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Reuse of Pickling and Chrome Tanning Liquor and Treatment of Tannery Effluent

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Abstract

Leather industries in Bangladesh are polluting water and air severely. Among all the operation carried out in the tannery, pickling and chrome tanning are the leading pollution causing processes. The prevalent standard operating procedure of pickling, and chrome tanning causes pollution since the tannery owners in Bangladesh often discharge untreated pickling liquor and add extra chromium salt to expedite the chrome tanning process instead of adding a catalyst. This study was carried out to evaluate the re-use capability of the pickling and chrome tanning liquor without compromising the quality of leather. Later, the discharged effluent was treated with the locally available chemicals, especially available in tannery for purification. The results showed that the addition of 0.2% sulfuric acid (10 times diluted) and 0.1% formic acid (10 times diluted) in the old pickling bath and the addition of 5% fresh basic chromium sulfate in the used chrome liquor made the liquors efficient to re-use in the new tanning process. A slight change in the design of the common effluent treatment plant (CETP) is required to collect the used pickling and chrome tanning liquor. After re-using the pickling and chrome tanning liquor, the discharged effluent was treated to purify with the help of chemicals and adsorbents available in a tannery. The change in the biochemical oxygen demand (BOD), chemical oxygen demand (COD), total solid and chrome removal efficiency of discharged effluent after treatment was 95.4%, 84.6%, 98.5% and 66.7%, respectively. These results revealed that the cost associated with the processes and reduction of pollutants would make it a practicable method in the local tanneries of Bangladesh.

Introduction

The leather industry is one of the largest export-oriented industry in Bangladesh. In 2012-13 fiscal year, the worth of export was 1.29 billion USD [1] and it is expected to cross the 5 billion USD mark by 2020 [1]. However, the age old tanning processes followed in maximum tannery are seriously damaging the environment, especially in the Hazaribagh area of the Dhaka city. These tanneries produce 22,000 m^3 effluent and 232 tons solid wastes [2]. The Hazaribagh canal and river Buriganga is heavily polluted by the nearby tanneries and other industries. The water is completely lost its suitability to use. During tanning operations, there are several processes involved in the production of leather from raw hides or skin. Among all the processes liming, pickling and chrome tanning processes pollute environment most severely [3]. In the present work, we emphasized to find out the feasibility of re-use of the pickling and chrome tanning liquor. Early attempts have been taken to treat and re-use tannery effluent using different methods, especially by embedding system [4].

Raising animals for food and leather requires huge amounts of feed, pastureland, water and fossil fuels. Animals on factory farms produce 130 times excrement than the entire human population. The U.S. Environmental Protection Agency (EPA) has acknowledged that livestock pollution is the greatest threat to our waterways [http://www.peta.org/issues/animals-used-for-clothing/leather-industry/leather-environmental-hazards/]. The chemical composition of untreated hides or skin waste (fleshing, trimmings, and splits) depends mainly on the kind and quality of the raw material, treatment type, and processing conditions. The main components are up to 10.5% both proteins and fats and 60% moisture content. These wastes contain small amounts of mineral substances (2–6%, w/w). While processing leather, pickling is done to acidify the collagen and to protonate the carboxyl groups. In this way, the reactivity is modified and longer preservation period of the pelt is attained [6]. The traditional recipe for pickling is 100% water, 10% NaCl, 1% sulfuric acid and 0.5% formic acid (acids are added in 1:10 dilution), 0.2% imprapel CO, 0.5% hypo based on pelt weight [6]. The pickling bath is highly acidic and the pH is kept 2.8 in the tanneries. After pickling, the chrome tanning is the most important process contains trivalent chromium salt, which later converts to hexavalent chromium when comes in contact with water. Hexavalent chromium is carcinogenic and affects nose, lungs, skins, and throat [https://www.osha.gov/OshDoc/data_General_Facts/hexavalent_chromium.pdf]. Chrome tanning and subsequent re-tanning are carried out for several reasons; among them some advantages are high shrinkage temperature, resistance to putrefaction by microorganism, the degree of permanence of the changes and soft leather, etc. [7]. In chrome tanning, half of the pickle bath is added to the chrome bath and the chrome bath contains 8.0% basic chromium sulfate, 1.0% sodium formate and 0.5% carbonyl sulfide. Chromic oxide content of leather is 0.5% and the rest of the chromium is discharged in nature along with chrome tanning bath. The chrome tanning liquor is also acidic; pH of the chrome bath is kept 3.7 in tanneries.

