Global NEST Journal, Vol 27, No 5, 06993

Removal of sulphide from real unhairing tannery wastewater by a sequential chemical precipitation-oxidation leaching process

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Received: 11/11/2024, Accepted: 12/04/2025, Available online: 28/04/2025
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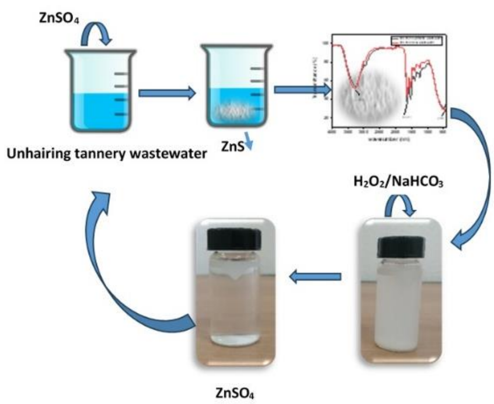
https://doi.org/10.30955/gnj.06993

Graphical abstract



Abstract

This study investigates the effectiveness of a combined precipitation and oxidative leaching process in reducing high concentrations of sulphides in unhairing bath tannery effluent from a major leather tanning plant in Batna, Algeria. First, the influence of various operational parameters and different zinc salts was evaluated in relation to the precipitation and settling rate of ZnS. Owing to its low solubility product (pK_s), ZnS proved to be highly effective under optimal conditions—specifically, a solution pH of 8–9, an initial stirring speed of 1000 rpm for the first five minutes followed by a reduction to 500 rpm, and the use of $ZnSO_4$ as the precipitating agent—achieving up to a 95% reduction in sulphide ion concentration. Moreover, Analysis of the treated unhairing wastewater revealed significant improvements in water quality, including reductions in pH (from 12.4 to 8.11) and turbidity (88%). Additionally, chemical oxygen demand (COD) analysis indicated the preservation of valuable and recoverable nitrogenous organic compounds, such as proteins, peptides, and free amino acids, post-treatment. The FTIR spectra analysis confirmed the good quality of the obtained precipitate. On the other hand, when hydrogen peroxide (H_2O_2) was added to zinc sulphide (ZnS) in the presence of sodium bicarbonate ($NaHCO_3$) at ambient temperature, the leaching of ZnS occurred, promoting the oxidation of sulphide ions to sulfate (97%). This process significantly reduced the production of metal sludge. As a clean and sustainable approach, it presents a promising strategy for sulphide mitigation in industrial wastewater treatment and holds strong potential for broader application in environmental management practices.

Keywords: Oxidation leaching; precipitation; sulphide removal; tannery effluent; water treatment

1. Introduction

Leather production, a cornerstone of the textile and handicraft industries since antiquity, remains vital to the economies of many developing countries (Lofrano *et al.*, 2013). Despite its economic importance, the industry is a significant source of environmental pollution (Zhao *et al.*, 2019, Tamersit *et al.*, 2018). The leather manufacturing process transforms animal hides into usable leather through several stages, beginning with unhairing, followed by tanning and finishing operations. The toxicity of tannery wastewater is primarily due to the presence of sulphides used during the unhairing-liming stage, as well as chromium salts introduced during the tanning process. The unhairing step involves an alkaline treatment of the epidermis and hair using a strong solution of lime ($Ca(OH)_2$) and sodium sulphide (Na_2S), which breaks down the hair structure at the root to facilitate its removal. During this phase, most unwanted components, such as non-structural proteins, fats, and hyaluronic acid, are eliminated, resulting in modifications to the intrinsic properties of skin proteins. However, the use of sulfur compounds presents several critical challenges. Hydrogen sulphide, in particular, is highly toxic and corrosive, posing a serious risk to infrastructure, especially concrete sewer systems. In addition, sulphides negatively impact the biological treatment of wastewater by inhibiting the activity of aerobic bacteria that are essential for biopurification processes. It has been observed that animal hides absorb only about 60% of the sulphide introduced during this stage (Tamersit *et al.*, 2018, Reyes-Serrano *et al.*, 2020), leading to a high concentration of chemicals in the wastewater. The resulting unhairing wastewater is characterized by a complex chemical composition, with high Chemical Oxygen Demand (COD) and sulphide concentrations often exceeding 2 g/L

(Tamersit and Bouhidel, 2020), poses considerable environmental challenges.

