

OXIDIZERS EFFECT OF SULPHIDE REMOVAL FROM HAIR DISSOLVING LIMING WASTEWATER IN TANNERY

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ABSTRACT

Hair dissolving is the conventional operation in the tannery where raw animal skins are treated with sodium sulphide and calcium hydroxide to remove keratin proteins e.g., hair and wool epidermis and to dissolve non-structural proteins. The hair dissolving liming process discharges wastewater containing soluble sulphide. In acidification, wastewater contains soluble sulphide creates toxic hydrogen sulphide, which is a great concern. In this present study, the efficiency of hydrogen peroxide (H₂O₂) and sodium chlorite (NaClO₂) oxidizers are compared to remove sulphide from the hair dissolving liming wastewater. The physicochemical parameters of the liming wastewater were: pH 12.3 and sulphide 3666.01 mg/L. The physicochemical parameters: sulphide and pH at optimum conditions of the treated liming wastewater for hydrogen peroxide (H₂O₂) and sodium chlorite were 109.2 mg/L, 6.1 and 98.3 mg/L, 7.0, respectively. The sulphide removal efficiency for H₂O₂ and NaClO₂ were 97.0% and 98.5%, respectively. The simple and easy method would be effective for treating hair dissolving liming in reducing soluble sulphide discharge from the tanneries.

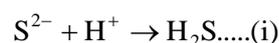
Keywords: *Tannery, Hair dissolving liming, Wastewater, Environment, Oxidizers.*

1. INTRODUCTION

The leather industry is one of the indispensable sectors for economic development contributing to high earning. In the world, 15 million tons of hides and skins are processing per year in this industry; the discharged wastewater is more than 1500 million litres/day in the average calculation (Rajamani, Chen, Zhang & Su, 2009). The amount and kind of waste created during leather production is variable and depends on numerous factors like breed, slaughter procedure, conservation of hides and the technology of used for hair removal (Souza & Gutterres, 2012). In Bangladesh, during liming operation in hair burning process, 208-623 metric ton sulphide is released (Hashem, Nur-A-Tomal, Ahsan & Bushra, 2018). It has been estimated that over 55,000 ha of land have been contaminated with tannery wastes and around 5 million people are affected by the low quality of the social environment and drinking water (CSIRO, 2001; Sahasraman & Jackson, 2005).

Now those days, in hair removal technology makes up 60-70% of the total pollution discharge from the leather industries (Xu, Zhang & Hao, 2009). Having of sulphhydryl (SH⁻) group in hair/wool, it leads to accumulation of heavy metals (Mondal, Hashem, Nur-A-Tomal & Aminur, 2016). The beam house operation naming liming and unhairing is functioned to remove hair, fatty substance, interfibrillary components, epidermis and to rupture the fibre structure (Covington, 2011). This technology depends upon the phenomenon of destroying or loosening and removal of hair by chemical and mechanical action; the keratinous materials (hair, hair root, epidermis, etc.) are removed from the pelts conventionally with the mixture of sulphides (Na₂S, NaSH) and lime (CaO) (Quadery, Uddin, Azad & Chowdhury, 2014).

The sulphur present into effluent comes from organic matter (especially hair) and from compounds used in the processing of hides of unhairing agents. Sulphur is found in the effluent in the form of sulphates (SO₄²⁻) and sulphides (S²⁻) (Souza & Gutterres, 2012). If the hair dissolving wastewater pH 8, soluble sulphide emits poisonous hydrogen sulphide (H₂S) gas (Dixit, Yadav, Dwivedi & Das, 2015) as the following equation (i):



The risk of H₂S formation during effluent treatment poses a serious environmental problem (Souza & Gutterres, 2012). Increasing salinization of rivers and groundwater has led to the loss of agricultural production and reduce the quality of drinking water (Money, 2008). The high pH concerned the liming water produce H₂S by mix up with low pH carried chrome tanning wastewater after discharge it from the industry (Hashem, Nur-A-Tomal, Ahsan & Bushra, 2018).

