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

Md. Abul Hashem*, Mst. Nazmin Zaman Khan, Protima Roy, Md. Anik Hasan

Department of Leather Engineering, Khulna University of Engineering & Technology (KUET), Khulna-9203, Bangladesh

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ABSTRACT

Liming and unhairing 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, the sulphide in wastewater generates toxic hydrogen sulphide, which has a negative impact on the environment. In this present study, the efficiency of hydrogen peroxide (H_2O_2) and sodium chlorite ($NaClO_2$) oxidizers are compared to remove sulphide from the hair dissolving liming wastewater. The soluble sulphide in the raw liming wastewater was 3666 mg/L. At optimized dose and pH for H_2O_2 and $NaClO_2$ soluble sulphide in the solution were 109.2 and 54.6 mg/L, respectively. The sulphide removal efficiency for $H_2O_2$and $NaClO_2$ were 97.0% and 98.5%, respectively at an optimum pH (pH 7). Before and after treatment the physicochemical parameters of the liming wastewater were analysed by observing different water quality parameters viz: pH, TDS, EC and salinity. At optimized condition TDS and salinity removal efficiency was 47.2%, 52.3% and 8.1%, 11.2% for H_2O_2 and $NaClO_2$, respectively. This simple and easy method would be effective for treating hair dissolving liming wastewater in reducing soluble sulphide discharge from the tanneries.

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

1. INTRODUCTION

The leather industry is considered one of the most potential sectors due to its enormous contributions to the world economy. In 2018, the leather industry contributes to the global market of US $80 billion and it is expected to the US $128 billion by 2022 (Sivaram & Banik, 2019). Due to producing a large number of solids, liquids and gaseous pollutants, the leather industry is negatively criticised (Pal *et al.* 2020). The quantity and kind of pollutants generated during leather processing depend on mainly two factors i) processing technology and ii) chemicals (Souza & Gutterres, 2012). On average every year, 15 million tons of hides and skins are processed which discharged more than 1500 million litres of wastewater (Rajamani *et al.* 2009). The discharged huge amount of wastewater accommodates a large number of different pollutants i.e. sodium, sulphide, chromium, chloride, nitrogen, total dissolved solids (TDS), biochemical oxygen demand (BOD), dyestuffs, and chemical oxygen demand (COD) (Chowdhury *et al.*2015). About 60-70% of pollutants of the leather industry are contributing from the unhairing and liming operation and this operation is considered as the highest pollution producing operation (Hashem *et al.* 2016). Besides dissolving the hair, wool, globulins, albumins, and subcutaneous layer, liming operation helps in swelling/plumping of the hide/skin and separating the non-structural proteins (Lofrano *et al.* 2013; Gutterres *et al.* 2011). The main chemicals used in the liming operation are lime (CaO) and sodium sulphite (Na_2S). Although lime is responsible for the production of a huge volume of sludge, it does not create other serious environmental problems (Saravanabhavan *et al.* 2003). On the other hand, Na_2S is considered one of the most dangerous chemicals used in leather processing operations because upon acidification its turns into hazardous substances e.g., toxic hydrogen sulphide, H_2S gas (Dixit *et al.* 2015) as the below equation (i).

$$S^{2-} + H^{+} \rightarrow H_2S.....(i)$$

The sources of sulphides in the liming wastewater are not only the Na_2S but also the sulphydryl (SH^-) group present in hair, wool (Xu *et al.* 2009). The sulphur may present in the liming wastewater in two forms sulphides (S^{2-}) and sulphates (SO_4^{2-}) (Souza & Gutterres, 2012). When the pH of the liming wastewater goes down below 8 it produces H_2S which is treated as one of the most influencing hazardous gas (Rubright *et al.* 2017). Sulphide gas not only creates environmental problems but also affects human health adversely like headache, nausea, irritation of eyes, and unconsciousness (Selvaraj *et al.* 2020). Nuvolone *et al.* (2019) reported that a high concentration of H_2S is responsible for premature death. De Kok *et al.* (2009) have observed that an elevated amount of H_2S has

*Corresponding Author: *mahashem@le.kuet.ac.bd*

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an adverse effect on seed germination and plant growth. Therefore, sulphide containing liming wastewater or wastewater should be treated to minimize those problems.

