

Enhancing Ammonia Nitrogen Removal from Saline Mining Effluents: A Hybrid Approach with Ozone Microbubbles and Precipitation

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Abstract

Mining activities generate effluents with high ammonia nitrogen (NH₃·N) concentrations, presenting substantial environmental risks. This study investigates the use of ozone microbubbles for ammonia removal from mining effluents. The treatment achieved over 99% ammonia removal in 15 L of effluent at a pH of 9, with treatment times ranging from 60 to 150 min. Ozone microbubbles demonstrated stable ammonia removal efficiency across varying salinity conditions, which were assessed to simulate the typical salinity levels of mining effluents. Following ozonation, Friedel's salt precipitation was applied to reduce chloride concentrations by 35% to 45%, addressing post-treatment concerns regarding effluent quality. These results suggest that ozone microbubbles, complemented by Friedel's salt precipitation, offer a promising solution for ammonia removal, particularly in cold climates where conventional methods face limitations.

Keywords: Ozone microbubbles, Ammonia nitrogen, Mining effluents, Advanced oxidation processes (AOPs), Salinity, Cold climates, Removal efficiency, Precipitation

Introduction

Mining operations are crucial for global mineral production, but they pose substantial environmental challenges, particularly in terms of effluent generation. Among the most concerning contaminants in mining effluents is NH3-N, which is highly toxic to aquatic life, even at low concentrations (0.4–3 mg/L) (CWQ 2010). Ammonia is introduced to waste streams in mining using the common blasting agent (ANFO-ammonium nitrate fuel oil) and emulsion-based products, as well as through cyanide degradation (Jermakka et al. 2015; Kuyucak and Mubarek 2013). regulations As environmental become increasingly stringent, the mining industry faces growing pressure to implement effective water treatment methods. The Metal and Diamond Mining Effluent Regulations (MDMER) require that discharged water must not be acutely toxic and set a criterion of 0.5

mg/L of NH3-N (Minister of Justice, 2024). At the provincial level in Quebec, mining companies must comply with the guidelines outlined in Quebec's Directive 019 for the mining industry (D019 2005; Ryskie et al. 2021). In addition to ammonia, salinity is another primary concern in mining effluents. Elevated salinity levels, as measured by total dissolved solids (TDS) or electrical conductivity (EC), pose considerable risks to aquatic life and the environment (Van Dam et al. 2014). Several advanced treatment technologies, including biological, physical, and chemical methods, have been employed to address ammonia and salinity in mining effluents (Elsahwi et al. 2022; Kuyucak and Mubarek 2013). Biological treatment methods are commonly used due to their cost-effectiveness; however, their effectiveness is often limited in colder climates, where low temperatures can inhibit microbial activity (Zha et al. 2020). However,

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ozonation with microbubbles effectively treats ammonia and other contaminants, generates no toxic byproducts, and adds no residual salinity (Neculita et al. 2020). Due to the presence of competing contaminants, such as cyanide and its derivatives from gold extraction, the ozonation process can be affected, necessitating further optimization of operational parameters. Additionally, pH levels have been found to play a critical role in ammonia removal, with optimal pH ranges of 9 to 11 yielding the most effective results (Ryskie et al. 2020). These findings underscore the need for continuous research to refine ozonation systems and adapt them to various effluent compositions and environmental conditions, particularly in colder regions. Controlling salinity levels remains a crucial challenge in managing mining effluents. Friedel's salt precipitation has been explored as a post-treatment to limit chloride and sulfate concentrations (Alhinaai et al. 2025; Wang et al. 2018), offering a means to control residual salinity in treated effluents and improve the quality of discharge water. By precipitating specific ions, Friedel's salt precipitation helps mitigate the environmental risks of high salinity, contributing to more responsible effluent management practices. This process works by reacting chloride ions with calcium or aluminium compounds to form Friedel's salts, which are insoluble and can be easily removed from the effluent.

