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Removal of ammonium and nitrate from cold inorganic mine water by fixed-bed biofilm reactors

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Abstract

Nitrogenous compounds, e.g. ammonium and nitrate, from various sources in extractive industry are often discharged with mine water to the aquatic environment. Ammonium and nitrate in blasting agents can dissolve in water from undetonated explosives and the nitrogenous compounds can negatively affect receiving water bodies. In this laboratory study, the removal of ammonium and nitrate from cold inorganic mine water was achieved by fixed-bed biofilm reactors at temperatures as low as 5 °C. Water from two underground mines was treated for ammonium removal in a nitrifying bioreactor. Ammonium concentration was from 2 to 83 mg NH_4^+–N/l. The sodium and chloride ion content was up to 0.8 and 2.2 g/l, respectively. At 5 °C, nitrification of up to 98% was reached at load of 0.33 g NH_4^+–N/m^2/d. The highest applied load was 2.42 g NH_4^+–N/m^2/d. The feed to the denitrifying bioreactor contained 12 to 86 mg NO_3^-–N/l. The anoxic methanol-fed denitrifying bioreactor reached up to 95% nitrate removal at loads as high as 0.91 kg NO_3^-–N/m^3/d and in combination with an anoxic unit a surface load of 4.26 g NO_3^-–N/m^2/d was applied at 5 °C. This is the first report on high-rate removal of ammonium and nitrate from cold inorganic mine water by fixed-bed biofilm reactors at low temperature.

Keywords: Bacteria; Biotechnology; Environmental; Mineral processing

1. Introduction

Ammonium and nitrate are usually discharged from mining operations to the aquatic environment. The main source of ammonium and nitrate in mine water originates from blasting agents such as ammonium nitrate fuel oil explosives (Forsberg and Åkerlund, 1999). Other sources of ammonium and nitrate in mine water are cyanide destruction, transformation of amines in flotation circuits, pH regulation agents, ammonium sulphate as eluent of uranium from ion exchange resins, ammonium hydroxide used in uranium precipitation, and ammonia used as lixiviant to recover copper and nickel in hydrometallurgical processes (EPA, 2003). In the European Union, no Best Available Technology has been defined for treatment of ammonium and nitrate in mine waters (EU, 2004). Several technologies exist for the removal of total nitrogen from water, including reverse osmosis (Awadalla and Kumar, 1994; Awadalla et al., 1994; Häyrynen et al., in press). The biological removal of total nitrogen by combined nitrification and denitrification is an established process for municipal and industrial wastewater treatment. Nitrification is the initial step of total nitrogen removal which proceeds by ammonium oxidation to nitrite (Eq. (1)) followed by nitrite oxidation to nitrate (Eq. (2)). Ammonia is oxidized by bacteria of the genera *Nitrosomonas* and *Nitrosospira* among others (Eq. (1))

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+ \qquad \text{pH decrease} \tag{1}$$

Nitrite is oxidized by bacteria of the genera *Nitrobacter* and *Nitrospira* among others (Eq. (2))

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$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \quad (2)$$

Biological denitrification proceeds by reduction of nitrate to dinitrogen gas by facultative, anaerobic, heterotrophic bacteria (Eq. (3))

$$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \rightarrow N_2O \rightarrow N_2 \quad (3)$$

For the denitrification in inorganic water, the heterotrophic bacteria require external carbon sources such as methanol (Eq. (4)). Methanol is often used, at a ration of 3 kg methanol/kg nitrate–nitrogen, due to its low cost and low excess biomass production (Tchobanoglous et al., 2003)

$$6NO_3^- + 5CH_3OH \rightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^- \quad (4)$$