Various methods have been explored to address this issue, and numerous reviews summarize chemical (Sawalha *et al*., 2020) (Feng *et al*., 2007), and biological techniques (Lofrano *et al*., 2013), as well as innovative treatment approaches (Saxena *et al*., 2017) (Mandal *et al*., 2010), for the removal of sulphides from leather unhairing wastewater. However, clean technologies such as membrane technologies (Drioli and Cassano, 2023, Gallego-Molina *et al*., 2013), remain the most effective, playing a critical role in promoting cleaner production and fostering sustainable industrial development. Currently, combinatorial technologies are effective in removing the primary contaminants from tannery wastewater to the required levels (Suresh and Rameshraja, 2011). These methods are widely employed to ensure compliance with environmental regulations and to meet the quality standards required for reusing treated wastewater in the unhairing process.

This study aimed to evaluate the effectiveness of a hybrid treatment method based on a novel combination of precipitation and oxidation leaching processes for the efficient removal of sulphide from unhairing tannery wastewater. In fact, direct oxidation of sulphide is not sufficiently selective, as the majority of the reagent is consumed in the oxidation of organic matter.

The precipitation step enables selective extraction of sulphide ions, while the oxidation leaching process transforms the highly polluting sulphide ions, contained in the ZnS precipitate, into non-toxic sulfate ions. This approach also reduces the buildup of excessive sludge, providing a more sustainable solution for tannery wastewater treatment.

In this study, we propose the use of zinc ions to precipitate sulphides. Zinc precipitation, widely used for both characterization and isolation purposes (Tamersit and Bouhidel, 2020) due to its high solubility product (pKs = 24.7). The primary goal is to identify the optimal conditions for the quantitative precipitation of sulphides. Zinc sulphide (ZnS), which forms as a white precipitate, exhibits variations in its appearance and sedimentation kinetics, mainly influenced by the pH of the solution.

Additionally, hydrogen peroxide (H_2O_2), at acid medium, is commonly employed as an oxidizing leaching agent in various research applications (Bahrami, 2006b, Aydogan, 2006, Mouna *et al*., 2023). In this study, we assess the efficacy of H_2O_2 in the presence of $NaHCO_3$ (as catalyst) for the leaching of ZnS and the oxidation of sulphides. This evaluation presents a comparative analysis of reaction efficiencies under various experimental conditions, which will be explored in detail in the following sections of this paper.

2. Material and methods

2.1. Chemical reagent

The sulphide stock solution (S^{2-}) was prepared by dissolving $Na_2S{\cdot}9H_2O$ (VWR Chemicals, 98%) in distilled water. Solid $ZnCl_2$, $ZnSO_4$, and $Zn(COO)_2$ were added to the graduated cylinder at the start of the mixing process. All chemicals used were of analytical grade and sourced from Sigma-Aldrich (Germany 99%).

2.2. Analysis methods

The total sulphide (S^{2-}) concentration in synthetic samples and tannery wastewater was analyzed by iodometric titration, where concentrations were obtained by the titration of the excess iodine using the $Na_2S_2O_3$ solution (Mendoza-Roca *et al*., 2010) (Rodier *et al*., 1996). The Chemical Oxygen Demand (COD) was measured using the dichromate reflux method (for 2 hours in a sulfuric acid medium), followed by colorimetric titration at 600 nm (Mendoza-Roca *et al*., 2010). pH, turbidity and conductivity were measured using an Inolab series WTW pH meter 270, Germany, a HACH 2100 P Turbid meter, United States and a Hanna series conductivity meter (Germany), respectively. The concentration of zinc in leaching solution was analyzed by a spectrophotometer UV-vis (Shimadzu UV-1700, Japan).