The tanned leather wastes are mainly useless splits, shavings, and trimmings. These waste groups differ mostly in size and shape and contain 3–6% (w/w) of fat and about 15% (w/w) of mineral components, including 3.5–4.5% (w/w) of chromium as Cr_2O_3 [8]. Another type of tannery waste is wastewater and sludge. Wastewater contains pollutants, such as unused chemicals, leached proteins, and products of hide and skin degradation. Biological oxygen demand (BOD) and chemical oxygen demand (COD) for 1 Mg of hides the processed amount are 35–105 kg and 88–280 kg, respectively [9]. Sludge from wastewater treatment plants contains mostly water (up to 65% (w/w)), organic substances (30% (w/w)) and chromium (III) compounds (about 2.5% (w/w)). Moreover, tanneries emit odors and other volatile compounds from the tanning processes as well as from biological decomposition processes that take place in stored raw hides, wastewater, etc. Such pollutants as ammonia, hydrogen sulfide, volatile hydrocarbons, amines, and aldehyde are present in the air at tannery plants. Currently, all these gaseous pollutants are emitted to the atmosphere [8, 10]. In this study, attempts have taken to evaluate the re-use capability of the pickling and chrome tanning liquor without compromising the quality of producing leather. Later, we have treated the discharged effluent with the locally available chemicals, especially chemicals available in the tannery.

Materials and methods

Sample collection

Sample collection for pickling and chrome liquor re-use

Three samples were collected for pickling liquor and chrome liquor re-use experiments from three different tanneries of Dhaka, Bangladesh, Reliance Tannery, Ruma Leather Industries Limited and Samina Tannery (PVT) Ltd, respectively. From each tannery, one pickle bath and one chrome liquor sample were collected. All six samples were collected in 1-liter plastic bottles and filled to its capacity.

Sample collection for effluent treatment

To determine the treatment technique of tannery effluent, three samples were collected from three different places of Hazaribagh canal, Dhaka, Bangladesh. The first sample was collected near the Hazaribagh bazaar, the second sample was collected from the canal flowing behind Samina Tannery (Pvt) Ltd and the third sample was collected from the canal's opening to the river Buringanga.

Analysis and preparation of samples

Analysis and preparation of samples for pickling liquor

In tanneries, the quality of pickle liquor depends on the pH value of the liquor. To re-use pickling liquor, we must find out the liquor physical and chemical properties. At first, the liquor was filtered with analytical grade filter paper (Double ring filter paper) to remove impurities like flesh, loose protein material and other impurities like dirt, particulate material, etc. Then the pH of the solution was measured using the pH meter (Thermo Scientific™ Orion™ Versa Star Pro™ benchtop meter, USA).

The pH value of all the pickle liquor samples was determined at both stages, namely fresh liquor and discharged liquor. After analysis, according to the results, the salt and acids were added in different ratios to find out the best ratio for the pickling liquor reuse.

Analysis and preparation of chrome tanning liquor

The chrome liquor was also assessed to find the capability of re-utilization of the liquor in the new chrome tanning process. At first, the liquor was filtered using the analytical grade filter paper (Double ring filter paper) to remove dirt, particulate materials, flesh, loose substances, etc. Then the samples were prepared for atomic absorption spectroscopy analysis. The sample was then acid digested [11] and analyzed to find out the amount of chromium was present in the liquor using the atomic absorption spectrometer (Perkin Einer-AAnalyst 800, USA).

