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COD Removal of Tannery Wastewater using Spent Tea Leaves

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Abstract – *Water pollution by industrial effluent both organic and inorganic is of serious environmental concern all over the world. In Bangladesh, 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 (spent tea leaves) 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.*

Key Words: Leather Tanning, Adsorption, Batch, COD, Spent Tea leaves

1. INTRODUCTION

The history of tannery industry in Bangladesh is not too old. The first tannery of Bangladesh established at Narayanganj by R.P. Shaha in 1940s. Later on, it was shifted to Hazaribagh area in Dhaka city. During the Pakistan period, in 1965 there were 30 tanneries in the then East Pakistan now Bangladesh. After independence, Bangladesh government took responsibilities all 30 tanneries. As a result, the sluggish activities of the factories occurred. For these circumstances, all those industries again returned to the private sector. Basically large scale Leather Industry developed in Bangladesh from 1970s. At the end of 1990 the leather industry got importance by foreign investment [1].In Leather tanning, huge amount of water are consumed and polluted by the various organic and inorganic chemicals used. Pure water is one of the essential elements for existence of life on earth and contamination of this valuable resource threatens our survival. Industrial wastewater differs in characteristics from the domestic wastewater. Industrial wastewaters result from spills, leaks and washing. Tannery also discharges wastes to the marshy land like rivers and canals which carry toxic chemical like H2S (Hydrogen sulphide), NH3 (ammonia), chromium (Cr), poisonous chlorine and nitrogen based gases, etc[2].

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 [3]. In the present study, it was aimed to carry out experiments using spent tea leaves (STL) 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 [4].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 [5]. Like other biomass residues, tea waste represents an unused resource and pose increasing disposal problem. For theses 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 tea consist of cellulose, lignin, carbohydrate which have hydroxyl groups in their structures .One third of total dry matter in tea 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 [6].

2. Materials and Methods:

2.1. Sample Collection

Samples were collected from the Hazaribagh Tanning area near the Institute of Leather Engineering and Technology (ILET), Hazaribagh, Dhaka. Sample 01 (S1) was collected from a cannel 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 tea waste was collected from teashops, restaurants, hotels, and offices, etc. Soluble and colored components were removed from tea by washing with boiling water. This is repeated until the water was virtually colorless. The tea leaves were then washed with distilled water and oven dried for 6-8 h at 1050C.

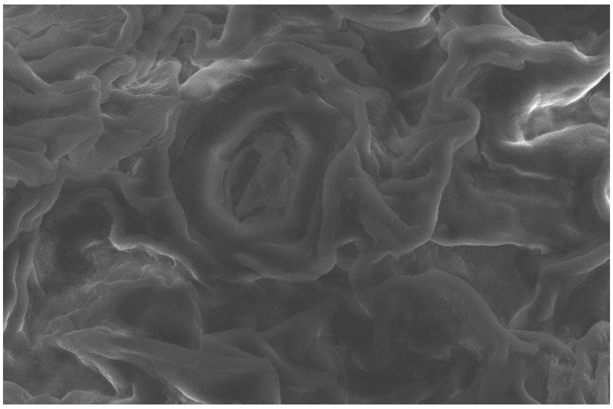

Figure 1: SEM images of Spent Tea Leave (15.0 kV 10.2 mm X 2.00 K SE)

Figure 1 shows the Scanning electron microscope (SEM) image of STL. SEM image was used to examine the surface morphologies. The surface of STL was found smooth and with uniform micro-porous structure.

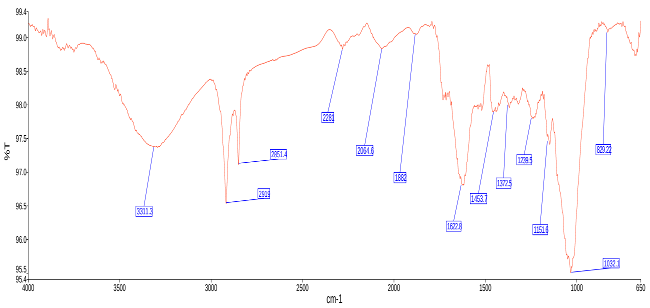

Figure 2: FTIR spectrum of Spent Tea Leave (STL)

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 [7]. The FTIR spectrum of STL 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 [8]. 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 tea waste were studied.