Several researcher groups have been carried out to remove as well as recover sulphide from industrial wastewater. By using electrochemical process sulphide could be recovered from industrial mixed wastewater (Selvaraj *et al.* 2016). Liu & Wang (2017) have observed that but using ionic liquid 100% H_2S could remove from wastewater within 2 hours. Nanoporous carbon can remove sulphide from wastewater through adsorption mechanisms (Gholampour & Yeganegi, 2014). Iron salts can remove sulphide from the municipal wastewater as ferrous sulphate by precipitation process (Zhang *et al.* 2008). Sergienko & Radjenovic (2020) have usedmanganese oxide-coated electrodes to recover as well as remove sulphide from the wastewater. All these methods have some disadvantages like creating secondary pollutants, required high capital investment, and sophisticated equipment. The efficiency of the biological treatment process has also been investigated to remove sulphide from the wastewater. Kurt *et al.* (2007) have observed that the biological process is less effective compare to electrochemical oxidation processes. Recently oxidation process has gained much popularity to remove sulphide from different industrial wastewater e.g., sewer wastewater (El Brahmi & Abderafi, 2021), petrochemical wastewater, and synthetic wastewater (Watsuntorn *et al.* 2019).In the present study, two oxidizers are used to remove sulphide from the hair dissolving liming wastewater of tannery.

The study aims to remove sulphide from the hair dissolving liming wastewater with low-cost oxidizers. The oxidizers hydrogen peroxide (H_2O_2) and sodium chlorite ($NaClO_2$) are used to remove sulphide from the hair dissolving liming wastewater and compare their performance.

2. METHODOLOGY

2.1 Sampling

The hair dissolving liming wastewater was collected three times into 5-litre capacity high-density polyethylene (HDPE) bottle on September 15, 2019 from the Superex Leather Ltd. Khulna, Bangladesh. The samples were taken immediately to the laboratory for experimentation.

2.2 Chemicals and Reagents

The reagents hydrogen peroxide (50%, TPL, Thailand), sodium chlorite (*Hoechst, Switzerland*), sulphuric acid (Merck, Germany), hydrochloric acid (Sigma Aldrich, Germany), potassium ferricyanide, barium chloride (UNI-CHEM, China), ammonium chloride (Loba Chemie, India), dimethyl glyoxime (Loba Chemie, India), iron(II) sulphate heptahydrate (Loba Chemie, India), ammonia solution (Loba Chemie, India), sulphuric acid (Merck Specialities Pvt. Ltd. India), ethanol (Merck KGaA, Germany) were purchased from a local scientific store, Khulna, Bangladesh. The buffer solution was prepared using 200 g ammonium chloride and 200 g ammonia solution per litre in deionized water. The indicator was prepared by mixing 10 mL of 0.6% ferrous ammonium sulphate, 50 mL of 1% dimethylglyoxime in ethanol and was 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

The hair dissolving liming wastewater was treated through the oxidation process. The preselected oxidizers H_2O_2 and $NaClO_2$ were used in the oxidation process. Figure 1 depicts the scheme for the treatment process of liming wastewater.