Since the chrome liquor used in tanneries normally use 8% chromium hydroxyl sulfate for tanning. We analyzed the liquor and found that the chromic oxide content was 0.8 mg/L; then we measured the value of chromic oxide of discharged chrome tanning effluent. After analysis, according to the result, the liquor was filtered and basic chromium salt and chrome stable fats were added in different ratios to find out the best ratio for the chrome liquor reuse.

Analysis of effluent

pH analysis

At first, the effluent was filtered with analytical grade filter paper (Double ring filter paper) to remove impurities like flesh, loose protein material and other impurities like dirt, particulate material, etc. Then the pH of the solution was measured using the pH meter (Thermo Scientific™ Orion™ Versa Star Pro™ benchtop meter, USA).

Total dissolved and suspended solid

Total dissolved solids (TDS) and total suspended solids (TSS) were determined gravimetrically following the standard methods of the American Public Health Association [12]. Sulfide level was determined by following the official method (SLC

202) of the Society of Leather Technologist and Chemists, 1996.

Biochemical oxygen demand

The biochemical oxygen demand (BOD) was measured through Oxitop measurement system (208214 OxiTop^{R}IS6, USA). The effluent sample (164 ml) was introduced in the BOD bottle and NaOH pellets were added in order to absorb the CO_2 produced from the oxidation. The method followed were DIN 38409T51 and DIN 38409T52 [13].

Chemical oxygen demand

For the chemical oxygen demand (COD), one ml sample was taken in 100 ml volumetric flask and diluted to 100 times by adding 99 ml distilled water. The method followed was DIN 38409 Part 41:1980 method [14].

Chromic oxide content

Chromic oxide content was measured prior to the analysis of utility capacity of chrome liquor. The method followed was SLC-8 (IUC-8, BS 1309:8); IUC-3 to determine the chromic oxide content.

Pickling and chrome liquor re-use experiment

Pickle liquor re-use

The collected samples were analyzed to find out the pH of the solution. In tanneries, generally the pH is kept 2.8 in pickling process and the pH is maintained strictly. We have found that the pH of the discharged liquor was 3.6 as it comes to contact with water during the washing of the tanning drums. We added H_2SO_4 and HCOOH in different ratios to find out in which ratio the pH is adjusted to 2.8. Moreover, the half of the liquor is only discharged and half of the liquor is used for adding chrome tanning bath. So we added fresh water and common salt collected from the desalting process of raw hides and skin. The selected recipe for pickling liquor was 80% water, 8% NaCl, 0.1% imprapel CO (run for 15 minutes), 0.5% formic acid (run for 15 minutes), 1.2% sulfuric acid (run for 150 minutes, left overnight) and 0.5% Hypo (run for 30 minutes). Half of the pickle bath was drained off.

Chrome liquor re-use

The amount of Cr_2O_3 content was measured using two different methods and the experiments were triplicated. At first, the chromic oxide content of the waste chrome liquor was measured using SLC-8 (IUC-8, BS 1309:8); IUC 3 method and from the result the amount of chromium present in the liquor was calculated. Secondly, we use atomic absorption spectroscopy (Perkin Einer-AAnalyst, USA) to measure directly the amount of chromium present in the liquor. The results obtained using both methods were identical. The selected recipe for chrome tanning added to the pickle bath was 4.0% Basic chromium sulfate (run for 30 minutes), 1.0% sodium formate, 0.5% carbonyl sulfide (OCS, run for 60 minutes and checked 100% penetration)**,** 50% Water**,** 1.2% sodium bicarbonate (1:20 dilution, run for 90 minutes**,** 0.2% preservative (1:5 dilution, run for 60 minutes and checked pH 3.7-3.8). Later, the liquor was drained off and piled up for one week to check polymerization reaction.

Effluent treatment

Filtration

The effluent was filtered using analytical grade filter paper to remove the coarse particle floating in the sample. Then the filter paper was dried and weighed to measure the amount of total suspended solid. Later, 100 ml filtered sample was evaporated at 100°C to determine the amount of total dissolved solid.

