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Sulfur-based autotrophic denitrification from the micro-polluted water

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ABSTRACT

Eutrophication caused by high concentrations of nutrients is a huge problem for many natural lakes and reservoirs. Removing the nitrogen contamination from the low C/N water body has become an urgent need. Autotrophic denitrification with the sulfur compound as electron donor was investigated in the biofilter reactors. Through the lab-scale experiment, it was found that different sulfur compounds and different carriers caused very different treatment performances. Thiosulfate was selected to be the best electron donor and ceramsite was chosen as the suitable carrier due to the good denitrification efficiency, low cost and the good resistibility against the high hydraulic loads. Later the optimum running parameters of the process were determined. Then the pilot-scale experiment was carried out with the real micro-polluted water from the West Lake, China. The results indicated that the autotrophic denitrification with thiosulfate as electron donor was feasible and applicable for the micro-polluted lake water.

Introduction

Many important lakes in China, like the West Lake, Taihu Lake, and Chaohu Lake, lie in the thickly populated agricultural areas. As nitrogen fertilizers are widely used in farming and planting, the nitrogen compounds are flushed into the rain, enter the nearby lakes, and finally cause the eutrophication. Moreover, the large amount of nitrogen in the water bodies also threaten the fishery and human health greatly because ammonium is toxic to aquatic organisms, and nitrite is a dangerous cancer inducer which may cause the disease of methemoglobinemia in infants. Therefore, nitrogen removal becomes a very important work. On the other hand, under the natural conditions all forms of nitrogen tend to transform into nitrate and exist stably in the surface water as nitrate, for example, nitrate in West Lake water accounts for 60%–70% of the total nitrogen. Hence denitrification becomes an urgent issue in preventing water eutrophication and controlling the nitrogen pollution.

As both nitrogen and carbon pollutants in the natural water bodies are of relatively low concentrations (that is why it is called micro-pollution), mostly no more than 10 mg/L, the treatment process has to be specially designed for this character. Nowadays the heterotrophic denitrification is the most commonly-used denitrification process. It needs the organic carbon to provide electrons for the reduction of nitrate, and at the same time, to provide carbon source for the metabolism of heterotrophic microorganisms. However, there are some problems in this process, including residual organic matters which may cause the secondary contamination, and the high amount of excess sludge which needs final disposal.

Autotrophic denitrification can be a useful alternative to the heterotrophic one. Autotrophic denitrification is accomplished by autotrophic denitrifying bacteria which utilize the inorganic

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materials as electron donors and carbon source. Although the slow growth of autotrophic bacteria may cause lower treatment efficiency, it brings about two important advantages for the autotrophic process (Soares, 2002; Rocca et al., 2007; Sierra-Alvarez et al., 2007). First, it needs no external organic carbon source (methanol, ethanol or acetate) which lowers the risk of secondary contamination. Second, lower cell yield and sludge production minimize the disposal of sludge. Presently studies on autotrophic denitrification have been divided into two directions: one is hydrogen-based (Lee and Rittmann, 2003; Wang and Qu, 2003), in which hydrogen gas is used, and the other is sulfur-based, in which sulfur compounds, such as sulfide and elemental sulfur, are utilized (Moon et al., 2004, 2006) as electron donors. Due to the danger and difficulties of handling hydrogen gas, the sulfur-based process has gained more and more attention. The stoichiometric equations of sulfur-based autotrophic denitrification can be described as follows (Koenig and Liu, 2001).

$$1.10S^0 + NO_3^- + 0.76H2O + 0.40CO_2 + 0.08NH_4^+ \rightarrow 1.10SO_4^{2-} + 0.50N_2 + 0.08C_5H_7O2N + 1.28H^+$$

$$0.844S_2O_3^{2-} + NO_3^- + 0.347CO_2 + 0.086HCO_3^- + 0.086NH_4^+ + 0.434H_2O \rightarrow 1.689SO_4^{2-} + 0.5N_2 + 0.08C_5H_7O_2N + 0.697H^+$$

$$0.421H_2S + 0.421HS^- + NO_3^- + 0.346CO_2 + 0.086HCO_3^- + 0.086NH_4^+ \rightarrow 0.842SO_4^{2-} + 0.5N_2 + 0.086C_5H_7O_2N + 0.434H_2O + 0.262H^+$$

