

Research Article

Tannery Waste Water Treatment through Aggregation of Bio-sorption and Chemical Coagulation Aided by Indigenous Coagulant

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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 220 MT raw hides and skins are taking for the production of leather in Bangladesh. The leather industry has crossed the record \$1-billion mark in exports in 2013-2014. According to the Department of Environment, the tanneries discharge 22,000 cubic meters of untreated liquid toxic waste daily. These pollution load and waste water should need treatment to make environmentally sustainable and living. From this point of view, we worked on tannery waste water processing. The paper highlights the initiation of Algal treatment with chemical coagulation process aided by natural coagulant for 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 4.48 mg/L at 33.6 °C (HQ 40d of HACH) where DO level was 0.24 mg/L at 33.6°C in raw mixer. In addition, the amount of alum as chemical coagulant was reduced in tannery waste water treatment by using indigenous snail shell powder as coagulant aid in conjunction with alum. In case of untreated sample after sedimentation required alum dosing was 6 mL/ 40 mL sample. After algal treatment, required alum dosing reduced to 4 mL/ 40 mL sample. By adding 3 mL/ 40mL liquid natural coagulant as coagulant aid, alum dosing was further minimized to 1 mL/ 40mL sample. The odour was more tolerable than raw mixer after algal treatment but after adding alum aided by natural coagulant, the odour was more acceptable than before. The diversified technique can hopefully reduce a reliable chemical cost in treatment process, considerable amount of pollution load & increase DO level and thus make effluent environment friendly to discharge. Finally, the DO level increases up to 6.56 mg/L at 33.7 °C and turbidity reduces to 183 NTU, pH reduces to 7.6, odour turns to be tolerable limit.

Keywords: Pollution load, algae, sedimentation, turbidity, DO, environment, coagulant.

1. Introduction

Tannery in Bangladesh seems a source of pollution load and waste water to all because there are 270 registered tanneries where approximately 220 MT raw hides and skins are taking for the production of leather in Bangladesh (Environmental Concerns, 2011). The leather industry has crossed the record \$1-billion mark in exports in 2013-2014 (Suman, 2015). According to the Department of Environment, the tanneries discharge 22,000 cubic meters of untreated liquid toxic waste daily (Human Rights Watch, 2012). Tanning is one of the oldest leather manufacturing process which is highly complex and characterized by high suspended solids, settle able solids, sulphide, chloride and chromium etc.

When untreated tannery effluents discharged directly into the water bodies or into the open lands cause irreversible damage to the environment. As a result, Tanning Industry which is considered as highly polluted industry (Lanteigne, 2010). Tanneries generate wastewater in the range of 30 - 35 L/kg skin or hide processed with variable pH and high concentrations of suspended solids. Major problems are due to waste water containing heavy metals, toxic chemicals, chloride, lime with high dissolved and suspended salts and other pollutants (Manivasagan, *et al*, 2011). Due to the inherent characteristics of tannery effluents, various physio-chemical techniques have been studied for the applicability to the treatment of tannery wastewater. Among these are coagulation, flocculation, ozonation, reverse osmosis, ion exchange and adsorption (Aboulhassan, *et al*, 2008).

Bio-sorption of heavy metals by algal biomass is an advantageous alternative, an appropriate and

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economically feasible method used for waste water and waste clean-up, because it uses algal biomass sometimes considered waste from some biotechnological processes or simply its high availability in coastal areas make it suitable for developing new by-products for waste water treatment plants (Brinza, *et al*, 2007). The use of dead cells offers several advantages: metal removal system is not subjected to metal toxicity, there is no requirement for growth media and nutrients, and adsorbed heavy metals can easily be desorbed and the biomass can be reused (Wike, *et al*, 2006). Algae have proved to possess high metal binding capacities due to the presence of polysaccharides, proteins or lipid on the surface of their cell walls containing some functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals (Gupta, *et al*, 2008).

Coagulation indicates the process which colloidal particles and very fine solid suspensions are destabilized, so that they can begin to agglomerate if the conditions are appropriate. Flocculation refers to the process by which destabilized particles actually conglomerate into larger aggregates so that they can be separated from the waste water (Farajnezhad, *et al*, 2012). Coagulant chemicals with opposite charges of suspended solids are added to the water to neutralize the negative charges on non-settable solids (such as clay and color-producing organic substances). Once the charge is neutralized, the small suspended particles are capable of sticking together. These slightly larger particles are called micro flocs, and are not visible to the naked eye (Prakash, *et al*, 2014). Aluminum sulfate (alum), ferrous sulfate, ferric chloride and ferric chloro-sulfate are commonly used as chemical coagulants (Farajnezhad, *et al*, 2012).

While the effectiveness of these chemicals as coagulants is well-recognized, there are many disadvantages associated with usage of these coagulants such as ineffectiveness in low-temperature water, relatively high procurement costs, detrimental effects on human health, production of large sludge volumes and the fact that they significantly affect pH of treated water. There is also strong evidence linking aluminum-based coagulants to the development of Alzheimer's disease in human beings (Kazil, *et al*, 2013). Therefore, it is desirable to reduce the amount of chemical coagulant for wastewater treatment. In this paper this is done by combining coagulation with bio-sorption.

