Proceedings of the
International Conference on Mechanical Engineeringand Renewable Energy 2015
(ICMERE2015) 26 – 29 November, 2015, Chittagong, Bangladesh

ICMERE2015-PI-019

INTRODUCTION OF ALGAL TREATMENT IN TANNERY WASTE WATER PROCESSING: BANGLADESH PERSPECTIVE

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Abstract*-Tannery in Bangladesh seems a source of pollution load and waste water to all because there are 270 registered tanneries where approximately 220MT raw hides and skins are taking for the production of leather in Bangladesh [1]. The leather industry has crossed the record $1-billion mark in exports in 2013-2014 [2]. According to the Department of Environment, the tanneries discharge 22,000 cubic meters of untreated liquid toxic waste daily [3]. These pollution load and waste water should need treatment to make environment sustainable and living. From this point of view, we worked on tannery waste water processing. The paper highlights the initiation of algal treatment in waste water processing in Bangladesh. The methodology of this process starts with mixing of waste water from different section of beam house operations at a definite ratio. The mixer takes nearly six hours to settle down. After sedimentation, the turbidity decreases at a reasonable amount i.e. 1428 NTU whereas before sedimentation it was 9050 NTU (2100P Turbid Meter of HACH). Later the supernatant was collected for algal treatment. After algal treatment the turbidity reduced to 530 NTU from 1428 NTU and the DO level increased up to 8.22 mg/L at 20°C (HQ 40d of HACH) where DO level was 0.24 mg/L at 20°C in raw mixer. The odor was also more tolerable than raw mixer after algal treatment. The algal treatment can hopefully reduce a considerable amount of pollution load & increase DO level and thus make effluent environment friendly to discharge.*

Keywords: pollution load, algae, sedimentation, turbidity, DO, environment

1. INTRODUCTION

Tanning industry is an old manufacturing sub-sector in Bangladesh with a long heritage of over six decades. The tanneries of Hazaribag started their journey from 1960. It was first introduced by Punjabi traders from what was then Pakistan. The industries expanded and after the independence of Bangladesh in 1971, the government took over the tanneries abandoned by the departing non-Bengali entrepreneurs and eventually made it a 'cash cow' to earn foreign currencies. The peak time of collection is during the Muslim festival of animal sacrifice, the Eid-ul-Adha. Leather manufactured from thisplace is being shipped to the US and Europe, and other parts of the world for further processing. With the latest trend of more focus towards ethical manufacturing process, countries are much interested towards the way in which their products are manufactured.

Tanning is the chemical process that converts animal hides and skins which are putrescible into leather which is non-putrescible and related products. Tanning is claimed to be second oldest trade in the world and considered as a noxious trade. The transformation of hides into leather is usually done by means of tanning agents and the process generates highly turbid, colored and foul smelling wastewater. The major components of the effluent include sulfide, chromium, volatile organic compounds, large quantities of solid waste, suspended solids like animal hair and trimmings[4].According to the Department of Environment, the tanneries discharge 22,000 cubic meters of untreated liquid toxic waste daily. In recent times, the leather industry is recognized as the prime industry of great economic significance. A current report exposed that leather and leather products are one of the major external trade sectors which contribute up to 1.39% share on the total export earnings [5]. But a great drawback of this sector is releasing of huge amount solid and liquid wastes, noxious gases etc. which are harmful to the environment, aquatic life and human beings. The extremely colored tannery wastewater is acidic in nature with high chromium content including other pollution loads such as chemical oxygen demand, biochemical oxygen demand, dissolved salts etc. So waste water gets more priority than others because the whole world contains a limited amount of pure and reliable water. In this respect, waste water should need proper treatment to make it sustainable to environment, aquatic life and human being. From this point of view, initiation of algal treatment in tannery waste water processing is a new thing. Algal treatment is the process where the application of algal biomass for the bio-sorption of heavy metals from wastewater. Both living and dead algal

biomass have the capability to uptake heavy metals from waste water. It is thought that bio-sorption on dead biomass involve a physical sorption phenomenon while bio-sorption on active biomass involve both physical and chemical sorption phenomena plus transmembrane and accumulation of heavy metals in the cell [6].In this experiment, algal dosing, performance properties of algae on the basis of amount, pH and time are investigated and feasible decision is taken for the treatment process of tannery waste water from tannery operations.