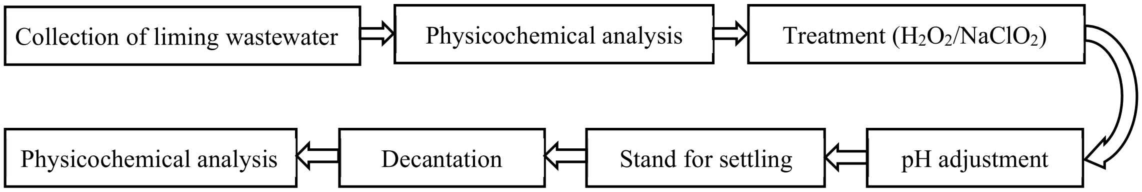

Figure 1: Scheme for the liming wastewater treatment process

The physicochemical parameters of the raw liming wastewater such as pH, total dissolved solids (TDS), soluble sulphide, salinity, and electrical conductivity (EC) were analysed. Then gradually preselected oxidizer (H_2O_2 and$NaClO_2$) was added with stirring at 150 rpm to eliminate the generation of toxic hydrogen sulphide (H_2S) gas. The pH of the mixture was adjusted with the help of diluted hydrochloric acid and the mixture was stirred for an additional 5 min and kept for settling. Finally, soluble sulphide and physicochemical parameters of the treated wastewater were analysed.

2.4 Analysis of Physicochemical Parameters

The electrical conductivity (EC), total dissolved solids (TDS), and salinity were measured following the standard methods of APHA (APHA, 2012). The EC, TDS, salinity was measured using an ion meter (CT-676, BOECO, Germany). The pH of the solution was measured, using a pH meter (UPH-314, USA). Before measuring all the meters were calibrated using the standard solution. The sulphide was measured following the official method of SLC 202 (Society of Leather Technologist and Chemists, 1996).

2.5 Measurement of Sulphide

The raw liming wastewater and treated liming wastewater (section 2.3) with oxidizers were used for sulphide determination. A 25 mL wastewater was pipetted into a 200 mL Erlenmeyer flask where 10 mL buffer, 1 mL indicator, and 2.0 mL barium chloride were added and stoppered the flask. The flask was left for 1 min to precipitate the sulphite as barium sulphite to mask the interference. Finally, the solution was titrated with 0.1 N potassium ferricyanide until the pink colour was disappeared.

2.6 Process Optimization

Assessments were carried out to optimize the treatment parameters pH and oxidizers dose. For optimization of oxidizers (H_2O_2 and $NaClO_2$) dose, varying doses of 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 g were used for batch treatment where other parameters remained unchanged. In the case of pH optimization, mildly acidic to mild alkali pH (6.0, 6.5, 7.0, 7.5, and 8.0) was investigated to obtain a higher sulphide removal efficacy.

3. RESULTS AND DISCUSSION

3.1 Optimization of Oxidizers Dose

Figure 2 illustrates the effect of oxidizers H_2O_2 and $NaClO_2$ dose on the sulphide removal efficiency. The experiment was conducted with varying oxidizer doses 0.2, 0.4, 0.8, 1.0, and 1.2 g for 50 mL wastewater while the pH remained unchanged (pH 7). It seems that with increasing the oxidizer doses, the sulphide removal efficiency was increased. For 0.2 g oxidizer dose for 50 mL liming wastewater, sulphide removal efficiency for H_2O_2 and $NaClO_2$ was 77.45% and 61.70%, respectively. For both oxidizers with the increase of the doses the sulphide removal efficiency was proportionally increased. The possible explanation is that with the increase of the doses the number of active sites of the oxidants was increased that's why it can accommodate more sulphide from the wastewater (Edathil *et al.*2021).