So far, many researchers worked on treating liming wastewater in various ways. For example, electrocoagulation (Sengil, Kulac & Ozacar, 2009); coagulation-electrocoagulation process (Hashem, Nur-A-Tomal, Ahsan, Momen, Hasan, Hasan & Sheikh, 2017); oxidation-coagulation-filtration method in sulphide removal (Hashem, Nur-A-Tomal & Bushra, 2016); simple coagulation filtration process (Barman, Juel & Hashem, 2016). Also, applying the techniques of flotation, electrochemical treatment, sedimentation, coagulation, ultra-filtration and reverse osmosis (Ates, Orhon, & Tunay, 1997; Song, Williams, & Edyvean, 2004). In those techniques, most often coagulants are used for the treatment of the hair dissolving liming wastewater are commercial aluminium sulfate (Al₂(SO₄)₃. 18H₂O), iron sulfate (FeSO₄.7H₂O), ferric chloride (FeCl₃.6H₂O) and lime (CaO) (Genovese, & Gonzalez, 1998). Likewise, in electrocoagulation (Hashem, Nur-A-Tomal, Ahsan, Momen, Hasan, & Hasan, 2017) electricity is used which is a costly and time-consuming process. The development of wastewater treatment techniques depends on several factors e.g., efficiency, cost-effective and environmental capability (Costa & Olivi, 2009).

In this study, an attempt was made to remove sulphide from the hair dissolving liming wastewater with low-cost oxidizers. The oxidizers hydrogen peroxide (H₂O₂) and sodium chlorite (NaClO₂) are used to compare their sulphide removal efficiency in simple and cost-effective.

2. METHODOLOGY

2.1 Sampling

The hair dissolving liming wastewater was collected into the high-density polyethylene (HDPE) bottle from the Superex Leather Ltd. Khulna, Bangladesh. The samples were taken immediately to the laboratory for the experiment.

2.2 Chemicals and Reagents

The reagents H₂O₂ (50%, TPL, Thailand), sodium chlorite (Hoechst, Switzerland) hydrochloric acid (Sigma Aldrich, Germany), potassium ferricyanide and barium chloride (UNI-CHEM, China); ammonium chloride (Loba Chemie, India), dimethyl glyoxime (Loba Chemie, India); iron(II) sulphate heptahydrate (Loba Chemie, India), ammonia (Loba Chemie, India), sulphuric acid (Merck Specialities Pvt. Ltd. India), ethanol (Merck KGaA, Germany) were purchased from a local scientific store. The buffer solution was prepared using 200 g ammonia chloride and 200 g ammonia per litre in deionized water. The indicator was prepared by mixing 10 mL 0.6% ferrous sulphate, 50 mL 1% dimethylglyoxime in ethanol which acidified with 0.5 mL concentrated sulphuric acid. The barium chloride solution was prepared by dissolving 12.5 g barium chloride in 1000 mL deionized water. The titrant 0.1 N potassium ferricyanide was prepared by dissolving 32.925 g potassium ferricyanide in 1000 mL deionized water.

2.3 Treatment of Hair Dissolving Liming Wastewater

Hair dissolving liming wastewater was treated with H₂O₂ and NaClO₂ oxidizers through the oxidation process. Scheme for the hair dissolving liming wastewater operation process by H₂O shown in Figure 1. Firstly, the process parameters of the untreated wastewater were analysed. Secondly, untreated wastewater was poured into a beaker, to which H₂O₂ was added and the mixture was stirred for 5 min to eliminate the evolved H₂S gas. Thirdly, the final pH of the mixture was assimilated with the help of dilute HCl and the final mixing was done by keeping on a stirrer for an additional 5 min. Finally, the mixture was allowed to settle. After settling, process parameters of the treated wastewater were analysed.