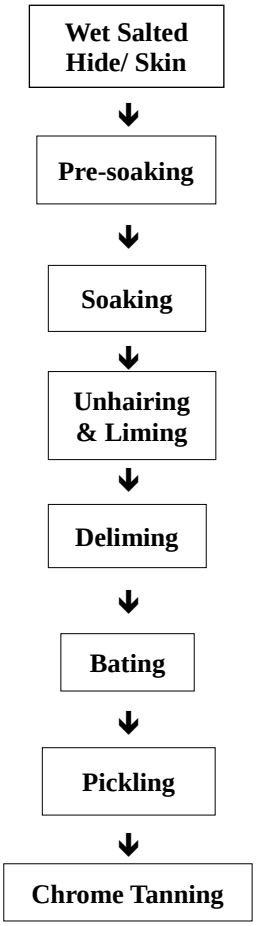
2. METHODOLOGY

2.1 Samples Collection

Samples were collected from a renowned tannery nearby KUET campus. Collected samples were different section of beamhouse operations i.e. soaking, liming, deliming & bating, pickling & chrome tanning.

2.2 Beamhouse Operations

Beamhouse operations are the initial stage of leather processing in tannery. The steps in the production of leather between curing totanning are collectively referred to as beamhouse operations. The stepwise processes namely pre-soaking, soaking, liming, deliming, bating, pickling and tanning are considered as beamhouse operation. The beamhouse operation has great importance for leather production. The flow chart for beamhouse operations from wet salted hide or skin is shown in the flow chart below [7**].**



Flow chart of beam house operations

2.3 Settling of Suspended and Insoluble Materials

Settling operation was the preliminary operation of this work. In this stage, samples were mixed in a beaker with a definite ratio 2:1:1:1 of different waste liquors i.e**.** soaking, liming, deliming & bating and pickle & chrome liquor. They were agitated properly to mix up well and kept up to 5-6 hours maximum for significant settling down. A continuous study represents that approximately 700 mL supernatant liquid was collected from the 1000 mL beaker where 300 mL was liquid & suspended mixture (Sludge). By considering the settled sample as raw, different environmental parameters of the raw sample were measured.

Fig. 1: Before settling.

Fig. 2: After settling.

2.4 Materials

The only material used for the desired treatment process is micro algae of Chlorophyta group. This type of algae is highly available in the rural area, urban area, ponds, lakes, rivers etc. The green algae are a large, informal grouping of algae consisting of the Chlorophyte and Charophyte algae. The algae were collected near KUET campus from a lake. The algae were washed well thoroughly by continuous water flow.They were dried for two days in an oven at 50-60 ^{0}C for conditioning to protect from fungal attack and putrefaction. After conditioning they were grinded carefully and isolated micro particles by sieving. In this way, materials were prepared for the treatment process. The algae contains alginate acid. The structure of alginate acid is shown in Fig.3.

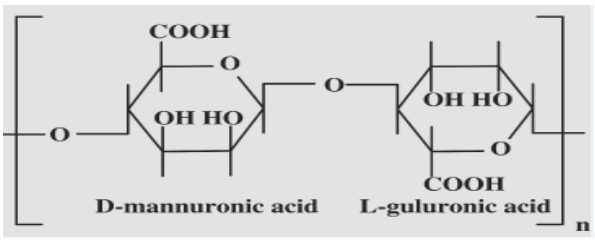


Fig. 3: Chemical structures of alginic acid

2.5 Algal Dosing

Algal dosing is the process of choosing optimum amount of required algae and given best performance on the basis of pH, time and some essential parameters. At first 40 mL of settled sample was taken into 50 mL beaker and kept it for 2.5hrs. Then 10mL of sample was taken from

the beaker for the determination of suspended solids and the rest of the sample was selected for the estimation of other environmental parameters. Optimum dosage of algae was selected on the basis of percentage adsorption of suspended solids by different amount of algae at different pH and time. To do so firstly, 6 beakers each of 50 mL volume were taken and each of all the beakers was poured to 40 mL of raw sample. Then 0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g algae were taken in different beakers and kept them for 2.5hrs. After that percentage adsorption of suspended solids by different amount of algae was calculated and was selected the best one. Secondly, 4beakers each of 50 mL size was filled by 40 mL of raw sample each was taken and was maintained different pH like 5.0, 6.0, 7.0 and 8.0 by using desired quantity of 0.1N hydrochloric acid. After that all the samples were treated with the above selected optimum amount of algae for 2.5hrs and percentage adsorption of suspended solids at different pH was calculated and was selected the best one. Finally, 5beakers each of 50 mL size with 40 mL of raw sample each were treated with the optimum mount of algae by maintaining the optimum pH at different times like 1hr., 1.5hrs, 2hrs, 2.5hrs and 3hrs and percentage adsorption of suspended solids by algae at different time was calculated and the best one was selected. By considering all the parameters, algal dosing was selected. The selected dose of algae is 0.3 g/ 40 mL i.e. 7.5 g per one liter of raw sample at pH 6.0 and time duration is 2.5 hours.

