Simultaneous nitrate and phosphate removal from wastewater lacking organic matter through microbial oxidation of pyrrhotite coupled to nitrate reduction

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ABSTRACT

This study investigated the efficiency of a pyrrhotite autotrophic denitrification biofilter (PADB) technology for simultaneous N and P removal from wastewater lacking organic matter. A PADB was constructed with natural pyrrhotite as the biofilter medium and inoculated with autotrophic denitrifies enriched from anaerobic sludge. Over an operating period of 247 days, PADB efficiently removed NO_3^- and PO_4^{3-} simultaneously from wastewater that lacked organic matter. The hydraulic retention time (HRT), and influent NO_3^- and PO_4^{3-} concentrations affected the removal of NO_3^- and PO_4^{3-}. A longer HRT led to lower concentrations of NO_3^- and PO_4^{3-} in the effluent. The PO_4^{3-} removal was influenced by NO_3^- removed; the more NO_3^- removed, the more PO_4^{3-} removed. As the synthetic wastewater containing NO_3^- —N of 28 mg L^{-1} and PO_4^{3-}—P of 6 mg L^{-1} in the absence of organic matter was treated by PADB at HRT of 24 h, total oxidized nitrogen (TON; NO_2^-—N + NO_3^-—N) and PO_4^{3-}—P concentrations of effluent were as low as 1.13 and 0.28 mg L^{-1}, respectively. When treatment of municipal wastewater treatment plant (WWTP) secondary effluent with TON of 21.11 mg L^{-1} and PO_4^{3-}—P of 2.62 mg L^{-1} at HRT of 24 h, the effluent TON was 1.89 mg L^{-1} and PO_4^{3-}—P was 0.34 mg L^{-1}. PO_4^{3-} was removed through the formation of secondary minerals with Fe and Ca. These secondary minerals contained elevated phosphorus, which presents a potential for P recovery from wastewater.

1. Introduction

The discharge of nitrogen (N) and phosphorus (P) from wastewater to water bodies is the main causes of eutrophication (Kim et al., 2012) so prior to wastewater discharge, removals of N and P are critical in order to reduce eutrophication (Conley et al., 2009). However, the costs associated with the removals of N and P are substantial (Schindler and Hecky, 2009). The primary concern for wastewater treatment is the removal of nitrate (NO_3^-) and phosphate (PO_4^{3-}) (Zhu and Jyo, 2005). Therefore it is necessary to develop efficient and cost-effective technologies that successfully remove N and P from wastewater.

Heterotrophic denitrification is the most efficient and cost-effective nitrogen removal process and has been widely used (Park and Yoo, 2009). However, the efficiency of heterotrophic denitrification is dependent on the availability of easily biodegradable organic matter in the wastewater. When wastewater does not contain sufficient readily biodegradable organic matter, the addition of external carbon sources (e.g. methanol) is required, thus increasing operational costs.

NO_3^- can also be removed from wastewater via sulfur autotrophic denitrification, in which reduced sulfur compounds, such as $S_2O_3^{2-}$, elemental sulfur (S^0), H_2S, etc., are used as electron donors (Batchelor and Lawrence, 1978). Recently sulfur autotrophic denitrification has attracted increasing interest for NO_3^- removal from wastewater in the absence of biodegradable organic matter due to its three major advantages over heterotrophic denitrification: no requirement for external carbon sources; lower sludge production; and lower operational costs (Sierra-Alvarez et al., 2007). S^0 is the
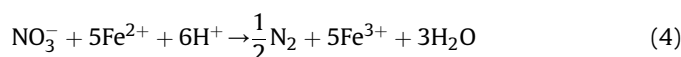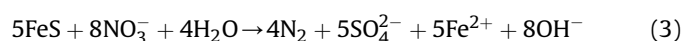
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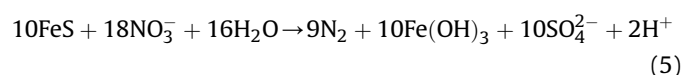
most extensively studied reduced sulfur compound in autotrophic denitrification because of its low cost and ease of use. Using S^0 as the electron donor and limestone as the pH buffer and inorganic carbon source, the sulfur-limestone autotrophic denitrification process (SLAD) has been shown to be effective in the removal of NO_3^- from wastewater (Zhang, 2002), groundwater (Soares, 2002), and landfill leachate (Koenig and Liu, 1996) in accordance with the following stoichiometric equations:

$$5S + 6NO_3^- + 2H_2O \rightarrow 5SO_4^{2-} + 3N_2 + 4H^+ \tag{1}$$

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \tag{2}$$
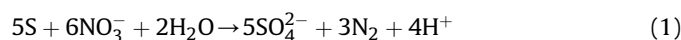
Iron sulfide (FeS) can function as an alternative reduced sulfur compound for autotrophic denitrification in the aquatic environment (Schippers and Jorgensen, 2002), and is even more efficient than S^0 (Trouve et al., 1998). The addition of synthetic FeS to sediments quantitatively enhanced denitrification (Golterman, 1989; Haaijer et al., 2007), and for a given concentration of NO_3^- the denitrification rate increased with the FeS concentration in sediments until saturation was reached (Garciagil and Golterman, 1993). Autotrophic denitrification using FeS as an electron donor is an important NO_3^- removal process and as much as one third of nitrate removal in a range of freshwater and marine environments is due to FeS autotrophic denitrification (Vaclavkova et al., 2014). FeS-based autotrophic denitrification can proceed in accordance with the following stoichiometric equations:

$$5FeS + 8NO_3^- + 4H_2O \rightarrow 4N_2 + 5SO_4^{2-} + 5Fe^{2+} + 8OH^- \tag{3}$$

$$NO_3^- + 5Fe^{2+} + 6H^+ \rightarrow \frac{1}{2}N_2 + 5Fe^{3+} + 3H_2O \tag{4}$$