2.3. Sampling and Characterization of unhairing tannery effluent

This study was conducted by preparing a synthetic solution through the dilution of a Na_2S stock solution to achieve a sulphide concentration of 2300 mg/L. Tannery wastewater was collected at the end of the unhairing process from an Algerian tannery (Batna unit) and stored at 4°C to prevent unwanted biological and chemical reactions. The analysis of the tannery wastewater is presented in **Table 1**.

Table 1. Unhairing bath tannery characteristics (Batna unit, Algeria)

Characteristics	average value
pH	12.4
Conductivity (mS)	14
Turbidity (NTU)	900
S^{2-}(mg/L)	2000
COD (mg/L)	30422

Table 1 presents the main physicochemical characteristics of the unhairing tannery effluent, highlighting the high levels of contamination found in the wastewater collected from a tannery. These parameters clearly demonstrate that, without adequate treatment, the release of this effluent could pose a severe environmental risk.

2.4. Experimental procedure

The precipitation experiments were performed to optimize various parameters, including the choice of precipitation agents, stirring speed, and pH. The procedure involved adding 100 mL of a synthetic solution containing 2300 mg/L of sulphide, while maintaining a fixed S^{2-}/Zn^{2+} molar ratio of 1 at room temperature. The solutions were stirred using magnetic stirrers for a predetermined period. Similar precipitation experiments were also conducted using real unhairing tannery wastewater under similar conditions.

3. Results and discussion

3.1. Optimization study (precipitation process)

3.1.1. pH effect

The pH can influence the precipitation of ZnS, to investigate the effect of pH on the precipitation and decantation of zinc sulphide, the concentration of sulphides in synthetic wastewater was maintained at a constant level (2300 mg/L, with an initial pH of 11). The process was carried out under neutral and alkaline conditions, with pH values ranging from 7 to 11 at 500 rpm of stirring speed. Acidic conditions were avoided to prevent the precipitation of proteins present in the real unhairing effluent (which occurs at a pH ≤ 4 due to their zwitterionic nature) and to avoid the formation and release of hydrogen sulphide (H_2S). The pH of the samples was adjusted within the 7 to 11 range using 0.1M HCl. The results are presented in **Figure 1**.

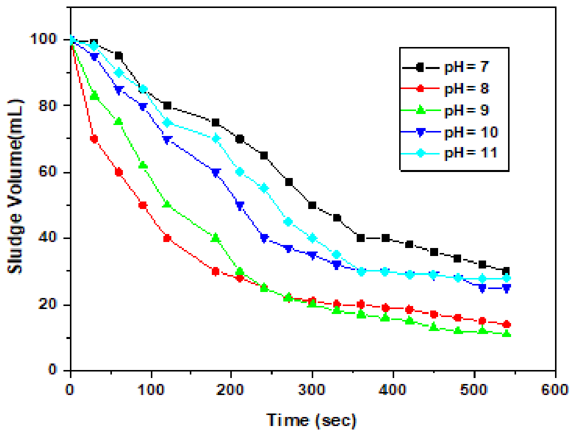
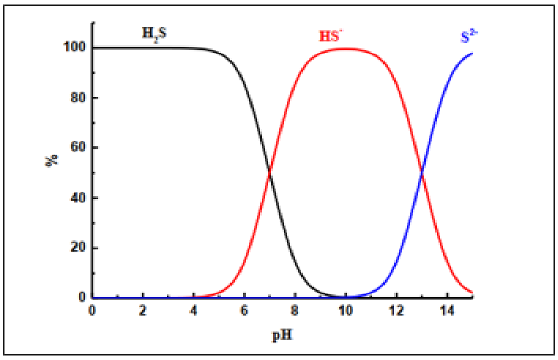