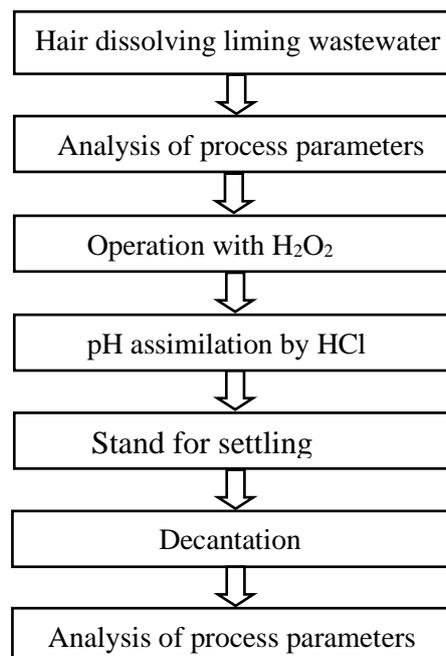


Figure 1: Scheme for the hair dissolving liming wastewater operation process by H₂O₂.

At the same time, the untreated liming wastewater was treated with NaClO₂. Scheme for the hair dissolving liming wastewater operation with the NaClO₂ is shown in Figure 2. At first, the process

parameters of the untreated liming wastewater were analysed. Then, the untreated lime was poured into a beaker, to which NaClO_2 was added in the liquid phase. Then, the mixture was stirred for 5 minutes and the final pH was assimilated by using diluted hydrochloric acid. After final mixing, keeping on a stirrer for an additional 5 min to oxidize perfectly and settling was done. Finally, again the process parameters were analysed.

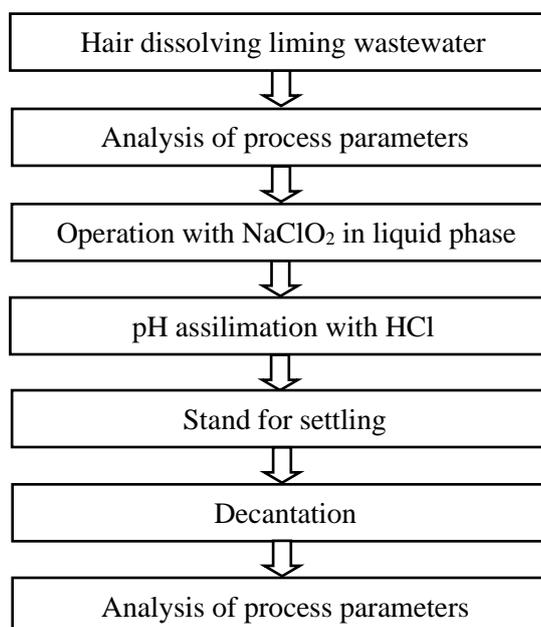


Figure 2: Scheme for hair dissolving liming wastewater operation process by NaClO_2

2.4 Analysis of Process Parameters

The electrical conductivity (EC), total dissolved solids (TDS), and salinity were measured by using an electrical conductivity meter (CT-676, BOECO, Germany). pH meter (UPH-314, USA) was used to measure the pH of the hair dissolving liming wastewater. Before measuring all the parameters, the meter was calibrated using the standard solution. EC, TDS, salinity was estimated gravimetrically following the standard methods of APHA (APHA, 2012). Sulphide level was measured by following the official method (SLC 202) of analysis (Society of Leather Technologist and Chemists, 1996).

2.5 Measurement of Sulphide

The soluble sulphide was determined by the titrimetric method following Society of Leather Technology and Chemist (1996) official method (SLC 202). A 25 mL treated hair dissolving liming wastewater without using filter paper and coagulant was pipetted into 200 mL conical flask. Then, 10 mL buffer, 1 mL indicator, and 2.0 mL barium sulphite were added and stopped the flask. The flask was left for 1 minute to precipitate the sulphite as barium sulphite to mask the interference. Then, the solution was titrated with the 0.1 N potassium ferricyanide until the pink colour was disappeared.

