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PILOT-SCALE INVESTIGATION OF AMMONIUM REMOVAL FROM GOLD MINE WASTEWATER BY PARTIAL NITRIFICATION AND ANAEROBIC AMMONIUM OXIDATION PROCESSES AT < 25°C

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Abstract: In this study, the treatment of ammonium-rich gold mine wastewater (Agnico-Eagle gold mine site, Laronde, Quebec, Canada) by partial nitrification/anammox (anaerobic ammonium oxidation) process was investigated, in a single-scale hybrid bioreactor, at temperatures below 25°C and HRT of < 4 days. The main objective was to determine the effect of operating and process conditions for the treatment of ammonium-rich wastewater. Batch and pilot-scale experiments were conducted with real wastewater containing 113 ± 13 mg/L, 7 ± 2 mg/L, and 8 ± 3 mg/L of ammonium, nitrite, and nitrate, respectively and 2478 ± 326 mg/L of sulfate. The ammonium and total nitrogen removal efficiencies of 87% and 81% were achieved during the stable operation period of 30 days. The batch tests results showed the main mechanism of ammonium removal was the nitrite dependent ammonium oxidation process. Nitrate and sulfate were used, respectively, as the main alternative electron acceptors, in the absence of nitrite. It was found that the control of pH at 7-8 was the critical operating parameter for a stable process at a temperature of 20°C as it minimized the fast pH decrease due to the rapid alkalinity consumption by microorganisms. This study confirmed the effective removal of ammonium from wastewater with these processes at temperatures of <25°C.

1. INTRODUCTION

Agnico Eagle Mines Ltd. is a senior Canadian gold mining company with exploration and development activities in Canada, since 1957. The company extracts and recovers gold from ores by a series of cyanide leaching, carbon adsorption, and acid washing processes. These processes produce wastewater with cyanides (CN^-) and derivatives, and sulfate- and nitrogen-based contaminants (e.g., thiocyanate (SCN^-), ammonium, nitrate). Currently, the company applies a series of chemical and biological processes by which consecutive conversion of cyanide to ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), and N_2 occur to remove toxic contaminants from the wastewater. The complete removal of contaminants with existing treatment processes is extremely efficient but can be challenging due to the complexity of water. An alternative to the existing treatment processes could be the application of recently discovered process known as anammox process (anaerobic ammonia oxidation) which directly converts ammonium to N_2 using nitrite as an electron acceptor (Mulder et al., 1995). The long-term treatment of high-strength ammonium from wastewater by partial nitrification (PN) and anammox processes have been successfully investigated at Concordia University using a single-stage hybrid airlift bioreactor (known as BioCAST) (Mohammadhosseinpour, 2016). Given the high concentration of ammonium in mine wastewater and the demonstrated high efficiency of the PN/anammox process in the treatment of ammonium-rich wastewater, the combined PN/anammox process was considered as a promising process for treatment of gold mine wastewater. This study, as a continuation of previous research, aimed to improve the cost-effective treatment of ammonium-contaminated wastewater by PN/anammox process. The main objective of the present project was to investigate the potential application of PN/anammox process for removal of nitrogen-based contaminants from real gold mine wastewater and to determine the important process and operational factors influencing these processes.

2. METHODOLOGY

2.1 Bioreactor structure and gold mine wastewater characteristics

The study used a single-stage pilot-scale hybrid airlift bioreactor containing both biofilm and suspension biomass. The bioreactor had three different environmental zones, including aerobic (dissolved oxygen, DO <1.2 mg/L), microaerophilic (DO <0.5 mg/L) and anoxic (DO = 0 mg/L), as well as a clarification compartment, for solid-liquid separation (Figure 1). These zones, with different dissolved oxygen levels and the suspended and attached media, provide optimal conditions for the growth and activity of aerobic nitrifiers and anaerobic anammox bacteria. The treatability of real gold mine wastewater was tested. Analytical measurements were conducted using test kits (Hach USA TNT 832, TNT 840, TNT 836, TNT 865, TNT 822). Total metal analysis (ICP-MS, Agilent) showed that the metal (e.g., Zn, Cu) content of the wastewater was below 1 mg/L which is in the range of anammox tolerance (Zhang et al., 2016). However, the contaminant of concern was sulfate (SO_4^{2-}) with a concentration of 2478 ± 326 mg/L, at pH 8 ± 0.7. Table 1 summarizes the BioCAST process/operating conditions and gold mine wastewater characteristics used in this study.

