COD removal was found 94.37 % at dose 5gm/l*

Keywords: Leather Tanning, Adsorption, Batch, COD, Groundnut shell

I. INTRODUCTION

The Indian leather industry has been one of the country's oldest and largest industries, contributing significantly to the country's economy. It is the second-largest employer after the agricultural sector in India. However, the Indian leather industry has not been able to realize its full potential due to several challenges. This article will analyze the Indian leather industry's current state, its future prospects, and the challenges that it needs to overcome in the next ten years to achieve sustainable growth.

Current State of the Indian Leather Industry:

The Indian leather industry is valued at \$17 billion and employs over 4 million people. It accounts for 12.9% of the world's leather production and is the third-largest exporter of leather and leather products globally, after China and Italy. The industry comprises various segments, such as tanning, footwear, leather goods, and accessories, among others. The Indian leather industry's main export destinations are the USA, Germany, UK, Italy, and France.

Challenges for the Indian Leather Industry:

The Indian leather industry faces several challenges that need to be addressed in the next ten years. The industry needs to address the issues of labor laws, lack of modernization, and environmental impact. The industry also needs to address the issue of skilled labor shortage. The tanning industry is labor-intensive, and there is a shortage of skilled workers in the country. The government needs to provide training programs to improve the skills of the workforce and make the industry more attractive to young people.

Another challenge for the Indian leather industry is the issue of environmental sustainability. The leather industry has a high environmental impact, particularly in the tanning process, which requires large amounts of water and chemicals. The Indian leather industry needs to focus on reducing its environmental impact by adopting sustainable practices such as using eco-friendly materials, reducing waste, and adopting cleaner production techniques. The industry can also benefit from government policies that promote sustainability, such as carbon pricing, water-use restrictions, and waste reduction targets.

The Indian leather industry also faces competition from other countries such as China, Vietnam, and Bangladesh. These countries have a large scale of production and lower costs, which makes them attractive to international buyers. The Indian leather industry needs to focus on improving its quality, increasing productivity, and reducing costs to remain



competitive in the global market. The industry can also benefit from entering into strategic partnerships with international brands and retailers.

Leather processing is an important economic activity around the world and uncontrolled release of tannery effluents to natural water bodies causes environmental degradation and increases health risks to human beings. The treatment of tannery effluent is a complex technological challenge because of the presence of high concentrations of organic and inorganic pollutants of both conservative and non-conservative nature. In the present study, it was aimed to carry out experiments using Groundnut shell (CH) for the removal of organic contaminants specially COD from the Tannery effluent.

A number of conventional treatment technologies have been considered for treatment of wastewater contaminated with organic substances. Among them, adsorption process is found to be the most effective and economical method. Adsorption as a wastewater treatment process has aroused considerable interest during recent years. Commercial activated carbon is regarded as the most effective material for controlling the organic load. However, due to its high cost and about 10 - 15% loss during regeneration, unconventional adsorbents like fly ash, peat, lignite, bagasse pith, wood, saw dust, periwinkle shells, etc. have attracted the attention of several investigations and adsorption characteristics have been widely investigated for the removal of refractory materials. Like other biomass residues, coffee waste represents an unused resource and pose increasing disposal problem. For these reason, strategies are being investigated to evaluate their possible use as an energy source or in other value-added application. The cell wall of waste coffee consist of cellulose, lignin, carbohydrate which have hydroxyl groups in their structures. One third of total dry matter in coffee leaves should have good potential as metal scavengers from solution and waste water because they contain functional groups. The responsible functional groups is lignin, tannin or other phenolic compounds are mainly carboxylate, aromatic carboxylate, phenolic hydroxyl and oxyl groups and could be a good sorbent for contamination.

II. MATERIALS AND METHODS

2.1. Sample Collection

Samples were collected from the Saleem leather and shoe exports Ranipet, Vellore. Sample 01 (S1) was collected from a canal which was located outside of the tanning area and sample 02 (S2) was collected from the outlet of a tannery. Pre-washed plastic bottles were used for sample collection.

2.2. Preparation of the adsorbent

The Groundnut shell was collected from coffeeshops, restaurants, hotels, and offices, etc. Soluble and colored components were removed from coffee by washing with boiling water. This is repeated until the water was virtually colorless. The coffee leaves were then washed with distilled water and oven dried for 6-8 h at 105°C.