Chrome removal

As the chrome liquor is highly acidic, to minimize the cost and make the process popular among tanners, lime was added to the liquor and an acid-base neutralization reaction took place. Later, the $Cr(OH)_3$ was removed by filtering the liquor.

Activated charcoal filter

Activated charcoal was used (Unichem, China) to finally remove the remaining impurities from the liquor. 100 ml liquor was stirred 30 minutes with 5g of activated charcoal and then filtered using the analytical grade filter paper.

Leather physical analysis

The leather produced using the treated pickle and chrome tanning bath was analyzed for physical parameters, for example, tensile strength, stitch tear strength, Bauman strength, and ball bursting test.

Tensile strength

Tensile strength indicates the overall strength of the leather. It was measured following the IUP-6 method [15]. The sample was cut into dumbbell shaped specimens (110 mm × 25 mm) and attach to the tensile strength testing machine (SATRA, Tensile Tester, Leeds, UK). The external force was applied to the specimen and in what amount of force the specimen was broken into two parts was observed. The strength depends on the moisture and fat content of the leather sample. Tensile strength was measured using the following formula:

Tensile strength = breaking load in kg/cross section (square cm)

Stitch tear strength

This strength was determined to know the strength of small seams of leather. This test was carried out using the DIN 53331 method [15]. The sample size was 50 mm × 25 mm and two holes were made each has 2 mm diameter. A soft 1 mm diameter steel wire bent to U-shape was inserted through the holes, then attached to the tensile strength testing machine (SATRA, Tensile Tester, Leeds, UK) and the load was applied until the sample specimen tore down between two cut holes. The stitch tear strength was determined using the following formula:

Stitch tear strength = tearing load in kg/leather thickness (cm)

Tearing/Bauman strength

The tearing strength gives the idea about the strength of the fiber. It was measured by the SATRA PM 162 method [15]. The sample was cut into 50 mm × 25 mm and two holders were inserted into the sample, then attach to the tensile strength testing machine (SATRA, Tensile Tester, Leeds, UK) and the load was applied until the sample tore down. The tearing strength was determined using the following formula:

Tearing strength = tearing load in kg/leather thickness (cm)

Ball bursting test

The bursting strength is an index of the overall strength of the leather and mainly determined for the shoe upper leather. This test was carried out by the IUP-9 method [15]. A circular specimen of 25 mm diameter was cut from the sample, attached to the lastometer (STM 104, SATRA, Leeds, UK) and the load was applied until the grain of leather was cracked; the test was further extended until the sample was busted due to high pressure. The strength was calculated using the following formula:

Grain crack strength = load in Kg/leather thickness (cm)

All the experiments were done thrice and the average is calculated.

Results and Discussion

Chemical analysis and reuse recipe

In the pickling and chrome tanning bath, we have added chemicals in different ratios to find out the suitable ratio to re-use the liquor in new pickling and chrome tanning process. The results are provided in Table 1 and Table 2 and the final ratio, which was used in the new pickling and chrome tanning processes is given with the original recipe in Table 3 and Table 4, respectively. Pickling was done to preserve the raw leather from putrefaction. This process is costly and pollutes environment due to the use of common salt, sulfuric acid, and formic acid. From the Table 1, we got the information about the pH values of the pickling liquors of different tanneries and the pH of discharged pickling liquor. Since all the tanneries depend on the pH value as the standard parameter for measuring the quality of pickling liquor, we had concentrated our focus on pH value too. Half of the pickle liquor was preserved for adding chrome tanning bath, only discharged half could be collected; hence adding fresh water according to the weight of the new batch of leather was required. Then salt and acids were added and through a trial and error method, we settled that the additives given in table-4 would be enough to lower the pH of the pickle liquor and would be good enough to be reused in the tanning process.

Chrome tanning is the most important and prevalent tanning process practiced all over the world. Although chrome tanning brought the best quality such as softness, suppleness, breathability of the leather, it does come at the cost of heavy environmental pollution [2, 3]. To reduce the

Table 1 Pickling liquor pH analysis results.