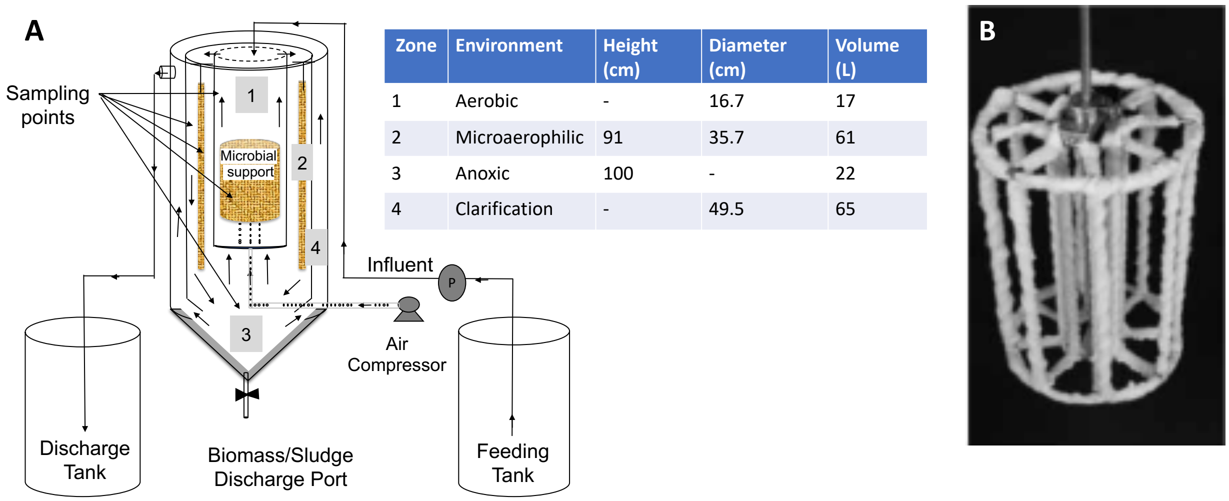
Table 1: BioCAST process/operating conditions and gold mine wastewater used in this study.

Parameter	Unit	This study
Reactor	-	Single-stage multi-zone hybrid airlift reactor
Biomass aggregation status	-	Suspended granule and attached biofilm
Wastewater	-	Real gold mine wastewater
Process type	-	Partial nitrification/anammox
TSS and VSS (suspended biomass in the BioCAST)	mg/L	4760 and 3870
Operating temperature	ºC	20 – 25
NLR, nitrogen loading rate	$g/m^3.d$	50 – 100
NH_4^+ in influent	mg/L	113 ± 13
SO_4^{2-} in influent	mg/L	2478 ± 326
COD in influent	mg/L	246 ± 34
Wastewater pH	-	8 ± 0.7

Note: TSS, total suspended solids; VSS, volatile suspended solids; COD, chemical oxygen demand

2.2 Bioreactor operating conditions

The anammox-bioreactor used in this study had established complete aerobic nitrifiers and anammox communities due to the long-term continuous operation with limited-nitrite high-ammonium wastewater. The experimental period of the current project was divided into two phases: (i) start-up of a 10-day operation period, at 25°C, for the rapid acclimation of the bacteria in the BioCAST reactor to the sulfate- and ammonium-rich gold mine wastewater; and (2) the operation at lower temperatures (e.g., 20°C) for the evaluation of the PN/anammox process performance and stability. Following the characterization of the real gold mine wastewater, the wastewater was fed, with no adjustment, into the pilot-scale bioreactor with a flow rate of 50 L/d, a hydraulic retention time of 2 days (calculated from the bioreactor volume and flow rate) and temperature of 25°C. Upon the achievement of a TN removal efficiency of greater than 70% at 25°C, the temperature was reduced step-wise from 25°C to 20°C over a period of 20 days. The operation was continued at 20°C for one month. At the onset of the experimental period, the pH of influent gold mine wastewater was above 7, thus the alkalinity of the real gold mine wastewater (100 $mgCaCO_3/L$) was not adjusted. However, over the course of this study, the alkalinity of influent was adjusted to 600 $mgCaCO_3/L$ (on day 19) and further to above 1000 $mgCaCO_3/L$ (on day 26), respectively, using potassium bicarbonate ($KHCO_3$) in response to a rapid pH drop (to below 6) and unstable pH in the bioreactor.



Zone	Environment	Height (cm)	Diameter (cm)	Volume (L)
1	Aerobic	-	16.7	17
2	Microaerophilic	91	35.7	61
3	Anoxic	100	-	22
4	Clarification	-	49.5	65

Figure 1: A) Schematic diagram of the BioCAST technology (B) and the structure of the microbial support.