Figure 1. Effect of pH on settling rate of ZnS



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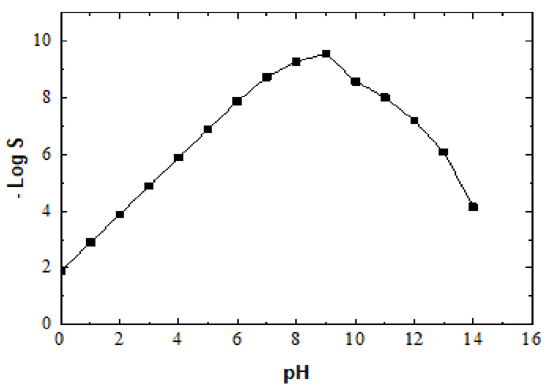

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Figure 2. a. Diagram of distribution of sulphide species as a function of pH and b. Diagram of Theoretical changes in the solubility of ZnS according to pH

The results indicate that precipitation and decantation were most effective at a pH of 8-9. At a pH of 7, sulphides exist as HS^- and H_2S, as shown in the species distribution diagram (see **Figure 2.a**). While precipitation can still occur at this pH, some hydrogen sulphide may evaporate, which is undesirable and could reduce the overall precipitation yield. At a pH of 8-9, sulphides predominantly exist as HS^-. Under these conditions, the precipitation of zinc with HS^- is rapid (Prokkola *et al.*, 2020), following the reaction:

$$Zn^{2+} + HS^- \rightleftharpoons ZnS(s) + H^+ \qquad pKs = 24.7 \qquad (1)$$

This finding was confirmed by the diagram of -Log Solubility as a function of pH (**Figure 2b**)

Beyond 9, the efficiency of precipitation and decantation decreases compared to that at pH 8-9. This decline is likely due to the formation of zinc hydrocomplexes, which affect the solubility of zinc sulphides at higher pH levels. Zinc is known to form two hydrocomplexes, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$(Rezaei *et al.*, 2022, Shemyakina *et al.*, 2015) , according to the following reactions:

$$Zn^{2+} + 3OH^- \rightleftharpoons Zn(OH)_3^- \qquad pK_{d1} = 13.14 \qquad (2)$$

$$Zn^{2+} + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} \qquad pK_{d2} = 14.66 \qquad (3)$$

3.1.2. Stirring speed effect

The stirring rate plays a crucial role in the crystallization process by enhancing both mass and heat transfer rates, which are essential for efficient crystallization (Susilowati *et al.*, 2023) Furthermore, it influences the size and morphology of the resulting crystals. This occurs through the interaction and contact between crystals during stirring, which affects their growth and development.

The effect of stirring speed on the kinetics of zinc sulphide precipitation was examined at various stirring speeds (100, 500, and 1000 rpm) at room temperature and at pH of 8, in solutions containing 2300 mg/L of sulphide. The comparative analysis of results (**Figure 3)** from various tests leads to the conclusion that the impact of agitation is particularly significant in the initial five minutes, where effective decantation is observed at a stirring speed of 1000 rpm. However, during the final phase of the process (the last five minutes), the decantation effects are nearly identical. Therefore, it is recommended to start the process at an agitation speed of 1000 rpm for the first five minutes and then reduce the speed to 500 rpm for the remainder of the procedure (Du *et al.*, 2015).

3.1.3. Precipitation agent effect

From literature, the anions do not participate in the chemical reaction during ZnS precipitation, while they may influence the charge on the aggregating particles, thereby affecting their growth rate and morphology (Eshuis *et al.*, 1999). The effect of different precipitation agents on sulphide removal was assessed by measuring precipitation settling rate at optimal conditions. (Misganaw *et al*., 2024). As shown in **Figure 4**, the settling rate with $ZnSO_4$ and $ZnCl_2$ is significantly higher compared to the other two agents. This is attributed to the granular, dense, and easily settleable nature of the sludge produced by $ZnSO_4$ and $ZnCl_2$. In contrast, the sludge formed by $Zn(NO_3)_2$ and $Zn(COO)_2$ is gelatinous and more difficult to filter.