2.3.1. Adsorbent Dose

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

SL	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 ›photometer	HACH DR/2010

Table-1: List of Used Instrument

3. 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

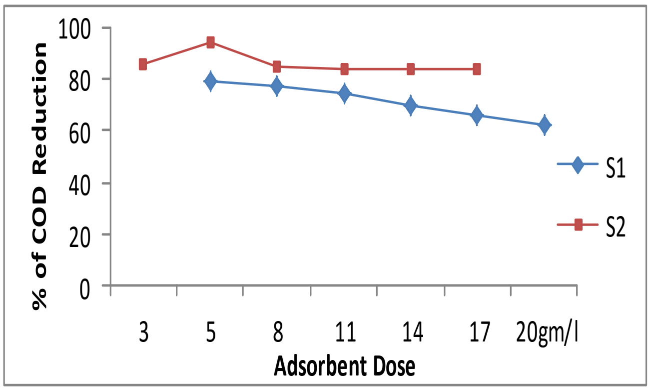

Figure 3: Effect of adsorbent dose on COD removal

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.Aabout79.12 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 [5] and Mukundan et al. 2015[9] found the similar trend.

Effect of Contact time

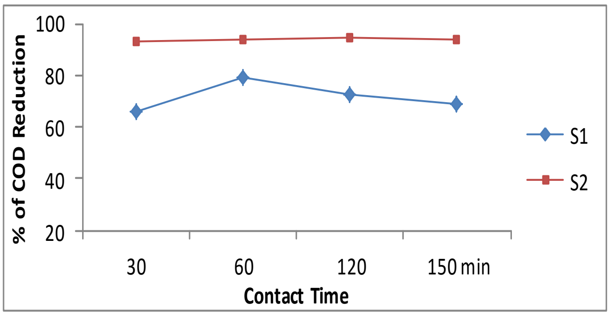

Figure 4: Effect of contact time on % removal of COD by tea waste adsorbent

Figure 4 shows the variation in the percentage removal of COD with contact time using 05gm/l of tea 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

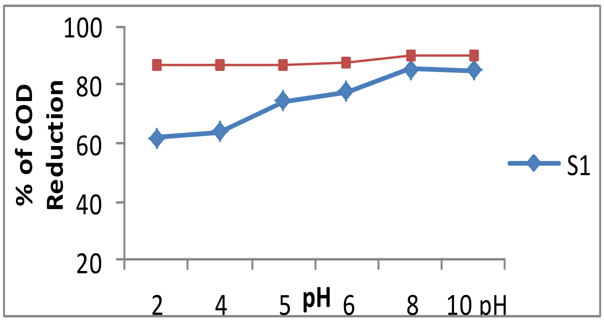

Figure 5: Effect of pH on % removal of COD by tea waste adsorbent

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 [10].

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 [11-12]. Freundlich and Langmuir isotherms are the earliest and simplest known relationships describing the adsorption equation [13]. Adsorption isotherm was an equilibrium plot of solid phase (qe) versus liquid phase concentration (Ce).

Table 3: Freundlich and Langmuir adsorption isotherm parameters

No	Ads. Dose, m, (gm/l)	Eq. conc. Ceq (mg/l)	Rev. x=Co-Ceq (mg/l)	qe=x/m, (mg/gm)	Rev. %	Log Ceq	Log x/m	1/Ceq	1/qe
1	0	21060	---	---	---	---	----	-----	------
2	3	1420	19640	6546.67	93.26	3.15	3.82	0.000704	0.000153
3	5	1410	19650	3930.00	93.30	3.15	3.59	0.000709	0.000254
4	8	1520	19540	2442.50	92.78	3.18	3.39	0.000658	0.000409
5	11	1550	19510	1773.64	92.64	3.19	3.25	0.000645	0.000564
6	14	1610	19450	1389.29	92.36	3.21	3.14	0.000621	0.00072
7	17	1650	19410	1141.76	92.17	3.22	3.06	0.000606	0.000876

Freundlich model with linear plotted log qe versus log Ce shown in the following equation;

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

Where Kf is, roughly, an indicator of the adsorption capacity (mg/g), Ce is the equilibrium concentration (mg/L) and 1/n is the adsorption intensity. A linear form of the Freundlich expression will yield the constants Kf 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 [14].