2.6 Process Escalation

Appraisals were carried out to optimize the treatment parameters: pH and oxidizers dose. The process parameters were engrafted by investigating the various physicochemical parameters e.g., sulphide, EC, TDS, and salinity of the treated wastewater. To optimize H_2O_2 dose, varying doses were used for each batch 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 where other parameters were left unchanged, such as pH (6.1). For the optimization of pH, mildly acidic to mild alkali pH (5.0 to 8.0) was preselected. And to optimize the NaClO_2 dose, varying doses were used for each batch 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 mL, where the other parameters were left unchanged (pH 7.0). Here, for the optimization of pH, mild acidic and mild alkali pH (6.0, 6.5, 7.0, 7.5 & 8.0) were preselected.

3. RESULTS AND DISCUSSION

3.1 Optimization of Oxidants Dose

From the assessment to determine the effect of oxidizers obtained result is represented in Figure 1 and Figure 2. Figure 1 shows the sulphide removal efficiency of H₂O₂ dose and in Figure 2 shows the sulphide removal efficiency of NaClO₂ dose. It was discerned that the sulphide removal percentage was gradually increased with the increasing dose of H₂O₂ and NaClO₂. Both oxidizers were applied at pH 7 and in both purpose removal percentage was increased to the 1.0 g of dose per 50 mL wastewater and after that the near about constant with the increasing dose of oxidizers. Here, it was realized that in same dose NaClO₂ gives a better result. At 7 pH, 1.0 g of oxidizers dose, 97.03% of maximum removal with NaClO₂ and 97.02 % of maximum removal with H₂O₂.

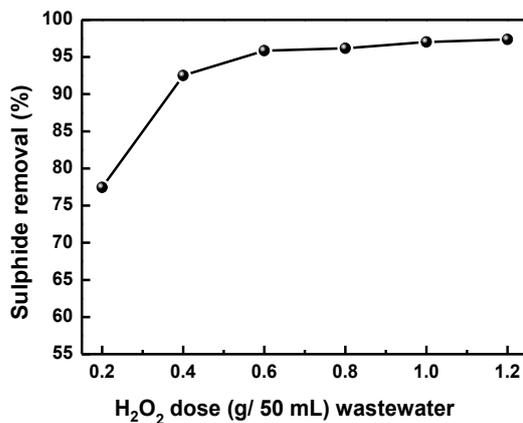


Figure 1: Sulfide removal with H₂O₂

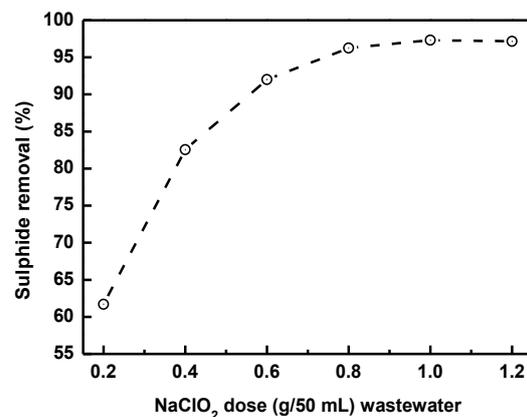


Figure 2: Sulfide removal with NaClO₂

3.2 Optimum pH for Sulphide Removal

The sulphide removal efficiency with increasing of pH on both oxidizers the same dose represented in Figure 3 and Figure 4.

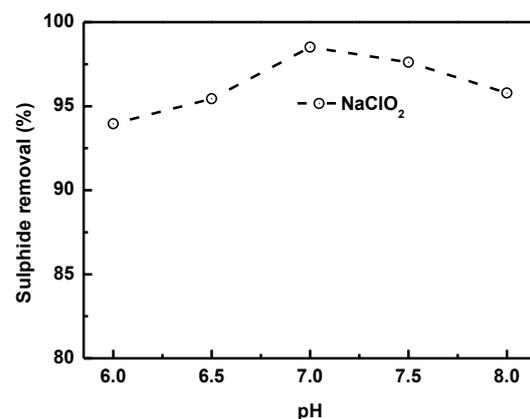
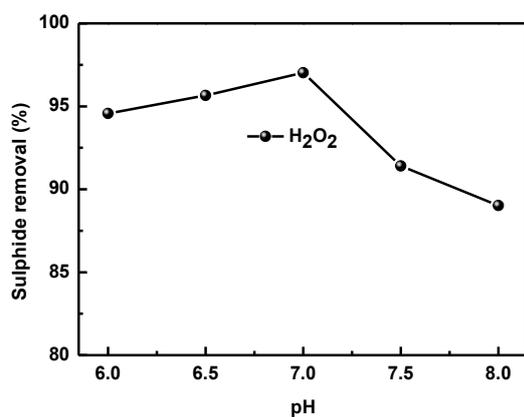