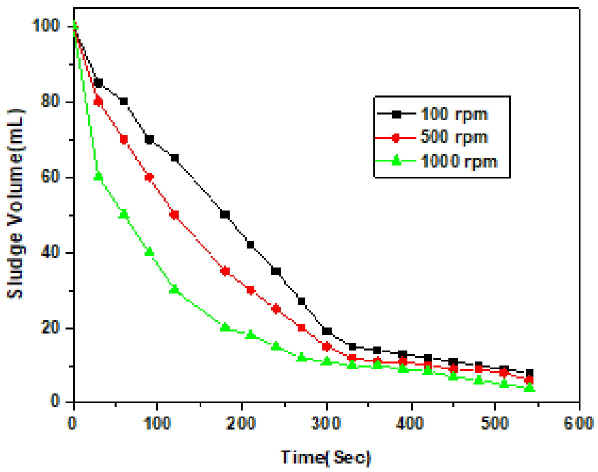

Figure 3. The settling rate of ZnS for different stirring speeds values

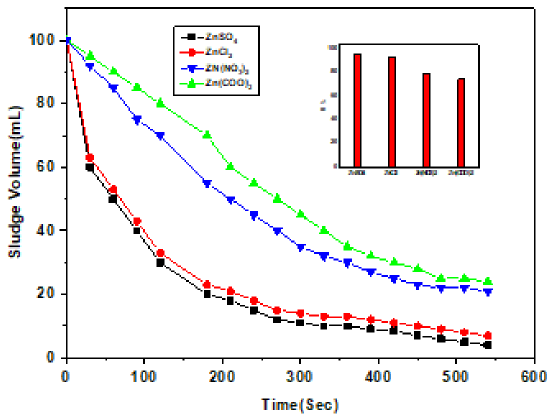

Figure 4. The settling rate of ZnS for the various precipitating agents and the effect of different precipitation agents on sulphide removal (f) (inset)

3.2. Oxidative Leaching of ZnS using H_2O_2

Hydrogen peroxide is an effective oxidizing agent, with a redox potential of (1.77v) (Antonijević *et al.*, 2004). Additionally, it is considered an environmentally safe reagent (Bahrami, 2006a). Reports indicate that during the oxidation of sulphide minerals using hydrogen peroxide, water is the only reaction product generated, making it a clean option. The redox potential of 1.77v is sufficient to oxidize nearly all metal sulphides (Antonijević *et al*., 2004).

In fact, the redox potential of H_2O_2/H_2O (1.77V) is sufficient to oxidize SO_4^{2-}/ZnS (-0.035V), the difference potential value ΔE (0.183 > 0) indicates that the oxidation of ZnS reaction by H_2O_2 occurs spontaneously. The oxidation of ZnS by H_2O_2 is based on the following reactions:

$$H_2O_2 + 2H^+ + 2\acute{e}\ \text{Ç}\ 2H_2O \quad E = 1.77\ V \tag{4}$$

$$ZnS + 4H_2O\ \text{Ç}\ Zn^{2+} + SO_4^{2-} + 8H^+ + 8\acute{e} \quad E = -0.035\ V \tag{5}$$

$$ZnS + 4H_2O_2 \rightarrow Zn^{2+} + SO_4^{2-} + 4H_2O \tag{6}$$

According to the literature, $NaHCO_3$ is commonly used as a catalyst (Aharon *et al.*, 2023) in the presence of H_2O_2, as bicarbonate ions effectively activate hydrogen peroxide. In this part of the experiment, we investigated a $NaHCO_3$ catalyzed peroxide oxidation process for the dissolution of ZnS and the oxidation of sulphide (Richardson *et al.*, 2000, Jawad *et al.*, 2016). The study specifically examined how varying the amounts of $NaHCO_3$, the volume of hydrogen peroxide and the mixing time influenced the dissolution/oxydation of ZnS.