2.6 Algal Treatment Process

The algal treatment process starts with the application of definite amount of algae in the supernatant liquid (waste water) obtained from settling operation. The treatment process was run into normal condition. In this process, the required essentials are

- Algae
- Beaker (50 mL)
- Analytical balance
- Filter (Locally available)
- pH meter
- Oven
- Measuring Cylinder (10 mL & 50 mL)
- Stirrer

At the beginning of treatment process, 40 mL of waste water was taken by the help of measuring cylinder (50 mL capacity) and poured into a beaker (50 mL capacity). Then adding hydrochloric acid to maintain solution pH 6.0. The optimum dose of algae selected for the 40 mL waste water processing is 0.3 g. That amount of algae was measured with the help of analytical balance. The measured amount of algae was poured into the waste water and mixed with the waste water by the help of stirrer. The mixture was kept for two and half hours for the treatment process. After treatment, turbidity, DO level, pH were measured. A pretty good result was obtained.

2.7 Mechanism of Algal Biosorption

Elucidation of mechanisms active in metal biosorption is essential is essential for successful exploitation of the phenomenon and for biosorbentregeneration in multiple re-useable cycles. The main uptake mechanisms suggest are ion exchange between protons and heavy metal ions at the binding site or light metals and heavy metals, chelation, adsorption by physical forces, electrostatic interactions, complexion, micro precipitation [8].

Extracellular polysaccharides (such as alginates and fucoidans) are the main components of cell wall responsible for metal uptake [9].

Because of their high content of such polysaccharides, brown algae may have a higher uptake capacity than other algae [10].

It is supposed that biosorption on dead biomass involves a physical sorption phenomenon where biosorption on active biomass involve both physical and chemical sorption phenomena plus transmembrane and collection of heavy metals in the cell. Bioaccumulation occurs in two stages, biosorption where metal ion transportation into the cellular interior [11].

3. RESULTS AND DISCUSSION

The amount of suspended solid was 47550 mg/L without algal treatment. The following tables represent the optimization of algal dosing for 40 mL solution.

Table 1: Effect of amount of algae

No of Beaker	Amount of Algae (g)	Absorbed (mg/L)	Percentage of absorbance (%)	Remarks
1	0.1	20680	43.49	
2	0.2	11070	23.28	
3	0.3	28450	60.00	Accepted
4	0.4	8580	18.00	
5	0.5	23360	49.13	

Table 1: Represents the effect of amount of algae on percentage of absorbance of suspended solid.

Table 2: Effect of pH on algae (0.3g)

No of Beaker	pH	Absorbed (mg/L)	Percentage of absorbance (%)	Remarks
1	5.0	23890	50.00	
2	6.0	30250	63.00	Accepted
3	7.0	20640	43.00	
4	8.0	24550	51.63	
5	Raw	25100	52.78	

Table 2 represents the effect of pH on algae of same amount.

Table 3: Effect of time on algae (0.3g)

No of Beaker	Time (hr.)	Absorbed (mg/L)	Percentage of absorbance (%)	Remarks
1	1.0	7960	16.74	
2	1.5	7790	16.38	
3	2.0	26610	55.96	
4	2.5	28880	60.73	Accepted
5	3.0	18950	40.00	

Table 3 represents the effect of time on algae of same amount.

From Table 1, 2 and 3 it is noticed that the percentage of absorbance fluctuated. There may be different reasons: algal bleeding, optimum condition, pH range, time and so on and the selected dose of algae is 0.3 g/ 40 mL of raw sample at pH 6 and time duration two and half hours. Different environmental parameters are measured of raw sample by the utilization of different devices. Some environmental parameters and the devices used for the measurement of raw sample are given in the Table 4.

Table 4: Measured environmental parameters of raw sample

Parameter	DO	Turbidity	pH
Raw Sample	0.25mg/L at 20.0 ^{0}C	873 NTU	9.1
Device	HQ 40d of HACH	2100P Turbid Meter of HACH	EZDO PH5011

After algal treatment different environmental parameters are measured of treated sample by the utilization of different devices. Some environmental parameters and the devices used for the measurement of treated sample are given in the Table 5.