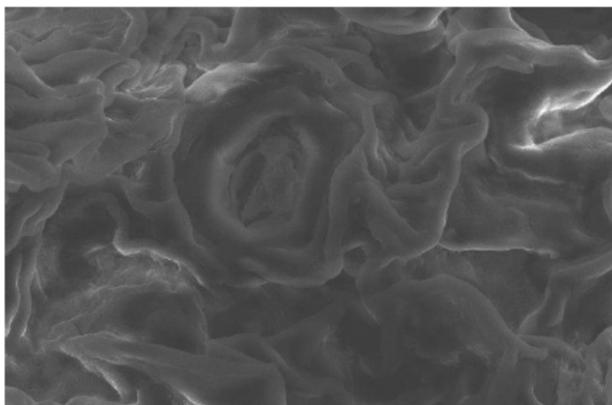


Figure 1: SEM images of Groundnut shell (15.0 kV 10.2 mm X 2.00 K SE)



Figure 1 shows the Scanning electron microscope (SEM) image of CH. SEM image was used to examine the surface morphologies. The surface of CH was found smooth

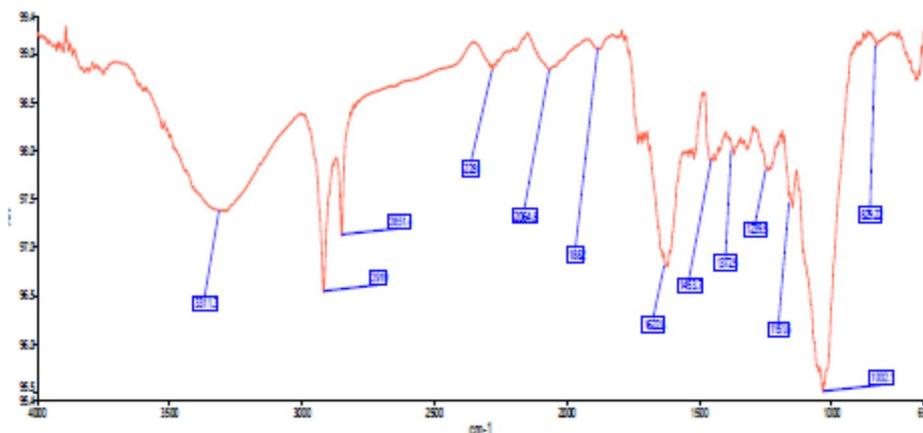


Figure 2: FTIR spectrum of Groundnut shell(CH)

Each specific chemical bond often shows a unique energy absorption band in FTIR analysis and it has been used as a useful tool to identify the presence of certain functional groups of the biosorbent. The FTIR spectrum of CH is shown in Figure 2. The surface contains various functional groups. The distinct broad and elongated 'U' shape peak around 3311.3 cm^{-1} in the spectrum indicates the free O-H group on the surface of the adsorbent and confirms the presence of alcohols and polyphenols in cellulose and lignin. Peak 2919 cm^{-1} and 2851.4 cm^{-1} as signing the-CH stretching mode from the aliphatic. Peak around 1622.8 cm^{-1} corresponds to C=O group. The band appeared at 1032.1 -1151.6 cm^{-1} can be due to C-O stretching in alcohols

2.3. Experimental procedure

The experiment was performed in a batch process in a series of beakers equipped with stirrers by stirring the tannery effluent. The batch technique was selected for its simplicity. At the end of predetermined time, the suspension was filtered and the remaining concentration of COD value in the aqueous phase was determined. The effect of various controlling parameters such as contact time, pH, and adsorbent dose of coffee waste were studied.

2.3.1. Adsorbent Dose

The studies were conducted with varying amount of adsorbent starting from 03 to 20gm/l. Tannery sample of 250 ml was treated with different amount of doses of coffee waste adsorbent.

2.3.2. Contact time

These studies were conducted by agitating 250 ml sample for different time period 30-150 min. After the predetermined time intervals, the samples were filtered and then analysed.

2.3.3. pH

pH effect was performed taking a specific concentration, adsorbent dose and contact time. The pH was varying using dilute NaOH/HCL solution. The samples were agitated for specific time, filtered and then analyzed.

2.4. Glassware and Apparatus used

All glassware's (Beaker, Conical flask, Pipette, Measuring cylinder, Test tube, etc) used were of Borosil / Ranken. The instrument and apparatus used throughout the experiment were listed below table.



S.NO.	Instrument	Brand
1	pH meter	Hanna
2	Digital Weight Balance	ViBRA AJ
3	Whatman filter paper no.	40
4	Automatic Stirrer	Lovibond
5	COD Digester	HACH
6	Portable Spectrophotometer	HACH DR/2010

Table-1: List of Used Instrument

Results and Discussion:

The tannery effluent sample was characterized with the parameters of pH, COD and BOD (Table 2).