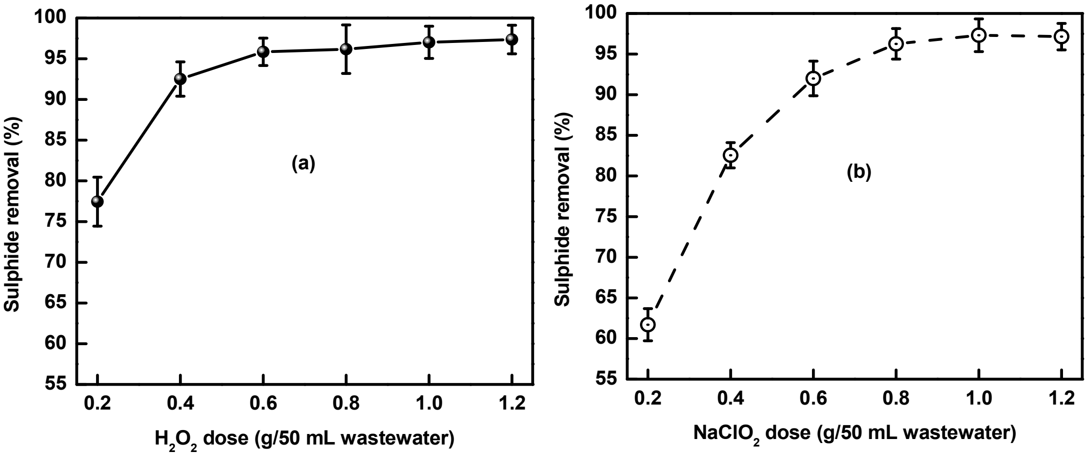

Figure 2: Oxidizers effect on sulphide removal a) H_2O_2 and b) $NaClO_2$

It is clear from Figure 2(a) that sulphide removal efficiency was significantly increased for H_2O_2 dose from 0.2 g to 0.6 g. Again, the H_2O_2 dose was gradually increased at 0.8, 1.0 and 1.2 g for 50 mL wastewater; sulphide removal percentage was insignificant. It is noticeable from Figure 2(b) that with increasing $NaClO_2$ dose from 0.2 to 0.8 g for 50 mL wastewater; sulphide removal percentage was remarkably increased. In the case of increasing $NaClO_2$ dose e.g., 1.0 and 1.2 g for 50 mL wastewater; the percentage of sulphide removal was not prominent. There is no significant difference in the removal of sulphide efficacy of the two oxidants. It is observable from Figure 2 that compares to H_2O_2; $NaClO_2$ has slight higher sulphide removal efficiency. For H_2O_2 and $NaClO_2$, the maximum sulphide removal efficiency was 97.4% and 97.3%, which was achieved at a dose of 1.2 g/50 mL and 1.0 g/50 mL, respectively.

3.2 Optimum pH for Sulphide Removal

According to Caliari *et al.* (2019), pH plays a vital role in the oxidation process. The effect of pH on the sulphide removal efficiency by two oxidizers (H_2O_2 and $NaClO_2$) was investigated and presented in Figure 3. At the initial stage with an increase in the pH, the percentage of sulphide removal was gradually increased for both the oxidizers. Above pH 7, sulphide removal efficiency started to decrease.