Sample No.	Fresh liquor pH	Discharged liquor pH	Average pH
1	2.8	3.57	
2	2.8	3.62	3.59
3	2.8	3.59	

Table 2 Chromic oxide content of fresh and discharged liquor.

Sample No.	Fresh liquor (mg/L)	Discharged liquor	
		Titration (mg/L)	AAS analysis (mg/L)
1	0.80	0.3035	0.3035
2	0.78	0.3030	0.3030
3	0.80	0.3035	0.3035

AAS = atomic absorption spectroscopy

Table 3 Chemical recipe for pickling liquor re-use experiment.

Components	Concentration
Water	50% fresh water based on the weight of new batch
Salt	40 g/kg
Formic acid	0.2% (1:10 dilution)
Sulfuric acid	0.1% (1:10 dilution)

Table 4 Chemical recipe for chrome liquor re-use experiment.

Component	Concentration	Chromic oxide content
Chrome powder	3%	0.61%
	4%	0.70%
	5%	0.78%
	6%	0.85%
	7%	0.93%
Chrome stable fat	0.5%	-

pollution, we needed to reduce the discharge of chrome liquor. Instead of applying complex, costly purification techniques, we could reuse the chrome liquor. To reuse the chrome liquor, chromic oxide content was measured since chromic oxide content is used as the standard of chrome liquor quality. From the analysis of fresh and used sample, it was found that significant amount of chromic oxide was used in the chrome tanning process, which is given in Table 2. We then follow the trial and error method to find out the amount of fresh chromium salt needed to add to get the 0.8 mg/L chromic oxide content. In Table 4, the results of chrome addition in different quantities are given. To reuse the chrome liquor, we need to add 5% basic chromium salt, which would make the chromic oxide content near to 0.8%. Therefore, the addition of 5% chrome powder is recommended.

There were several attempts to reuse the chromium and treated wastewater in tanning process again; however, the utilization of pickling liquor was not attempted in large scale. Electrochemical oxidation methods [16] were tried and the process was successful, yet that procedure is very difficult to implement in tanneries in Bangladesh. Since the pickle liquor contains a large amount of salt and acid, hence, it actively contributes to higher chemical oxygen demand and low pH both of which are polluting the fresh water. The results of this study showed that using simple procedures, pickling liquor can be reused and can be easily implemented at the tanneries in Bangladesh.

In this project, we tried to keep the system simple and aligned with tannery operations, for it can be adopted by the tanneries with minimum change of machinery. However, there were attempts by other researchers to recover and reuse the chromium by seaweed [17] where the chrome effluent was treated with pre-treated seaweed. Although this method was able to recover 11 mg chromium/g seaweed at pH 3.5-3.6 [17], which is a substantial amount of chromium, the complex process and the cost associated with the process would make the tanners unwilling to follow the process. The chromium can be recovered from the spent liquor by magnesium oxide and sulfuric acid treatment [17] since the process needs additional setup and the initial cost of setup and operating the system is about USD 88,000 associated with the process would make the owners of tanneries unwilling to follow the process [18]. The process which is given in Table 2 and Table 5 to reuse chrome tanning liquor was specially developed for the tanneries located in Bangladesh, where ease of operation and cost effectiveness both are highly required criteria for a process to be followed.

Leather physical analysis

Since the quality of produced leather cannot always be measured by the chemical analysis, hence we have carried out significant physical tests to ensure the quality of leather produced from reused pickling and chrome tanning liquor. The results are given in Table 5. Tensile strength indicates the overall strength properties of the leather which is very important for producing leather products such as footwear, garments, bag, etc. Though 100 kg/cm^2

Table 5 Physical analysis result of leather after the re-use of pickling and chrome tanning liquor.

Physical test	Method	Experiment result	Standard values
Tensile Strength	IUP-6	207 kg/cm^2	200kg/cm^2
Stitch Tear Strength	DIN-53331	83kg/cm	80-100kg/cm(shoe upper)
Bauman Strength	SATRA PM 162	31 kg/cm	30kg/cm
Ball Bursting Strength	IUP-9	23kg/cm	20kg/cm

Table 6 Effluent results before and after treatment.