During the experimental setup, the solution had a solid content of 100mg/20 mL and was stirred for 10 minutes in the presence of 0.03 g of $NaHCO_3$, while the progress of the ZnS leaching process was monitored through turbidity analysis. **Figure 5** illustrates the crucial role of the catalyst in sulphide oxidation. The use of a catalyst in combination with hydrogen peroxide significantly enhances its effectiveness as an oxidizing agent by accelerating the reaction rate and improving selectivity. The results show a marked improvement in oxidation efficiency, increasing from 55% to 90% with the addition of the $NaHCO_3$ catalyst. $NaHCO_3$ serves as a pH buffer (Zhang *et al.*, 2024), helping to maintain an optimal environment for hydrogen peroxide and preventing its premature decomposition. It may also promote the generation of reactive oxygen species, such as hydroxyl radicals (Liu *et al.*, 2021), which accelerate the oxidation of ZnS. Additionally, $NaHCO_3$ can enhance oxygen transfer, as evidenced by several studies (Shilov *et al.*, 2008, Aharon *et al.*, 2023), further improving the efficiency of the leaching process and leading to a significant increase in oxidation efficiency.

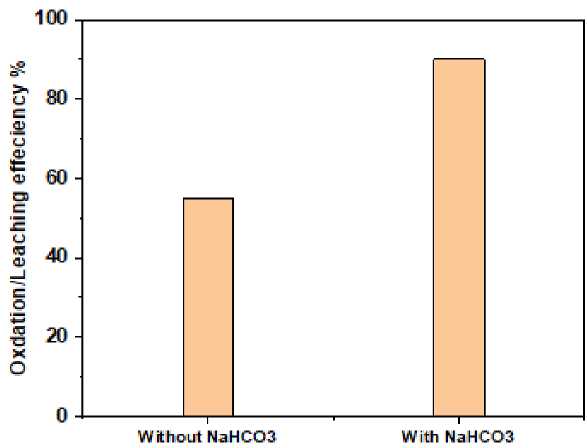

Figure 5. Oxidative Leaching of ZnS with and without catalyst

In this study, the leaching of ZnS using hydrogen peroxide (H_2O_2) in the presence of $NaHCO_3$ as a catalyst resulted in an impressive yield of approximately 90%. Comparing these results with those reported in the literature, Shams Latif (Latif, 2017) observed a leaching efficiency of 87% for

ZnS dissolution in sulfuric acid with hydrogen peroxide, which is similar to our findings but slightly lower. Nima Sadeghi (Sadeghi *et al*., 2017), also using H_2O_2 in sulfuric acid, achieved a significantly lower yield of 60%, suggesting that the $NaHCO_3$ catalyst used in our study plays a critical role in achieving much higher leaching efficiency. In contrast, R. Zárate-Gutiérrez *et al* (Zárate-Gutiérrez *et al*., 2015) found that ZnS did not dissolve in hydrogen peroxide when citrates were present, emphasizing the importance of different catalysts in ZnS leaching efficiency. The addition of $NaHCO_3$ in our experiment clearly enhances both the oxidation and dissolution of ZnS, demonstrating it to be a more effective catalyst than citrates and leading to a significant improvement in oxidation efficiency.

3.2.1. Mixing time effect

Figure 6 depicts the impact of the mixing time on the leaching of ZnS using H_2O_2, facilitated by the addition of 0.03g of $NaHCO_3$ at room temperature. In addition, the results show that the presence of H_2O_2 and $NaHCO_3$ is clearly important in the leaching process, as the zinc extraction rate increases rapidly within the first 4 minutes, suggesting rapid oxidation kinetics that convert ZnS into $ZnSO_4$.