Langmuir model with linear plotted 1/qe versus 1/Ce shown in the following equation:

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

Where qe is the equilibrium adsorbate concentration insolution; qmax is the maximum adsorption capacity (mg/g) which is determined from the slope; Ce is the equilibrium concentration (mg/L) and KL 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 [14, 15].

Freundlich adsorption isotherm

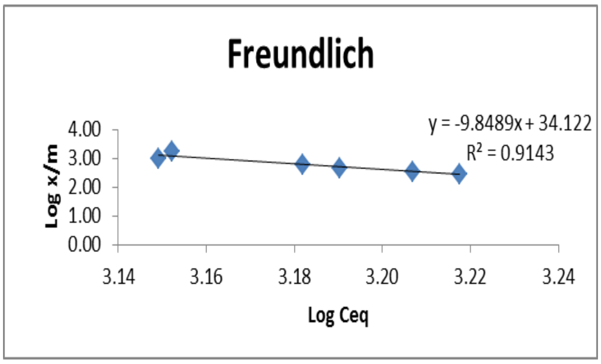

Figure 6: Freundlich isotherm of spent tea waste

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

Langmuir adsorption isotherm

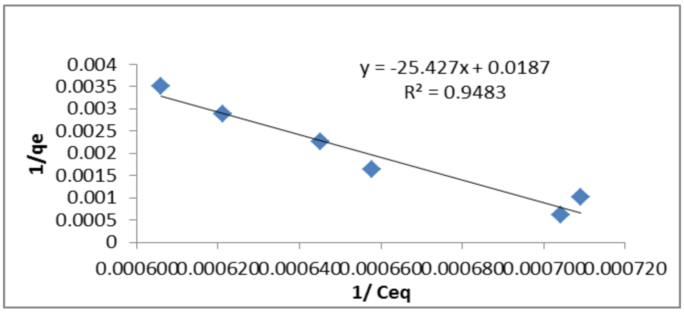

Figure 7: Langmuir adsorption isotherm of spent tea waste

From the Langmuir isotherm model as shown in Fig. 7, constants obtained are: Langmuir constant KL is 0.0187and 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, RL, as an essential feature of the Langmuir Isotherm to predict if an adsorption system is "favourable" or "unfavourable", which is defined as [16]:

$$RL = 1 / (1+bC0)$$

Where, C0= reference fluid-phase concentration of adsorbate (mg/l) (initial concentration), b = Langmuir constant (L/ mg)

Value of RL indicates the shape of the isotherm accordingly as shown in Table 4 below. For a single adsorption system, Co is usually the highest fluid-phase concentration encountered.

Table 4: Characteristics of adsorption Langmuir isotherm

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

The value of separation factor (RL) 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		
	qmax(mg/g)	KL (L/mg)	R2	Kf(mg/g)	1/n	R2
Spent Tea waste	25.427	0.0187	0.948	34.122	-9.849	0.914

From the table 5, the correlation coefficient (R2) of Langmuir (0.948) is higher than that of Freundlich adsorption isotherm.

4. Conclusion

The result of present study showed that spent tea leaves 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 absorbent, 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 (R2) of Langmuir and Freundlich adsorption isotherms were 0.948 and 0.914 respectively. This result shows that adsorbent made from agricultural waste (spent tea leaves) 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.

REFERENCES

[1] Leather industry of Bangladesh; http://emergingrating.com/wp-content/uploads/2016/08/Leather-industry-of-Bangladesh-Vol-I.pdf

[2] Nur-E-Alam M, Sayid Mia MA, RahmanLutfor M and RahmanMahizurM,'Impacts of Tanning Process on Surface Water Quality of Hazaribagh Tanning Area Dhaka, Bangladesh',Journal of Environmental Science, Computer Science and Engineering & Technology (JECET),June 2017- August 2017; Sec. A;Vol.6. No.3, 176-186.