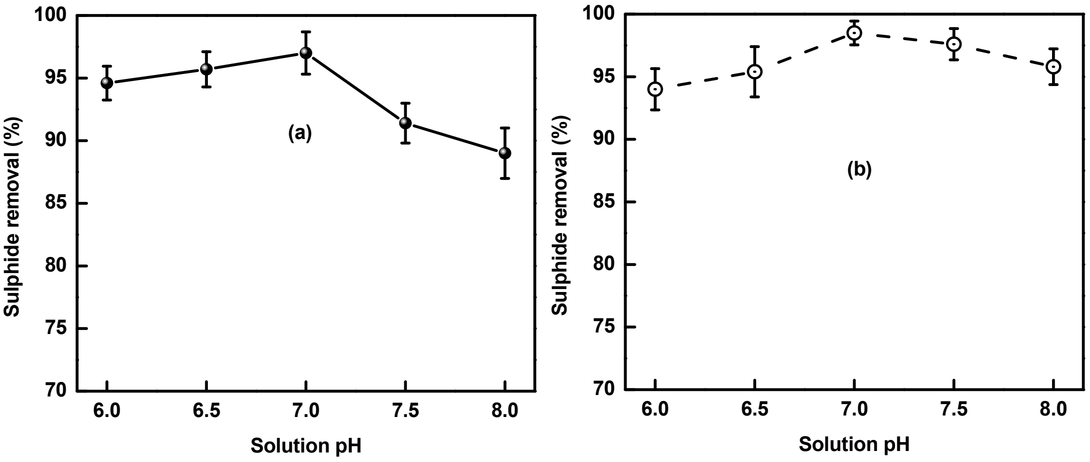

Figure 3: pH effect on sulphide removal a) H_2O_2 oxidizer b) $NaClO_2$ oxidizer

For both oxidizers H_2O_2 and $NaClO_2$, sulphide removal efficiency at neutral pH (pH 7) was 97.0% and 98.5%, respectively. At pH 8.0 for both oxidizers, gradually sulphide removal efficiency was decreased and was 89.0% and 98.8%, respectively. The results indicate that sulphide may convert to hydrogen sulphide (H_2S) at lower pH. However, the originated H^+ ion could be neutralized by the OH^- at the higher pH, which is mainly responsible for decreasing the H_2S formation and its removal from the solution (Saad *et al.* 2021). The same phenomena were observed in other studies (Wang *et al.* 2011; Dutta *et al.* 2008). Hence, the maximum sulphide removal efficiency was found at pH 7 for both oxidizers, therefore, pH 7 was chosen as an optimum pH.

3.3 Efficient Comparison of Oxidizers

Before and after treatment the physicochemical parameters of the wastewater were assessed and the obtained results were compared with the standard as shown in Table 1. The physicochemical parameters of the raw liming wastewater were far above the standard. Except for electrical conductivity, all the parameters were reduced at a significant level after treating with H_2O_2 and $NaClO_2$.

Table 1: Removal of pollution load from liming wastewater

Parameters	Initial	Treatment with		ECR (1997)	Unit
		$NaClO_2$	H_2O_2		
pH	12.3±0.04	7.03±0.03	7.0±0.02	6-9	-
TDS	16.3±0.04	14.9±0.2	8.6±0.06	2.1	g/L
Sulphide	3666.01±9.3	98.3±3.6	109.2±4.2	1.0	mg/L
EC	33.8±0.07	34.3±0.5	19.8±0.06	1.2	mS/cm
Salinity	21.4±0.6	19.0±0.4	10.2±0.1	--	ppt

In the case of sulphide removal, $NaClO_2$ showed better results compare to H_2O_2 but for the other entire water quality parameters, H_2O_2 exhibit more superior results than $NaClO_2$. The electrical conductivity of the $NaClO_2$ treated wastewater was higher than the raw wastewater. This phenomenon was occurred due to the production of counter ion Na^+, H^+, Cl^- while $NaClO_2$ reacts with HCl (Trautmann *et al.* 2021). After treatment with $NaClO_2$ and H_2O_2 the physicochemical parameters pH, TDS, **s**ulphide, EC, and **s**alinity of the treated wastewater were: 7.03**,** 14.9g/L**,** 98.3 mg/L**,** 34.3mS/cm, 19.0 ppt and 7.00, 8.6 g/L, 109.2 mg/L, 19.8 mS, 10.2 ppt, respectively. Although in the treated wastewaters' TDS, sulphide and EC values were 4, 109, and 16 times higher than the acceptable limits of ECR (1997) which were much lower than the raw wastewater sample.

4. CONCLUSIONS

In the present study, the hair dissolving liming wastewater was treated with two common oxidants H_2O_2 and $NaClO_2$. The performance of both the oxidants was compared by assessing the physicochemical parameters. The results revealed that in the case of sulphide removal $NaClO_2$ showed better results than H_2O_2. The maximum sulphide removal was obtained at pH neutral pH (7) for both oxidizers. The pH was within the permissible level. The removal efficiency of sulphide, TDS, and salinity at optimized conditions for H_2O_2 and $NaClO_2$ were 97%, 47.2%, 52.3% and 98.5%, 8.1%, 11.2%, respectively. The EC was a little increased for $NaClO_2$. The treated wastewater quality parameters indicate that both the oxidizer is effective in removing the pollution load parameters from hair dissolving liming wastewater. This investigation will help to treat sulphide-containing liming wastewater before discharging it into the environment.

DECLARATION

This is to declare that a part of this paper has been presented in ICCESD 2020 conference.

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