This study aims to evaluate the effectiveness of microbubble ozonation in removing NH3-N from mining effluents, with a focus on the impact of varying chloride and sulfate salinity levels. It also examines the application of Friedel's salt precipitation as a post-treatment method to mitigate residual salinity. By evaluating synthetic and real mining effluents, the study seeks to contribute to the development of more efficient and sustainable treatment technologies, ensuring compliance with environmental regulations and minimizing the impact on aquatic ecosystems.

Methods and materials

Microbubble ozonation unit for effluent treatment

Trials were carried out using a pilot unit for microbubble ozonation, consisting of a medical oxygen cylinder supplying the Primozone GM1 ozone generator, which has an ozone production capacity adjustable between 20% and 100% of its full output (equivalent to 35 g O₃/h at 20% wt concentration, or 300 g/Nm³ at 20% wt) (Ryskie et al. 2023). The generator has a cooling system, as the ozone production reaction is exothermic. The system also features a microbubble pump and a static mixer, which work together to enhance and control the size of the bubbles, thereby optimizing ozonation efficiency. The ozonation reactor has an 18 L capacity and is made of polycarbonate. The gas flow rate for the tests was 1.3 L/min, and the ozone generator produced ozone at a rate of 22 g/h. The reactor was maintained at 10 °C using the cooling system to preserve ozone solubility, as temperature increases would otherwise reduce it. A total of 15 L of effluent was treated. The pH was maintained at 9 using a 2.5 N NaOH solution, with a hydraulic residence time (HRT) ranging from 1 to 2.5 h.

Synthetic and real effluents for ozonation tests

Two distinct types of effluents were utilized in two separate experimental series for the ozonation tests. Synthetic effluents: The first experimental series was performed using synthetic effluents (solutions) prepared from deionized water and high-purity ACSgrade chemicals (Thermo Fisher Scientific). Ammonia nitrogen was introduced in the form of NH₄Cl or (NH₄)2SO₄, while sodium thiocyanate (NaSCN) was added in select cases to achieve a targeted concentration of thiocyanate (SCN⁻). To simulate varying salinity levels, appropriate salts such as NaCl and Na₂SO₄ were incorporated, depending on whether the salinity was attributed to chloride (Cl⁻) or sulfate (SO₄²⁻) ions. The primary objective of this series was to assess the efficiency of microbubble ozonation in treating synthetic effluents, each containing varying concentrations of NH₃-N, SCN, and different salinity profiles. A summary of the elemental concentrations used in these tests is provided in Table 1. Real effluents: The second series of four tests involved three real effluents, R1, R2, and R3, along



with a 40% diluted version of effluent R3 (denoted as R4), all sourced from several mines in Canada (Table 1). These effluents varied in chemical composition, ammonia concentrations, and salinity sources. For effluent R_1 , with high metal concentrations, the metals were precipitated before ozonation to prevent interference with the ammonia removal process. This pre-treatment prevents metal interference in microbubble ozonation; however, its industrial-scale necessity requires further evaluation.

Salinity treatment via Friedel's Salt precipitation: Jar test procedure

A jar test was conducted to investigate chloride precipitation as Friedel's salt, specifically testing the effect of salinity treatment on effluent R₃, which has high chloride salinity, following ozonation. A 250 mL sample of effluent R3 was treated with NaAlO₂ and Ca(OH)₂ using a Ca/Al/Cl molar ratio of 2/1/1, with constant stirring at 150 rpm for 24 h. During the experiment, liquid samples (1 mL each) were collected at regular intervals: every 5 min during the initial hours and every 30 min thereafter. All samples were filtered through a 0.45 µm filter before liquid analysis. At the end of the experiment, the solution was filtered through a Buchner funnel in an Erlenmeyer flask using a cellulose filter (0.22 µm; Mixed Cellulose Ester filter, Filter-Lab), and the solid was separated. All chemicals used in the experiments were of ACS-grade quality (Thermo Fisher Scientific).