Table 2: Characteristics of Sample

Parameter	Sample (S1)	Sample (S2)
pH	6.5	8.2
COD mg/l	2,490	21,060
BOD mg/l	1,700	12,600

Effect of Adsorbent Dose

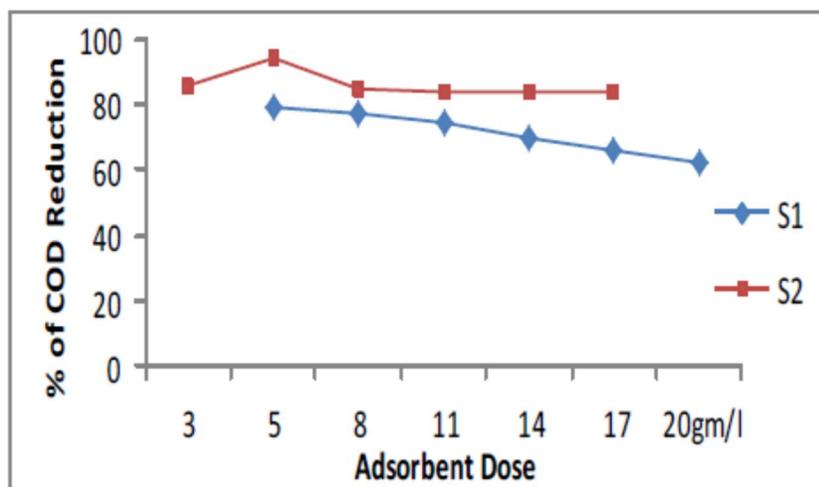


Figure 3: Effect of adsorbent dose on COD removal

Figure: 3 show the effect of adsorbent on COD removal. For sample 01 (S1) adsorbent dose was selected from 05-20 gm/l and for sample 02 (S2) it was 03-17 gm/l. The samples were run for 60 min. The result shows that the optimum dosage of adsorbent for COD was 05 gm/l for of both the sample.About 79.12 and 94.02 %removal were obtained for S1



and S2 respectively. After the optimum dose, percentage of COD removal was declining significantly in sample S1 than S2. Aluyor et al. 2008 and Mukundan et al. 2015 found the similar trend.

Effect of Contact time

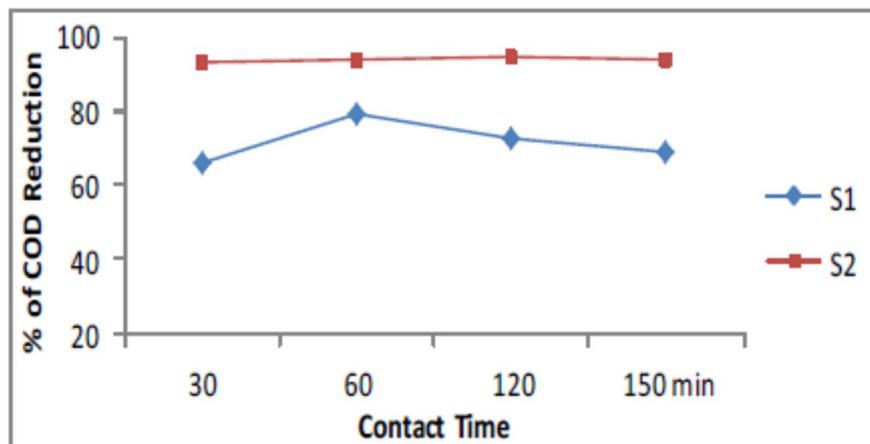


Figure 4: Effect of contact time on % removal of COD by coffee waste adsorbent

Figure 4 shows the variation in the percentage removal of COD with contact time using 05gm/l of coffee waste adsorbent dose. The result obtained shows that maximum COD removal occurred at time of 60 min and 120 min for S1 and S2 which were 79.12 and 94.37 % removal respectively. After 60 min, the % of COD was decreasing in sample S1 while for sample S2 it was stable. The lowest % of COD removal obtained at time of 30 min.