The enhanced oxidation rate can likely be attributed to the catalytic effect of $NaHCO_3$ in combination with H_2O_2, which promotes the oxidation of the sulphide. The synergistic interaction between these reagents not only accelerates the reaction but also improves the overall efficiency of the leaching process. Therefore, this finding highlights the importance of optimizing the conditions under which these agents are applied to achieve optimal leaching results.

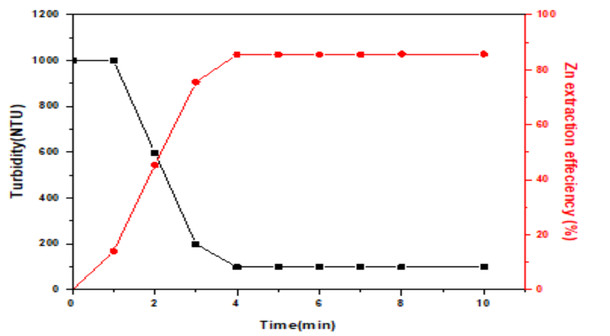

Figure 6. Effect of mixing time on the Oxidation/Leaching of ZnS

3.2.2. Amount of $NaHCO_3$ effect

The effect of varying amounts of $NaHCO_3$ on the leaching of 100mg of ZnS sludge was investigated using quantities ranging from 0.01 to 0.05 g of $NaHCO_3$ at room temperature in a solution containing 20 mL of 30% hydrogen peroxide for 4 min. As shown in **Figure 7**, the leaching efficiency of ZnS increased with the increase of $NaHCO_3$ amount. Within the range studied, 0.04 g was identified as the optimal amount for maximum leaching efficiency.

This finding suggests that there is an optimal balance between the catalyst and reactant, where an excess or deficiency of the catalyst can reduce the leaching efficiency of ZnS.

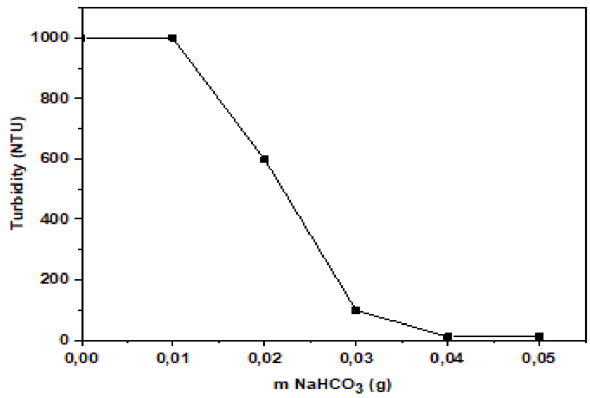

Figure 7. Effect of NaHCO3 amount on the Oxidation/Leaching of ZnS

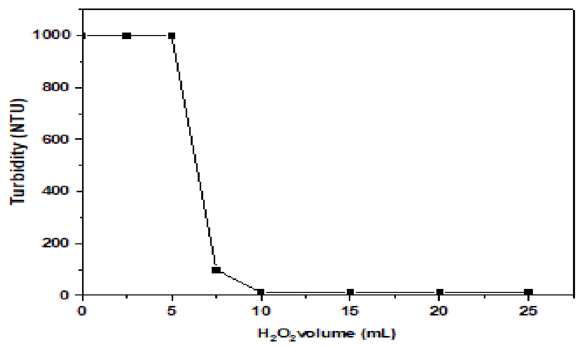

Figure 8. Effect of H_2O_2 Volume on the Oxidation/Leaching of ZnS

3.2.3. H_2O_2 volume effect

To evaluate the impact of H_2O_2 volume on the leaching efficiency of ZnS, experiments were conducted with varying H_2O_2 volumes ranging from 2.5 to 25 mL at room temperature in solutions containing 0.04 g of $NaHCO_3$ over 4 min period. **Figure 8** demonstrates a steady increase in disintegration efficiency, shown by a substantial decrease in turbidity from 1000 NTU to 12.1 NTU as the H_2O_2 dosage rises from 5 to 10 mL. Since 10 mL of H_2O_2 is sufficient to achieve near-complete dissolution (99%), this dosage is considered optimal.