The nitrification is affected by temperature (Chen et al., 2006) and nitrification rates double with 10 °C increase (Tchobanoglous et al., 2003). Denitrification is also strongly dependent on temperature, with denitrification rates doubling with every 4 °C increase (Given and Meyer, 1998). In municipal wastewater treatment plants, the total nitrogen removal performance is usually about 1 kg N/m^3/d (Tchobanoglous et al., 2003). The biological removal of ammonium and/or nitrate from mine water has been applied at a few mines in North America (Given and Meyer, 1998; Given et al., 1998; Reinsel and Plumb, 1999; Reinsel, 2001). Nitrification as part of biological cyanide destruction has been extensively studied (e.g. Akcil, 2003; White and Schnabel, 1998). However, the combined removal of ammonium and nitrate from water of mining and mineral processing plants has only been studied in suspended biomass systems as part of cyanide destruction. Since 1996, the Homestake's Nickel Plate mine in British Columbia, Canada, successfully applied a full-scale suspended sludge process for cyanide and thiocyanate removal from effluents of tailing facilities (Given and Meyer, 1998; Given et al., 1998). The biological destruction of cyanide and thiocyanate generates ammonium, which is biologically converted to dinitrogen gas via nitrification and denitrification. The bacteria involved in the nitrification and denitrification have long generation times and low cell mass yields. Therefore, in the applied suspended sludge process a high sludge age has to be maintained to achieve good performance results. The activated sludge process was designed for total nitrogen removal of about 20 mg N/l at flow rates of 0.7–1.1 m^3/min. The ammonium concentration is from 20 to 50 mg N/l and the nitrate content is from 100 to 130 mg N/l (Given and Meyer, 1998; Given et al., 1998). At Nickel Plate mine, nitrification requires temperature above 11 °C and the heating costs are about 5% of the total operational costs of about 0.01 euro/m^3. Methanol is used as a carbon source in the denitrification at a ratio of 3 kg methanol/kg nitrate–nitrogen and accounts for another 5% of treatment costs. However, reagents costs are only about 10% of the treatment costs with labor as the main costs of 40% (Given and Meyer, 1998; Given et al., 1998). Although plants treating water by suspended biomass processes perform successfully with organic wastewater, they are limited in treating dilute inorganic wastewaters. Reactors with biomass growing attached onto a carrier material, i.e. a biofilm, have several advantages over suspended biomass water treatment systems. These advantages are a relatively short treatment time, low maintenance costs, slow excess biomass generation with generally no waste biomass, and good resistance against low temperature, toxification and changing feed quality (pH, salinity, metals, biological and chemical oxygen demand content) (Rowan et al., 2003). The attachment property of bacteria to the carrier material in the biofilm reactor is a major parameter and minimizes biomass washout of slow-growing microorganisms at high flowrates. Further, biofilm reactors yield higher removal rates in smaller units. Attached bacteria usually show higher specific activity than suspended bacteria (Singh et al., 2006). Dictor et al. (1997) studied fixed-bed reactors for biological cyanide conversion to ammonium. So far laboratory studies have only applied synthetic mine effluents to study biological ammonium and nitrate removal at room temperature (e.g. Koren et al., 2000).

This study aims to: (i) establish and maintain nitrifying and denitrifying biofilms in bioreactors treating actual cold inorganic mine water, i.e. low in organic compounds, (ii) achieve high nitrogen removal rates in nitrifying and methanol-fed denitrifying biofilm reactors at temperature as low as 5 °C, and (iii) study the effect of two different mine waters on the performance of the biological nitrification.

2. Materials and methods

2.1. Bioreactor feed

Water was collected from the dewatering system of the ScanMining Ltd. Pahtavaara Gold Mine (mine I) and the Outokumpu Ltd. Kemi Chromite Mine (mine II) (Table 1). The two sites were chosen as representatives of underground mining in cold climate, i.e. Finnish Lapland. The mine water was sampled into 30 l or 220 l barrels and stored in the cold. The pH of the feed was about 8 (Table 1), which is favourable for the treatment of weakly buffered waters in nitrifying bioreactors (see Eq. (1)). During some tests on nitrification, the feed was at spiked with NH_4NO_3 to reach higher loading of the bioreactor. The nitrate content in the influent of the denitrifying bioreactor was increased by addition of HNO_3 and KNO_3 on day 301 and 307. The denitrifying bioreactor was supplemented with methanol as an external electron donor/carbon sources since the feed, i.e. mine water II, contained only minor amounts of organic carbon determined as chemical oxygen demand (COD_{Cr}) of 26.9 mg O_2/l. Furthermore, phosphate sources were supplemented to the feed of the denitrifying bioreactor after day 102.

2.2. Fixed-bed biofilm reactors

The nitrifying bioreactor combined a trickling filter, 12.8 dm^3, and a submerged fixed-bed reactor, 5.7 dm^3