Effect of Ph

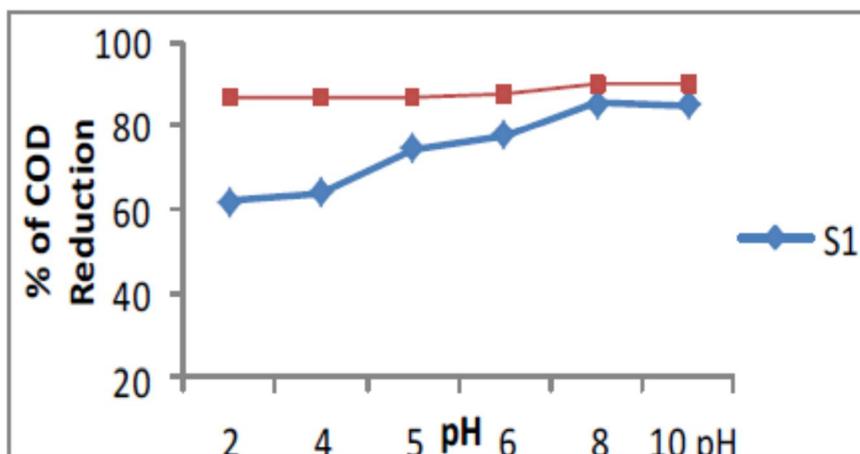


Figure 5: Effect of pH on % removal of COD by Groundnut shell adsorbent

About more than 80 and 90% COD removal were achieved at pH 8-10 for sample S1 and S2 respectively. After pH 4, COD removal was increasing (Figure 5). The reason for the better adsorption observed at higher pH attributed to the co-precipitation of the organic matters and the other chemicals responsible for COD with the colloidal Cr(OH)₃. At comparatively lower pH, formation of Cr(OH)₃ was not sufficient and hence not suitable for coagulation .



3.1. Adsorption Isotherms

Equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which is usually the ratio between the quantity adsorbed and that remained in solution at equilibrium at fixed temperature. Freundlich and Langmuir isotherms are the earliest and simplest known relationships describing the adsorption equation. Adsorption isotherm was an equilibrium plot of solid phase (q_e) versus liquid phase concentration (C_e).

Table 3: Freundlich and Langmuir adsorption isotherm parameters

No	Ads. Dose, m, (gm/l)	Eq. conc. C_{eq} (mg/l)	Rev. $x=Co - C_{eq}$ (mg/l)	$q_e=x/m$, (mg/gm)	Re v. %	Lo g C_e q	Lo g x/m	1/ C_{eq}	1/ q_e
1	0	21060	---	---	---	---	---	---	---
2	3	1420	19640	6546.67	93.26	3.15	3.82	0.00704	0.000153
3	5	1410	19650	3930.00	93.30	3.15	3.59	0.00709	0.000254
4	8	1520	19540	2442.50	92.78	3.18	3.39	0.00658	0.000409
5	11	1550	19510	1773.64	92.64	3.19	3.25	0.00645	0.000564
6	14	1610	19450	1389.29	92.36	3.21	3.14	0.00621	0.00072
7	17	1650	19410	1141.76	92.17	3.22	3.06	0.00606	0.000876

Freundlich model with linear plotted $\log q_e$ versus $\log C_e$ shown in the following equation;

$$\log q_e = \log K_f + 1/n \log C_e$$

Where K_f is, roughly, an indicator of the adsorption capacity (mg/g), C_e is the equilibrium concentration (mg/L) and $1/n$ is the adsorption intensity. A linear form of the Freundlich expression will yield the constants K_f and $1/n$. Freundlich isotherm model assumes a non-ideal adsorption on heterogeneous surfaces in a multilayer coverage. It suggests that stronger binding sites are occupied first, followed by weaker binding sites. In other words, as the degree of site occupation increases, the binding strength decreases.

Langmuir model with linear plotted $1/q_e$ versus $1/C_e$ shown in the following equation:



$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} K_L C_e}$$

Where q_e is the equilibrium adsorbate concentration in solution; q_{\max} is the maximum adsorption capacity (mg/g) which is determined from the slope; C_e is the equilibrium concentration (mg/L) and K_L is Langmuir constant related to of the binding sites and determined from the intercept, (L/mg). The Langmuir isotherm model is valid for monolayer adsorption onto surface containing a finite number of identical sorption sites. This model assumes that adsorbed molecules cannot move across the surface or interact with each other .