The overall reaction is expressed as follows:

$$10FeS + 18NO_3^- + 16H_2O \rightarrow 9N_2 + 10Fe(OH)_3 + 10SO_4^{2-} + 2H^+ \tag{5}$$

One of the main methods for removing PO_4^{3-} from wastewater in wastewater treatment plants is chemical precipitation with compounds containing Fe^{2+}, Fe^{3+}, Al^{3+} and Ca^{2+} (De-Bashan and Bashan, 2004). PO_4^{3-} precipitation with Fe^{3+} proceeds in accordance with the stoichiometric equation as follows:

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4 \downarrow \tag{6}$$
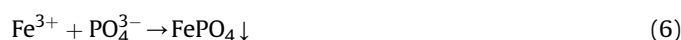
In the SLAD process, Ca^{2+} is released and PO_4^{3-} is primarily removed by the formation of calcium phosphate precipitates. However, the pH of the SLAD effluent is usually around 6.5, far lower than 12 which is the optimal pH for the formation of calcium phosphate precipitates (Wang and Nancollas, 2008), so PO_4^{3-} removal is limited in the SLAD process (Li et al., 2014).

According to Eqs. (3)–(5), FeS autotrophic denitrification produces Fe^{2+}, Fe^{3+} and $Fe(OH)_3$, which are capable of removing PO_4^{3-} from wastewater with a broad range of pH values (Parsons and Smith, 2008; Ruihua et al., 2011; Wei et al., 2008). Therefore, autotrophic denitrification with synthetic FeS as the sulfur source can efficiently remove N and P simultaneously from wastewater despite the absence of easily biodegradable organic matter, as previously reported in batch experiments (Li et al., 2013b).

Pyrrhotite, one of the most abundant reduced sulfur mineral sources in nature, has a non-stoichiometric composition of $Fe_{1-x}S$, where x varies from 0 (FeS) to 0.125 (Fe_7S_8) (Belzile et al., 2004). Pyrrhotite is much less expensive than S^0. It is reasonable to hypothesize that pyrrhotite autotrophic denitrification could be advantageous over S^0 autotrophic denitrification, for example, less

production of H^+ and SO_4^{2-}, and efficient PO_4^{3-} removal. However, compared with a number of studies on S^0 and synthetic FeS autotrophic denitrification for wastewater treatment, very few studies have focused on pyrrhotite autotrophic denitrification for the removals of N and P.

From an application prospective, it is probable that the natural pyrrhotite mineral can be used as the filling media of the biofilters which can simultaneously remove NO_3^- and PO_4^{3-} from wastewater lacking easily biodegradable organic matter through pyrrhotite autotrophic denitrification. In the present study, a pyrrhotite autotrophic denitrification biofilter (PADB) was constructed with the natural pyrrhotite mineral as the filling media. The main objectives of this research were to establish a PADB with autotrophic denitrifiers enriched from anaerobic sludge, and investigate the simultaneous removal of NO_3^- and PO_4^{3-} from wastewater lacking organic matter and the mechanisms of NO_3^- and PO_4^{3-} removals. A multi-disciplinary approach, based on environmental engineering, mineralogy, microscopy, and spectroscopy techniques, was used to investigate the efficiency of PADB. These techniques included X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and cloning and sequencing analysis.

2. Materials and methods

2.1. Pyrrhotite and limestone

Pyrrhotite (obtained from Tongling City, Anhui Province, China) was fragmented in a jaw crusher and sieved into particles of 2.36–5.12 mm in size. Pyrrhotite particles were placed in a 10% (v/v) HCl solution for 2 h for the removal of oxides formed on the surface, and rinsed with deionized water until the pH of the rinse reached 7 ± 0.1. The clean pyrrhotite particles were dried at 20 °C in a vacuum drying oven for 24 h and subsequently stored in airtight bags, which were flushed with nitrogen gas to prevent oxidation.

The pyrrhotite sample for XRF analysis was ground into a powder and subsequently analyzed in accordance with the manufacturer's instructions (ARL-9800XP, ARL, Switzerland). The XRF analysis identified the chemical composition of the pyrrhotite as follows: Fe 56.69%, S 38.46%, Si 1.22%, Cu 0.74%, Ca 0.34%, Mg 0.24%, Al 0.21%, Cl 0.10%, W 0.05%, K 0.03%, Zn 0.02%, Mn 0.02%, Cr 0.01%, and the residue was O. The combined total content of Fe and S was 92.43%, with a molar ratio of Fe to S of 0.948. X-ray diffraction (X'TRA, ARL, Switzerland) analysis indicates that the pyrrhotite mineral was composed of pyrrhotite mineral phase (Supporting Information Fig. S2). Pulverized limestone was obtained from Galway, Ireland and was sieved into particles of 2.36–5.12 mm. All reagents used were analytical grade (Trace Metal Grade, Fisher, UK).

2.2. Biofilters

Three identical biofilters were constructed and each was an anoxic upflow fixed-bed reactor comprising a stainless column with an internal diameter of 10 cm, a height of 27 cm, and a working volume of 1800 mL. The three biofilters were packed with: limestone (biofilter B1); pyrrhotite (biofilter B2); and a combination of both pyrrhotite and limestone (volume ratio of 1:1) (biofilter B3). The porosity of every biofilter was approximately 45% with a capacity of 810 mL for wastewater in each column. The hydraulic retention time (HRT) was calculated as follows:

$$HRT = \frac{24Vn}{Q} \tag{7}$$

where, HRT: hydraulic retention time, h; V: Volume of the filling