Physicochemical measurements and analytical laboratory techniques

This study used various analytical techniques to monitor the physicochemical properties of synthetic and real effluent samples throughout the experimental treatment process. Initial concentrations of the effluents were measured before the experiment began, establishing baseline values for comparison. During the experiment, liquid samples were collected from synthetic and real effluents at regular intervals for analysis every 15 min, depending on the treatment process (ozonation or Friedel's salt precipitation). NH₃-N concentrations were measured using an ammonia-selective electrode (ISE Orion ThermoFisher Scientific) to track ammonia levels. Anion concentrations, including Cl⁻, NO₃⁻, and SO₄²⁻, were analyzed using ion chromatography at the experiment's start and end. SCN- concentrations were determined by UV-VIS spectrometry at 460 nm after the addition of nitric acid (HNO₃) and ferric nitrate (Fe(NO₃)₃), which formed a cyano ferric complex. pH was continuously monitored using a pH electrode connected to a multimeter (Symphony B30PCI). The initial and final concentrations of the effluents, along with the observed changes during the experiment, were used to assess the effectiveness of the treatment process. These analyses provided crucial data on the chemical dynamics throughout the treatment under varying conditions.

Effluent	Туре	рН	[Cl ⁻] (mg/L)	[N-NH ₃] (mg N/L)	[SCN ⁻] (mg/L)	Br ⁻ (mg/L)	SO4 ^{2.} (mg/L)
S1	Synthetic	6.40	-	55.0	50.0	-	2400
S2	Synthetic	6.16	-	100.0	50.0	-	2400
S3	Synthetic	8.03	-	110.0	-	-	2400
S4	Synthetic	6.86	2400	110.0	-	-	-
S5	Synthetic	5.93	18000	110.0	-	-	-
R1	Real	7.88	247	67.5	54.9	3.3	1899
R2	Real	9.88	220	76.0	52.7	2.2	2221
R3	Real	7.88	36329	392.3	<1	260.8	1208
R4	Real	7.12	14237	153.8	<1	102.2	325

Table 1 Composition of synthetic and real effluents.

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Data treatment and calculation of treatment efficiency

The treatment efficiency of different elements (e.g., NH_3 -N) was calculated using the equation 1:

$$Efficiency = \frac{c_i - c_f}{c_i} \times 100 \tag{1}$$

where C_i and C_f represent the concentrations of NH_3 -N before and after treatment, respectively.

The mass of elements (e.g., N-NH₃) treated was calculated using the equation 2:

Mass treated = $(C_0 - C_x) \times V$ (2)

where C_0 is initial concentration, C_x is the remaining concentration, and V is the volume treated.

The ozone consumption (O3) was calculated using the equation 3:

Ozone consumption $=\frac{T_1}{60} \times Q \times \frac{Mass Treated}{1000} = (3)$ where T_1 is the treatment time, and Q is the ozone flow rate.

Results and discussion

Ozonation tests using synthetic effluents

Fig. 1 shows the treatment efficiency and ozone consumption for five synthetic effluents (S1 to S5). The treatment duration ranged from 90 to 165 min, successfully reducing NH₃-N concentrations to below 0.5 mg/L. Effluent S1, which contained 62.09 mg N/L of NH₃-N and 50.61 mg N/L of SCN⁻, required 2 h to remove 99.4% of NH₃-N, with SCN⁻ rapidly oxidized within the first 30 min. In effluent S2, with an initial NH₃-N concentration of 103.9 mg N/L and 44.7 mg