Coagulant aids are used to water during coagulation to improve agglomeration, build a stronger, more settle able floc, reduce the amount of coagulant and reduce the amount of sludge production. Here, the amount of chemical coagulant is further abated by using indigenous snail shell powder as a natural coagulant.

2. Methodology

2.1 Sample collection

Samples were collected from a renowned tannery nearby KUET campus. Collected samples were from different sections 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 to tanning are collectively referred as beamhouse operations. The consecutive 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 below (Hashem, *et al*. 2014).

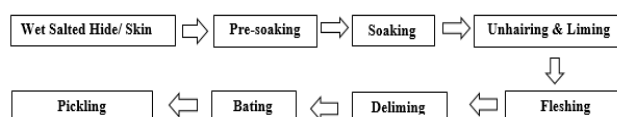


Fig. 1 Flow chart of beam house operations

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 settle 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. 2 Before settling **Fig. 3** After settling

2.4 Materials

The materials used for the desired treatment process are micro algae of Chlorophyte group, alum as coagulant and snail shell powder as coagulant aid. These algae are 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 Cryophyte algae. The algae were collected from a lake of KUET campus. The algae were washed well thoroughly by continuous water flow. They were dried for two days in an oven at 50-60 °C for conditioning to protect from fungal attack and putrefaction. After conditioning they were grinded carefully and isolated micro particles by sieving. Reagent grade alum was used in the treatment process. Alum is grinded well and prepared a solution of alum in the concentration of 10 g/L. Snail shell was collected from rural area. It was washed well with continuous water flow and dried well. Then it was grinded well and prepared snail shell power solution in the concentration of 10 g/L. In this way, materials were prepared for the treatment process.

2.5 Algal dosing

Algal dosing is the process of choosing optimum amount of required algae for best performance on the basis of pH, contact time, amount etc. Optimum dose of algae was selected on the basis of suspended solids adsorption percentage 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 2.5 hrs. After that percentage of suspended solids adsorption by different amount of algae was calculated and was selected the best one. Secondly, 4 beakers each of 50ml 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 0.1 N hydrochloric acid. After that all the samples were treated with the above selected optimum amount of algae for 2.5 hours and percentage of suspended solids adsorption at different pH was calculated and was selected the best one. 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 with 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 40 ml waste water processing was 0.3 g. That amount of algae was measured with the help of analytical balance. Then measured amount of algae was poured into the waste water and mixed with 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 Coagulant dosing for raw sample

After settling operation, raw sample of 6.0 was treated with different amount of alum as chemical coagulant to select dosing. From raw sample, 40 mL of raw sample was taken for each beaker. Alum solution was added to each beaker in sequential manner 3 mL, 4 mL, 5 mL, 6 mL and 7 mL and vigorously stirred for five minutes. Then stirred the sample slowly for 10 minutes. After stirring, had rest for thirty minutes and checked out whether settling starts or not. Then 10 mL of upper solution was taken for suspended solids measurement.

2.8 Coagulant dosing for algal treated sample

At first five beakers about 50 mL were taken. Then the beakers were conditioned in oven and measured the weight of each beaker after drying. About 40 mL algal treated sample was taken in each beaker. Then alum dosing was made in the treated sample in each beaker. Then 1mL, 2mL, 3mL, 4mL, 5mL solution of alum were added sequentially in the five beakers and vigorously stirred the sample for five minutes. Then the sample was stirred slowly for 10 minutes. After stirring, had rest for thirty minutes and checked out whether settling starts or not. Then 10 mL of upper solution was taken for the measurement of suspended solids.

2.9 Optimization of chemical coagulant by using snail shell powder as natural coagulant

The amount of alum for the processing of algal treated waste water can be partially reduced by adding snail shell powder as coagulant aid. Three beakers were taken and conditioned properly. In first beaker, 40 mL treated sample was taken and add Alum with snail shell powder with the ratio of 50:50 (Alum: snail shell powder). In second beaker, Alum with snail shell powder solution was added in 40 ml sample with the ratio of 45:55 (Alum: snail shell powder). In third

beaker, Alum with snail shell powder solution was added in 40 ml sample with the ratio of 33:67 (Alum: snail shell powder). Then 10 mL of upper solution was taken for the measurement of suspended solids. The amount of alum was reduced in tannery waste water treatment by using snail shell powder as coagulant aid in conjunction with alum (Bina, *et al*, 2009).

3. Results and discussion

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

From table 1, 2 it is noticed that the percentage absorbance of suspended solids by algae is 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 was two and half hours

The total amounts of suspended solids for different dosing of alum are given in table 3

The total amounts of suspended solids for different dosing of alum after algal treatment are given in table 4.