Table 5: Measured environmental parameters of treated sample

Parameter	DO	Turbidity	pH
Raw Sample	8.22mg/L at 20.0 ^{0}C	530 NTU	6.9
Device	HQ 40d of HACH	2100P Turbid Meter of HACH	EZDO PH5011

By comparing Table 4 & 5, it is observed that a pretty good result is obtained. The DO level of treated sample is increased4.48 mg/ L at 20 ^{0}C from 0.25 mg/L at 20 ^{0}C of raw sample (waste liquor). The DO level is increased up to 8.22 mg/L at 20 ^{0}C through aeration. Another two parameters measured are also reduced to a significant amount; i.e. the former turbidity was 873 NTU and after algal treatment it reduced to 530 NTU. So almost an amount of 343 NTU is reduced. The pH is also in a safe level. The discharge limit of water to environment is 6-9 pH [12].

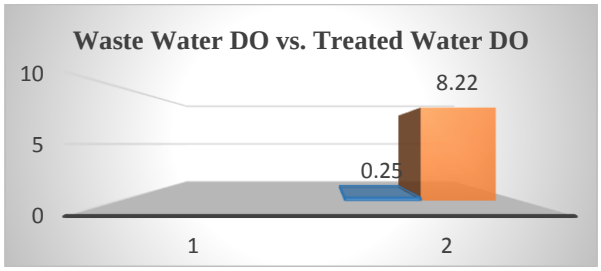


Fig.4: Waste water DOlevel vs. Treated water DO level (after aeration)

= Waste water

= Treated water

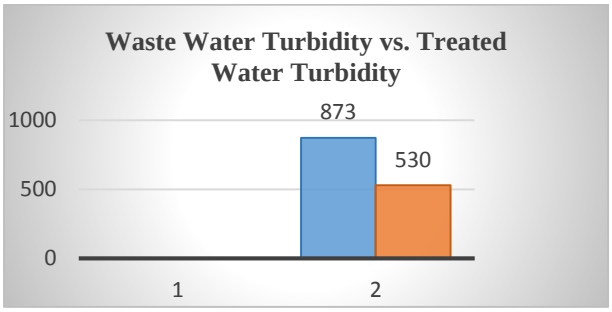


Fig.5: Waste water turbidity level vs. Treated water turbidity level

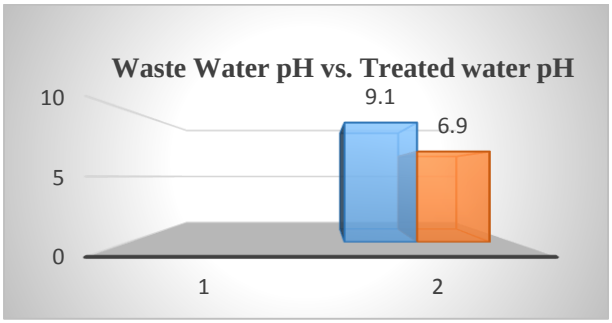


Fig.6: Waste water pH level vs. Treated water pH level

The picture of untreated sample, treated and treated vs. untreated sample are shown in figure below.

Fig.7: Untreated sample

Fig.8: Treated sample

Fig.9: Treated sample vs. untreated sample

4. CONCLUSIONS

This study is the introduction of algal bio-sorption for treatment of tannery waste water. Here the assessment of the best adsorption parameters and the improvement of different environmental parameters of tannery waste water by microalgae of Chlorophyta group were done. Optimum conditions for biomass adsorption revealed that at pH 6.0; maximum adsorption of suspended solids was 60.73% by 0.3 g of biomass for 40 mL of raw sample and the contact time was 2.5 hrs. This study also showed that DO level of the treated sample was improved to 4.48 mg/L (after aeration 8.22 mg/ L) from 0.25mg/L of the raw sample. The turbidity and the pH of the treated sample were reduced to 530 NTU and 6.9 respectively from 873 NTU and 9.1. Dead algal biomass is a useful alternative to conventional adsorption products for suspended solids uptake from tannery effluents. The expenses of the process is lesser compared to other techniques. But the development of bio-sorption processes using algal biomass requires further investigation, with particular attention to: Selectivity of algal species, Regeneration and reusability of algal biomass, Simulation and modeling of processes etc.

5. ACKOWLEDGEMENT

Authors would like to express their profound gratitude, sincere appreciation and a deep sense of indebtedness is also conveyed to Rajan Kumar Raha, Lecturer, Department of Leather Engineering, Khulna University of Engineering & Technology for his continuous supervision, detailed comments, encouragement and sympathetic assistance.

Authors would be very much delight to express their deep gratitude to authority "SAF LEATHER" for their kind permission to collect tannery waste water.

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7. NOMENCLATURE

Symbol	Meaning
DO	Dissolved Oxygen
g	Gram
mg	Milligram
L	Liter
mL	Milliliter
NTU	NephelometricTurbitiy Units