N/L of SCN, the treatment achieved 99.6% removal efficiency after 150 min, decreasing NH_3 to 0.378 mg N/L. The presence of SCN⁻ in both S1 and S2 extended treatment times, as SCN⁻ consumed ozone during the oxidation process. Effluent S3, containing 117 mg N/L of NH₃-N and SO₄²⁻, achieved 99.7% NH₃-N removal in 105 min, with ozone consumption measured at 77.2 g O₃/g N-NH₃. Effluent S4, which contained 2.4 g/L of Cl⁻ and 118.3 mg N/L of NH₃, reached nearly 100% NH₃-N removal in 105 min, with ozone consumption of 68.3 g O_3/g NH₃. The NO₃⁻ concentration increased from 32.9 mg/L to 191 mg/L in S4, indicating effective NH₃ oxidation. Effluent S5, which had 17.7 g/L of Cl⁻ and 116.8 mg N/L of NH₃-N, required 90 min to achieve near-complete NH₃ removal. reaching 99.9% efficiency, with ozone consumption of 57.8 g O_3/g NH₃. The addition of SO_4^{2-} and Cl⁻ across all effluents did not crucially affect treatment efficiency. No chlorinated by-products, such as chlorates (ClO₃) or perchlorates (ClO_4) , were detected, even at high concentrations of Cl⁻. These results demonstrate that microbubble ozonation is highly effective for treating saline and nonsaline effluents. The presence of SCN⁻ was the only factor contributing to longer treatment times, but it did not deteriorate treatment efficiency. According to previous studies (LeBourre 2020; Ryskie 2017), the treatment duration required for synthetic effluents containing 246 mg N/L and 100 mg N/L of NH₃, respectively, were similar in effluents that only contained NH₃-N, without the



Figure 1 a) Treatment efficiency as a function of time for five synthetic effluents containing different concentrations of NH_3 , SCN⁻, and various salinities (S1 to S5), b) O_3 consumption as a function of time for the same synthetic effluents (S1 to S5).



addition of salts. This indicates that treatment times were almost identical for saline and non-saline synthetic effluents, and the treatment efficiency remained consistently high. Therefore, the introduction of SO₄²⁻ and Cl⁻ did not reduce the effectiveness of the microbubble ozonation process. The relatively longer treatment times observed in effluents S1 and S2 can be primarily attributed to the presence of SCN, which consumed ozone during the oxidation process. Moreover, trials with synthetic effluents demonstrated no important effect from sulfates or chlorides, and no chlorinated by-products were detected, even at high concentrations of Cl-. These findings underscore the robustness of the microbubble ozonation process across various effluent compositions. To further validate the process's effectiveness, additional trials with real effluents, which were more complex, were conducted.

Ozonation tests with real effluents

Ozonation tests were conducted on three real effluents: R1, R2, R3, and R4 (R3 was tested at a 40% dilution prior to treatment). These effluents differ in their concentrations of NH₃-N and have various sources of salinity. Additionally, thiocyanates are present in two effluents (Fig. 2). In all cases, the treatment efficiency was around 99%, and an NH₃-N concentration of less than 0.5 mg N/L was achieved. In the first stage for effluent R1, high metal concentrations were precipitated to prevent interference with the ozonation process. The precipitation effectively reduced

the residual metal levels (data not presented). Afterwards, ozonation was performed, during which SCN⁻ rapidly oxidized, dropping from 54.9 to 0 mg N/L within 30 min. This oxidation contributed to a slight increase in NH₃-N concentration, from 67.5 to 71.4 mg N/L during the same period. The treatment efficiency for NH₃-N was high, decreasing from 67.5 to 0.3 mg N/L, representing a 99.5% efficiency within 2 h. This was accompanied by an O_3 consumption of 44.3 g O_3/g N-NH₃. Concerning effluent R2, which has a similar NH₃-N composition to R1, the treatment time was longer, reaching 135 min. The initial pH was high, around 9.88, and NaOH was added only after the first 15 min. Initially, the NH₃-N concentration increased slightly from 75 to 77 mg N/L due to the transformation of SCN-, which degraded within 30 min, dropping from 52.74 to 0.05 mg N/L. The treatment of this effluent was also effective, reducing the NH₃-N concentration from 76 to 0.2 mg N/L, with an average O₃ consumption of 56.2 g O₃/g N-NH₃, as shown in Fig. 2b. At the start of the test, the effluent was white and opaque, gradually turning pink by the end. This color change is likely due to the formation of metal oxide nanoparticles, which could pose a toxicity risk to Daphnia magna (Ryskie et al. 2023). For effluent R4 (R3 at 40% dilution), which had a salinity mainly due to the presence of chloride at 14 g/L and did not contain SCN⁻, the treatment was nearly 100% effective in just 60 min, with an O₃ consumption of 50.7 g O₃/g N-NH₃. Between 45 and 60 min, the N-NH₃ concentration