3. RESULTS AND DISCUSSION

3.1 Nitrogen and sulfate removal under inorganic condition

Figure 2 shows the NH_4^+, TN and SO_4^{2-} removal efficiencies of gold mine wastewater during the experimental period. The feasibility of ammonium removal from a gold mine wastewater by PN/anammox process was evaluated in a single-stage hybrid bioreactor. One day after the introduction of the real gold mine wastewater to the bioreactor, the NH_4^+ and total nitrogen (TN) removal efficiencies reached 59% and 42%, respectively. The N-removal efficiencies gradually increased to 64% and 54% and further to 70% and 81% at the end of this period (days 1-10). At the same time, nearly 45% of the SO_4^{2-} was removed within the same period. The average concentration of nitrite in this period reached to an average of 2.6 mg/L (0.5 - 15.5 mg/L), and the average concentration of nitrate reached to 24 mg/L (14.5 - 32 mg/L). Achieving a satisfying N-removal and in an attempt to provide treatment conditions similar to the existing wastewater treatment system in the gold mine site, the temperature was gradually reduced from 25°C to 23°C. In this period (days 11 to 30) the NH_4^+, TN and SO_4^{2-} removal efficiencies considerably reduced to 30%, 20% and 20%, respectively. Given the low and unstable pH in this period, the influent alkalinity was increased (day 16) from 100 mg/L to 650 mg/L which improved the NH_4^+ and TN removal efficiencies. On day 30 of the experimental period, the temperature was further reduced to 20°C, while the HRT was increased to 4 days. The influent alkalinity was increased and maintained above 1000 mg/L, until the end of the experimental period, in response to the unstable and low pH (e.g., pH <7), as an indication that the alkalinity was not sufficient. In this phase (days 32 - 52), the NH_4^+ and TN removal efficiencies progressively increased from 57% and 42%, respectively, to 95% and 65%, while the SO_4^{2-} removal efficiency remained below 20%. The average concentration of nitrite in this period was 1.14 mg/L and the average concentration of nitrate was 28 mg/L.

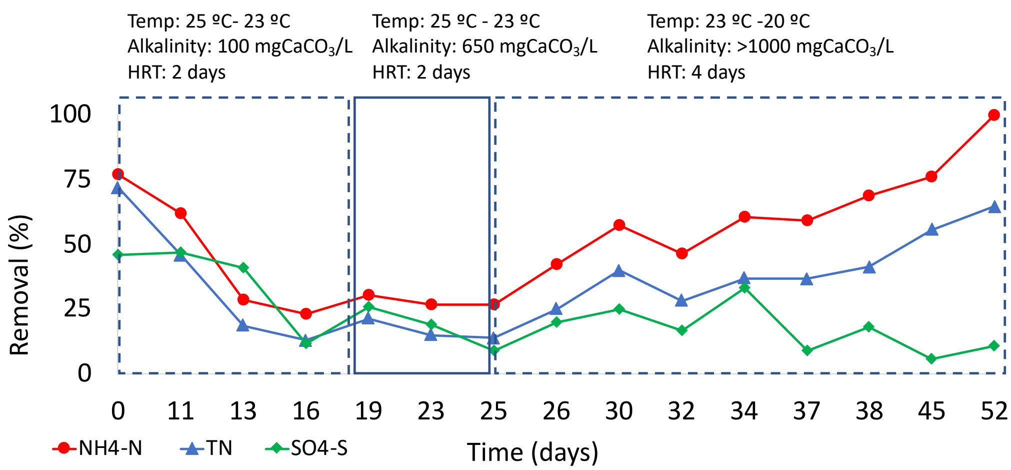


Figure 2: Ammonium, total nitrogen and sulfate removal efficiencies of gold mine wastewater containing NH_4^+ and SO_4^{2-} concentrations of 113 ± 13, and 2478 ± 326 mg/L, respectively, treated by PN/anammox process in the multi-zone hybrid bioreactor during the experimental period.

4. CONCLUSIONS

This pilot-scale study investigated the application of PN/anammox process for removal of ammonium from gold mine wastewater as one of the primary efforts for sustainable and economically viable treatment of gold mine wastewater in Canada. Determining the effect of process and operating parameters provided important information for the less challenging integration of this process for the industrial applications. This pilot-scale study advanced our understanding of the feasible application of the anammox process for removal of ammonium from sulfate-rich gold mine wastewater. This study showed that the acclimatization of aerobic nitrifiers and anaerobic anammox communities to high sulfate (> 2500 mg/L) can occur if the optimal conditions for the activity of aerobic nitrifiers and anaerobic anammox were provided. This study showed that providing proper buffering capacity (e.g., alkalinity) has a strong effect on the successful application of the PN/anammox process at the temperature of 20ºC. The main limitations identified in this study were (i) a relatively high nitrate concentration of (e.g., 35 mg/L) in the effluent that negatively impacted the TN removal efficiency and (ii) the high HRT of 2 - 4 days, which was not in line with the low HRT (e.g. 6 h) of the nitrification/denitrification process of the existing wastewater treatment plant (WWTP). These limitations will be further addressed before the integration of the PN/anammox process in the existing WWTP. Therefore, further studies are required to meet the industry's needs.

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