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 2. Effect of pH on algae

No of Beaker	pH	Absorbed (mg/L)	Percentage of absorbance (%)	Amount of algae (g)	Remarks
1	5.0	23890	50.00	0.3	
2	6.0	30250	63.00	0.3	Accepted
3	7.0	20640	43.00	0.3	
4	8.0	24550	51.63	0.3	
5	Raw	25100	52.78	0.3	

Table 3. Coagulant dosing for raw sample

No of Beaker	Amount of Alum (mL)/ 40 mL [Solution Concentration 10 g/L]	Amount of Suspended Solids (mg/L)	Remarks
1	3 mL	29046	
2	4 mL	28356	
3	5 mL	26750	
4	6 mL	24900	Accepted
5	7 mL	24578	

Table 4. Coagulant dosing after Algal Treatment

No of Beaker	Amount of Alum (mL)/ 40 mL [Solution Concentration 10 g/L]	Amount of Suspended Solids (mg/L)	Remarks
1	1 mL	14370	
2	2 mL	12890	
3	3 mL	11050	
4	4 mL	9920	Accepted
5	5 mL	9610	

Table 5 Optimization of chemical coagulant by using snail shell powder as natural coagulant

No of beaker	Amount of Alum with snail shell powder (mL)/ 40 mL [Solution Concentration 10 g/L]	Alum: Snail Shell Powder Solution	Amount of Suspended Solid (mg/L)	Remarks
1	2.0 mL + 2.0 mL	50:50	8425	
2	1.4 mL + 2.6 mL	44:56	8100	
3	1mL + 3mL	33:67	7820	Accepted

Table 6 Environmental parameters (raw sample) and devices

Parameter	DO	Turbidity	pH	Salinity	Conductivity
Raw Sample	0.25 mg/L at 33.7 °C	873 NTU	9.1	24.4 ppt. at 33.7 °C	45.00 mS/ m at 33.6 °C
Device	HQ 40d of HACH	2100P Turbid Meter of HACH	EZDO PH5011	BOECO CT-676	BOECO CT-676

Table 7 Environmental parameters (treated sample) and devices

Parameter	DO	Turbidity	pH	Salinity	Conductivity
Treated Sample	6.56 mg/L at 33.6 °C	183 NTU	7.6	18.1 ppt. at 33.7 °C	33.46 mS/m at 33.6 °C
Device	HQ 40d of HACH	2100P Turbid Meter of HACH	EZDO PH5011	BOECO CT-676	BOECO CT-676

**Fig. 4** Before Treatment**Fig. 5** After Treatment

From table 3, 4, 5 it is noticed that the amount of suspended solids reduced in a sequential manner. Finally, the amount of suspended solids was reduced to 7820 mg/ L from 47550 mg/ L.

Different environmental parameters are measured of raw sample by the utilization of different devices. Some environmental parameters of raw sample and the devices used for the measurement are given in the table 6.

After combined treatment i.e. algal treatment and chemical coagulation aided by natural coagulant some environmental parameters of treated sample were measured by the utilization of different devices. Some environmental parameters of treated sample and used devices for measurement are given in table 7.

By comparing table 6 & 7, it is observed that a pretty good result was obtained. The DO level of treated sample is increased 6.56 mg/ L at 20 °C from 0.25 mg/L at 20 °C of raw sample (waste liquor). Another two parameters are also reduced to a significant amount; i.e. the former turbidity was 873 NTU and after treatment it is reduced to 183 NTU. The pH is measured i.e. 7.6 which is in a safe level. The discharge limit of water to environment is 6-9 pH.

The total amounts of suspended solids through optimization of chemical coagulant by using natural coagulant are given in fig. 4 and 5.

Conclusions

Dead algal biomass is a useful alternative to conventional adsorption products for heavy metal

uptake from tannery effluents. Here the following points are concluded from this work:

- 1) Development of bio-sorption processes with algal biomass requires further investigation, like Selectivity of algal species, Regeneration and reusability of algal biomass, Simulation and modelling of processes etc.
- 2) After the usage of green algae as bio-sorbents with chemical coagulation process aided by indigenous coagulant shows good efficiency of reducing pollution load from tannery waste water.
- 3) During the research work, we used 0.3 g algae at pH 6.0 within 2.5 hours' duration for treating 40 mL sample. After treatment of sample with algae, amount of waste particles reduced from 47550 mg/L to 28880 mg/L. That means 60.73% absorbance obtained by using such amount of algae. Therefore, it can be concluded that green algae can be used as bio-sorbents in treatment process.
- 4) Snail shell powder can be used as coagulating aid in waste water treatment process. Here 4 mL alum solution used as optimum dose. By using such amount in algal treated sample, the amount of total waste particles reduced to 9920 mg/L. After the infusion of coagulation aid the amount of waste particles reduced to 7820 mg/L. Thus, the alum dosing can be reduced for waste water treatment.
- 5) The use of this approach can confer solutions for the reduction of pollution load from waste water of tannery without being exposed to potential health hazard.

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