Freundlich adsorption isotherm

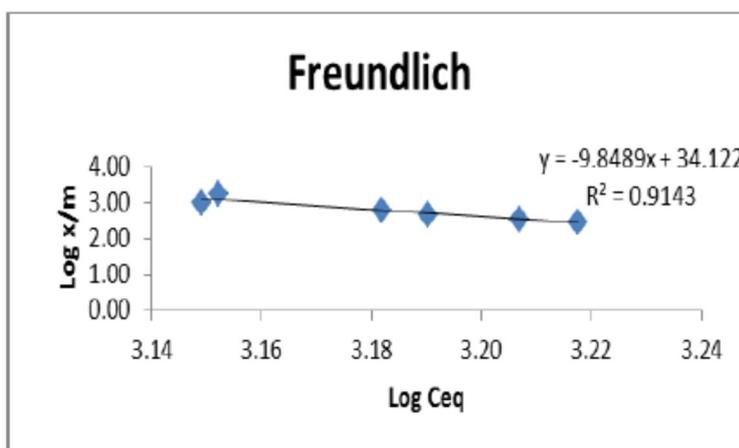


Figure 6: Freundlich isotherm of Groundnut shell

From the Freundlich isotherm model as shown in Fig. 6, constants obtained are: adsorption capacity, K_f , is 34.122 and adsorption intensity, $1/n$, is -9.849. The regression coefficient is 0.914.

Langmuir adsorption isotherm

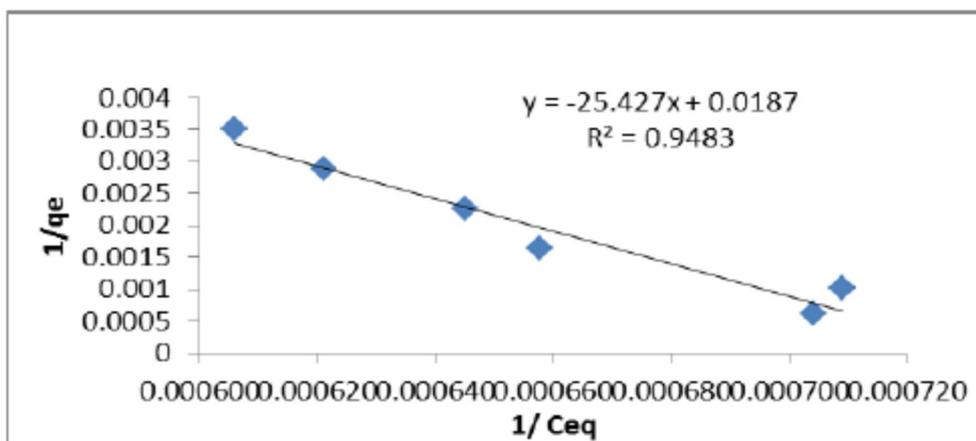


Figure 7: Langmuir adsorption isotherm of Groundnut shell



From the Langmuir isotherm model as shown in Fig. 7, constants obtained are: Langmuir constant K_L is 0.0187 and maximum adsorption capacity is 25.427. The regression coefficient is 0.948.

The effect of isotherm shape is discussed from the direction of the predicting whether and adsorption system is "favorable" or "unfavorable". Hall et al (1966) proposed a dimensionless separation factor or equilibrium parameter, R_L , as an essential feature of the Langmuir Isotherm to predict if an adsorption system is "favourable" or "unfavourable", which is defined as : $R_L = 1 / (1+bC_0)$

Where, C_0 = reference fluid-phase concentration of adsorbate (mg/l) (initial concentration), b = Langmuir constant (L/mg)

Value of R_L indicates the shape of the isotherm accordingly as shown in Table 4 below.

For a single adsorption system, C_0 is usually the highest fluid-phase concentration encountered.

Table 4: Characteristics of adsorption Langmuir isotherm

Separation factor, R_L	Characteristics of adsorption Langmuir isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The value of separation factor (R_L) for the present study is 0.0025 indicating that the shape of the isotherm is favorable.

Table 5: Adsorption Isotherm constants and coefficient of determination

Adsorbent	Langmuir Isotherm constants			Freundlich Isotherm constants		
	q_{max} (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	$1/n$	R^2
Spent Tea waste	25.427	0.0187	0.948	34.122	9.849	0.914

From the table 5, the correlation coefficient (R^2) of Langmuir (0.948) is higher than that of Freundlich adsorption isotherm.

IV. CONCLUSION

The result of present study showed that Groundnut shell can be used as an effective adsorbent in the removal of COD from tannery wastewater. The maximum COD removal was found at 5gm/l of adsorbent, i.e., 94.37 % removal of COD. Based on the batch adsorption study, the removal of COD was well fitted with Langmuir and Freundlich isotherm model. The correlation coefficient (R^2) of Langmuir and Freundlich adsorption isotherms were 0.948 and 0.914 respectively. This result shows that adsorbent made from agricultural waste (Groundnut shell) can be used with effectiveness for organic matter removal from tannery wastewater. This would be of benefit not only to the manufacturing industry in terms of minimizing cost of COD treatment, but also to minimize the impacts to the environment.



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