Parameter	Before treatment	After treatment	Standard discharge limit	Percent change
pH	3.6-3.7	7.8	6-9	110.8%
Total dissolved solid	141870 ppm	1643 ppm	2100 ppm	98.8%
Total suspended solid	70080 ppm	127 ppm	150ppm	99.8%
Chemical oxygen demand	4736 ppm	726 ppm	200ppm	84.6%
Biochemical oxygen demand	1487 ppm	68 ppm	50ppm	95.4%
Chromic oxide	0.3 ppm	0.1ppm	0.1ppm	66.67%

tensile strength is enough, it is recommended that leather must have the double tensile strength to ensure the quality [19].

Stitch tear strength was measured to know the strength of small seams of leather. During the production of football, garments, gloves where the stitching is mandatory, this test gives substantial information about the eligibility of a leather to use for manufacturing football, garment products or gloves. Tensile strength and stitch tear strengths give the idea about the leather, whereas the Bauman strength gives an idea about the strength of its fiber [19]. Ball bursting test was carried out to find out the overall strength of leather and its fiber in every direction since the machine applies force to all directions uniformly of the sample. The results of physical tests after the reuse of pickling and chrome tanning liquor were satisfactory that the strength of leather that was produced from used liquor was constantly achieving the standard values set for each physical test given in Table 6 [19]. In the leather industry, physical test's results are valued, therefore, we recommend reusing discharged effluent to produce leather.

Effluent treatment

Effluent treatment process was secondary objective and mostly chemicals available in the leather processing industries were used. In the treatment process, the effluent was filtered first. Filtration could reduce most of the BOD_5 and COD if properly carried out. Later, Fe(II) and Fe(III) salts were used and then chrome was precipitated as chromium hydroxide by adding lime. Finally, activated carbon treatment was used to remove the remaining impurities. The results of the effluent treatment experiment are given in Table 6. For effluent treatment, different parameters were measured. After laboratory analysis, it was found that the discharged water was highly contaminated with polluting substance and the pH was in the acidic range. The pH, total dissolved solid, total suspended solid and chromic oxide content reduction were found satisfactory since they contribute to make the water acidic in nature, deplete the amount of oxygen and intoxicated the water for the aqueous life and human those who use this water. However, a high concentration of biochemical oxygen demand and chemical oxygen demand could not be reduced to the minimum standard level due to the increase of the treatment cost which was an important consideration throughout the project work.

Undoubtedly, leather industries in Bangladesh are causing great damage to the environment by discharging effluent without prior treatment. However, there was no active effluent treatment plant in Hazaribagh (recently closed by Bangladesh government and relocated tannery estate to Savar, Dhaka where an effluent treatment plant is built) and this causes huge pollution to Hazaribagh canal, The river Buriganga, the people reside in that part of the town and tannery workers. In different parts of the world, several treatment processes have been tried [19-23] and had positive results; however, these works were completely focused on one or two parameters described in Table 7. In this work, a significant amount of pH, total dissolved solid, COD, BOD_5, chromic oxide content were reduced, yet chemical oxygen demand and biochemical oxygen demand did not reduce up to the standard discharge limit, which was reduced in the processes described in other research literature [24-26]. Still, considering the cost associated with the processes and reduction of pollutants in other parameters would make it a practicable method in the local tanneries of Bangladesh.

Conclusions

To prevent pollution; the leather processing industries in Bangladesh should re-use the effluent as much as possible. The solid wastes like buffing dust, leather trimmings might be used to produce heat energy by burning; furthermore, they might be developed to the adsorbent. If the tanneries follow these processes, they would be able to reduce cost as well as pollution. For the effluent treatment, tannery should have an internal treatment plant. At least, the tanning effluent should not mix together, rather those should be divided into different flows and collected to reuse. Only when it is not feasible to use, then the effluent should be discharged by maintaining proper rules and regulations.

Conflict of interest

The authors declare that there is no conflict of interest.

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