Figure 2 a) *Treatment efficiency as a function of time using real effluents (R1, R2, R3 and R4 (R3 at 40% dilution)). b)* O_3 *consumption as a function of time using the real effluents.*



dropped sharply from 31.2 to 0.02 mg N/L. The oxidation of N-NH₃ was accompanied by an increase in the NO₃⁻ concentration, which increased from 252 mg/L (relatively high relative to R1 and R2) to 338 mg N/L. For undiluted effluent R3, the treatment duration was relatively short despite the high initial NH₃-N concentration of 392.3 mg N/L. The ozonation with microbubbles lasted 150 min, decreasing the NH₃-N concentration from 392.3 to 0.008 mg N/L, indicating near 100% efficiency. The O₃ consumption was 295.6 g O₃/g N-NH₃. Between 120 and 135 min, the N-NH₃ concentration dropped from 61.2 to 4.2 mg N/L. Thus, despite high salinity, higher initial NH₃-N concentrations result in faster kinetics, while the presence of contaminants like SCN- may increase treatment time due to their faster oxidation. Future studies should examine solution aging and complexation in real effluents, as these factors may impact treatment effectiveness.

Salinity treatment with Friedel's salt

Following the ozonation of effluent R3, high chloride salinity was treated using Friedel's salt precipitation, resulting in a chloride removal efficiency of $35 \pm 6\%$, indicating some decrease in chloride levels. The chemical reaction responsible for the formation of insoluble Friedel's salt, triggered by the addition of Ca(OH)₂ and NaAlO₂ to the chloride-rich effluent, is as follows (Wang *et al.* 2018):

 $CaCl_{2} + 3Ca(OH)_{2} + 2NaAlO_{2} + 8H_{2}O \rightarrow 2Ca_{2}Al(OH)_{6}Cl \cdot 2H_{2}O + 2NaOH$ (4)

This reaction is based on the theoretical molar ratio of Ca:Al:Cl of 2:1:1. In addition to chloride removal, the treatment led to a reduction in sulfate concentrations, underscoring the broader potential of Friedel's salts for salinity management in mining effluents. Despite the promising results, further investigations are necessary to optimize and enhance chloride removal efficiency.

Conclusion

This study focused on enhancing NH3-N removal from saline mining effluents through a hybrid approach combining microbubble ozonation and precipitation. Initial tests were conducted with synthetic effluents in batch mode to simulate real-world conditions, followed by trials with effluents from various Canadian mines. The results revealed a high treatment efficiency of 99% across all tests. The main variation in treatment times was attributed to the rapid oxidation of SCN-, which occurred before NH₃-N oxidation. SO²⁻ and Cl⁻ ions did not considerably influence the treatment time or the overall effectiveness of ozonation. Notably, no chlorinated by-products were detected during the ozonation of chloride-containing effluents, likely due to the operating temperature of approximately 10°C, which is not conducive to ClO₃-formation. Furthermore, post-treatment of ozonated effluent R3 using Friedel's salts demonstrated moderate chloride removal, showcasing the potential of combining ozonation with precipitation techniques. This hybrid approach presents a promising solution for addressing both ammonia nitrogen and salinity challenges in managing mining effluents. While tests demonstrate high NH3-N removal efficiency, scaling up may pose challenges that require further study.

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