Table 2. Unhairing tannery characteristics before and after ZnS precipitation

Characteristics	Before precipitation	After precipitation
pH	12.4	8.11
Conductivity (mS)	12.02	8.78
Turbidity (NTU)	825	99
S^{2-}(mg/L)	2050	61
COD (mg/L)	24800	18200

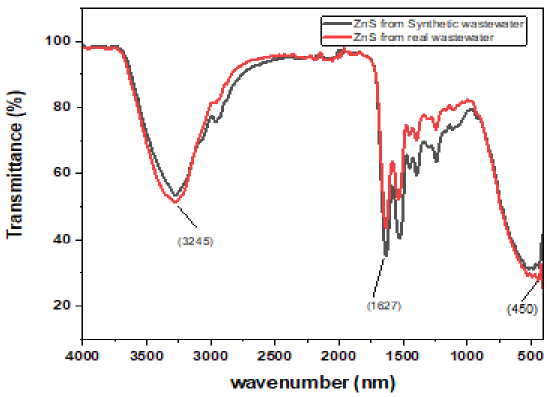

Figure 9. FTIR spectra of ZnS from synthetic and real unhairing wastewater

3.3. Real wastewater treatment

To assess the effectiveness of this treatment method in real-world applications, wastewater from the unhairing process of a tannery (**Table 2**) was selected. In this experiment, the optimal conditions identified from the treatment of the synthetic solution were applied.

The results demonstrated a high sulphide ion extraction efficiency of 97% (**Table 2**), along with significant reductions in pH and turbidity.

4. FTIR characterization

The FTIR spectra depicted in Figure 9 provide a comparative analysis of ZnS obtained from synthetic wastewater (illustrated by the black line) and real unhairing wastewater (depicted by the red line). Both spectra demonstrate comparable overall profiles. Specifically, the peak at 3245 cm^{-1}, a dominant feature in both samples, is indicative of O-H stretching modes, a result of water molecules adsorbed on the ZnS surfaces. Moreover, a significant absorption band at 1627 cm^{-1} corresponds to H-O-H bending vibrations, and the distinctive ZnS vibrational peaks are apparent between 420–550 cm^{-1}. These observations align with documented findings in the literature (Kiani *et al*., 2021, Panchavarnam *et al*., 2016, Tabatabai Yazdi *et al*., 2019).

A comparison of the FTIR spectra of ZnS (**Figure 9**) obtained from both synthetic and real solutions confirms the high quality of the precipitate, as indicated by the similar spectral patterns. As a result, the treated wastewater is rich in clean, recoverable organic matter.

Furthermore, oxidative leaching of ZnS using H_2O_2 in the presence of $NaHCO_3$ as a catalyst, under optimal conditions, led to a substantial oxidation/leaching of sulphide to sulfate (97%) within just 4 minutes of mixing time. Moreover, the resulting zinc sulfate solution can be reused in subsequent sulphide precipitation cycles, providing a distinct advantage and benefit to the overall treatment process.

5. Conclusion

The treatment of unhairing wastewater from an Algerian tannery (Batna unit) was carried out using an integrated chemical precipitation-oxidation leaching process. Initially, selective sulphide extraction was achieved through chemical precipitation under optimized conditions, resulting in a 95% reduction in sulphide ions. The integration of the oxidation leaching process with chemical precipitation further enhanced sulphide removal, achieving up to 97%, while also preventing sludge production. Additionally, the resulting $ZnSO_4$ solution can be recycled for use in a new precipitation cycle.

Acknowledgements

The authors express their sincere gratitude for the collaboration, and support provided by the Algerian Ministry of Higher Education and Scientific Research (DGRSDT/MESRS).

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