[3] Sabumon PC (2016) Perspectives on Biological Treatment of Tannery Effluent. Adv Recycling Waste Manag 1:104. doi:10.4172/2475-7675.1000104

[4] Lakdawala M.M.; Lakdawala M.J., Comparative Study of Effect of PAC and GAC on Removal of COD Contributing Component of Sugar Industry wastewater.Research Journal of Recent Science.Vo.2(ISC-2012), 90-97(2013).

[5] Aluyor O. Emmanuel and Badmus A. M. Olalekan, COD removal from industrial wastewater usingactivated carbon prepared from animal horns. African Journal of Biotechnology Vol. 7 (21), pp. 3887-3891, 5 November, 2008.

[6] Nandal M., Hooda R. and Dhania G.Tea Wastes as a Sorbent for Removal of Heavy Metals from wastewater, International Journal of Current Engineering and Technology, E-ISSN 2277 – 4106, P-ISSN 2347 – 5161

[7] Shrestha B., Kour J.,Homagai L.P., Pokhrel R.M. and Ghimire N.K.,Surface Modification of the Biowaste for Purification of Wastewater Contaminated with Toxic Heavy Metals —Lead and Cadmium, Advances in Chemical Engineering and Science, 2013, 3, 178-184, http://dx.doi.org/10.4236/aces.2013.33022

[8] Bhavsar K and Patel P. Efficiency Evaluation of Tea Waste for Adsorption of Hexavalent Chromium from Industrial Effluent. International Journal of Science and Research (IJSR), Vol. 3 Issue 7, July 2014.

[9] Mukundan. U. and Ratnoji. S.S. 'Cod Removal from Sewage by Activated Carbon from Rice Husk-An Agricultural By Product.' International Journal of Innovative Research in Science, Engineering and Technology, Vol. 4, Issue 6, Jume 2015.

[10] Sabur. M.A., Rahman. M.M. &Safiullah. S. 'Treatment of Tannery Effluent by Locally Available Commercial Grade Lime', journal of Scientific Research (JSR), 5(1),143-150 (2013), doi: http://dx.doi.org/10.3329/*jsr*.v5i1.12557

[11] El-Halwany MM (2007) Development of Activated Carbon from EgyptianRice Hull: Evaluation of Adsorption Properties (Part I). International ChemicalScience Conference Sharm El-Sheikh 16-19 April.

[12] Muhamad N, ParrJ, Smith DM, Wheathey DA (1998) Adsorption of heavymetals in show sand filters in: Proceedings of the WEDC Conference Sanitationand Water for All Islamabad Pakistan 346-349.

[13] IGWE C.J., ONYEGBADO O.C., and ABIA A.A.,ADSORPTION ISOTHERM STUDIES OF BOD, TSS AND COLOUR REDUCTION FROM PALM OIL MILL EFFLUENT (POME) USING BOILER FLY ASH, Ecl. Quím., São Paulo, Vol. 35 - 3: 195 - 208, 2010, www.scielo.br/eq

[14] JamhourM. A. Q. Rasheed, Ababneh S. Taher, Al-Rawashdeh I. Albara, Al-Mazaideh M. Ghassab, Al Shboul1, M. A Tareqand Jazzazi M. A Taghreed, Adsorption Isotherms and Kinetics of Ni(II) and Pb(II) Ions on New Layered Double Hydroxides-Nitrilotriacetate Composite in Aqueous Media, Advances in Analytical Chemistry 2016, 6(1): 17-33

[15] Mostafapour F. K., Bazrafshan E.,Farzadkia M. and AminiS. Arsenic Removal from Aqueous Solutions bySalvadorapersicaStemAsh,Journal of Chemistry, Hindawi Publishing Corporation,Volume 2013, Article ID 740847

[16] Dhanakumar S.,Solaraj G.,Mohanraj R. and Pattabhi S. Removal of Cr (VI) from aqueous solution by adsorption using cooked tea dust. Indian Journal of Science and Technology, Vol.1No.2 (Dec.2007), 1-6.

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