Figure 3: pH effect on sulphide removal by H₂O₂ Figure 4: pH effect on sulphide removal by NaClO₂

The important parameter of the process is pH which has a great contribution to the proper functioning of the oxidizers and removal of physicochemical parameters. In Figure 3, it was perceived that the maximum removal percentage at pH 7 per 50 mL of wastewater. In the same condition, the maximum percentage of sulphide removal with NaClO₂ was given a better result than operating with H₂O₂. The removal percentage with NaClO₂ and H₂O₂ were 98.5 % and 97.0 %, respectively. The maximum removal percentage was got at pH 7. When displaced from the normal pH condition (7 pH). the removal percentage was decreased. It may be caused by recreating of S²⁻ from the production of sulphur.

3.3 Efficient Comparison of Oxidizers

In the optimum and same condition, the result of the treatment process with H₂O₂ and NaClO₂ is compared in Table 1. Before treatment of the liming wastewater, the initial physicochemical parameters were: pH 12.3±0.04; TDS 16.26±0.04 g/L; sulphide 3666.01±9.3 mg/L; EC 33.83±0.07 mS and salinity 21.4 ±0.61 ppt. After completed all step treatment with H₂O₂ the physicochemical parameters were: pH 7.00±0.02; TDS 8.59±0.06 g/L; Sulphide 109.2±4.2 mg/L; EC 19.83±0.06 mS and salinity 10.2±0.14 ppt.

Table 1: Removal of pollution load from liming wastewater

Parameters	Initial	Treatment with		ECR (1997)	Unit
		NaClO ₂	H ₂ O ₂		
pH	12.3±0.04	7.03±0.03	7.00±0.02	6-9	-
TDS	16.26±0.04	14.94±0.18	8.59±0.06	2.1	g/L
Sulphide	3666.01±9.3	98.28±3.6	109.2±4.2	1.0	mg/L
EC	33.83±0.07	34.31±0.47	19.83±0.06	1.2	mS
Salinity	21.4±0.61	19.0±0.42	10.2±0.14	--	ppt

The physicochemical parameters, after treatment with NaClO₂ were: 7.03±0.03; TDS 14.94±0.18 g/L; sulphide 98.28±3.6 mg/L; EC 34.31±0.47 mS and salinity 19.0±0.42 ppt. In overall observation, it could be said that treatment with H₂O₂, sulphide removal percentage was lower but other parameters removal was higher than the treatment with NaClO₂. On the other hand, treatment with NaClO₂ the sulphide removal percentage was higher though other parameters removal percentage was lower than treatment with H₂O₂. In the case of treatment with NaClO₂, EC was increased. Because NaClO₂ react with HCl produces ClO₂ which evaporate over time. Further, NaClO₂ react with HCl and produce Na⁺, H⁺, Cl⁻ for counter ion. Therefore, treatment with NaClO₂ increased salinity.

4. CONCLUSIONS

The present study reveals that hair dissolving liming wastewater treatment with simple oxidation method. The physicochemical parameters were reduced for both the oxidizers. The pH was within the permissible level. The removal efficiency of sulfide, TDS, EC and salinity at optimized conditions for hydrogen peroxide were 97%, 47.2%, 41.4% and 52.3%, respectively. The removal efficiency of sulfide, TDS and salinity at optimized conditions for sodium chlorite were 98.5%, 8.1% and 11.2%, respectively. The EC was a little increased. The study could be useful to treat hair dissolving liming wastewater to reduce sulphide simple hydrogen peroxide oxidation method as well as to reduce the other physicochemical parameters.

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