So far the studies of sulfur-based autotrophic denitrification have been mostly on using elemental sulfur as electron donors. Park et al. (2002) proved the feasibility first. They investigated the impact of influent concentration and nitrogen loading rate (NLR), and verified that 95% of nitrate could be removed when the influent nitrate achieved 175 mg/L and the NLR reached 2.46 kg N/(m^3·day). Nitrogen removal was closely related to the influent concentration and the NLR. Moon et al. (2006) found that the size of sulfur granules greatly affected the denitrification process. Smaller granules brought better efficiency, but if the granules were too small, they might be flushed out, together with bacteria on them. Due to the consumption of alkali in the process, lime is often used in the form of sulfur-limestone in order to provide the sufficient alkalinity. Later, Sierra-Alvarez et al. (2007) found that the 7.3 mmol/L nitrate was removed by 95.9%, and the nitrite in the effluent was very low. The production of nitrogen gas followed the stoichiometric equation that Koenig and Liu (2001) put forward. A few species of autotrophic denitrifiers have been found to utilize elemental sulfur meanwhile reducing nitrate to nitrogen gas, such as *Thiobacillus denitrificans* (Moon et al., 2008; Koenig et al., 2005) and *Thiomicrospira denitrificans* (Brettar et al., 2006).

Using sulfide as electron donor represents another experience for the simultaneous removal of nitrate and sulfide from wastewaters. For example, Vaiopoulou et al. (2005) found that almost all the 110 mg/L sulfide was removed while the denitrification efficiency achieved 100%, and *S/N* ratio and sulfide concentration were crucial impact factors in this process. Lu (2009) studied the mechanism of this process and revealed that at high NLR the sulfide was first partly oxidized into elemental sulfur, but at the low concentration and long hydraulic retention time (HRT), most sulfide was oxidized into sulfate directly. However, Fajardo et al. (2014) studied the influence of some factors on the denitrification process and found that sulfide concentration of 200 mg/L could inhibit the process, and nitrite of 48 mg/L could inhibit it by 50%. Moraes et al. (2012) also have similar conclusion about the inhibition of sulfide.

Eutrophication is a chronic disease for many natural lakes and rivers. The characters of micro-pollution, that is, low concentrations of pollutants and low C/N ratio, make the biological treatment even more difficult. Sulfur-based autotrophic denitrification may provide a cure for this disease. However, its real application has never been reported. On the other hand, very few studies put attention on another possible electron donor, thiosulfate. In order to understand the applicability of sulfur-based autotrophic denitrification, this study focuses on the nitrate removal from micro-polluted water, aiming to find out the optimal type of sulfur-based electron donor, the suitable working conditions, and the feasibility of real application.

1. Materials and methods

1.1. Experimental set-up

Five lab-scale up-flow biofilters, as shown in Fig. 1, were used for the continuous denitrification from the nitrate-rich water. Four reactors (named as L1, L2, L3 and L4) were identical, consisting of a cylindrical glass tube with the inner diameter of 88 mm, effective height of 0.5 m and effective volume of about 3.0 L. The fifth (L5) reactor was of the same volume but with the inner diameter of 62 mm and height of 1.0 m. Two pilot-scale biofilters were used to verify the applicability. The first (named as P1) up-flow biofilter was made of PVC, with the inner diameter of 300 mm, height of 4.2 m, the effective volume of 300 L, and designed full treatment capacity of 12 m^3/day. The second pilot-scale (P2) reactor was a down-flow biofilter, a used rectangle tank made of concrete. It was divided into two cells, each with length of 4 m, width of 3 m, effective depth of 3 m (2 m of filter carrier and 1 m of extra height), and designed full treatment capacity of 900 m^3/day.

Tap water was used in the lab-scale reactors as its nitrogen content was very similar to the micro-polluted surface water. Soluble sulfur compound, Na_2S or $Na_2S_2O_3$, was added at the *S/N* (*mol/mol*) ratio of 1.0, according to the nitrate concentration. Tap water in this city was acidic (pH about 6.0–6.2) so alkali was added during the domestication period, to adjust pH to 6.5–7.0. The water temperature around the year was from 5 to 30°C. For the pilot-scale reactors, the source water comes from Qiantang River and is pretreated with coagulating sedimentation process in a water pretreatment plant located by West Lake, Hangzhou, China. The pretreated water was pumped from the sedimentation tank into the pilot-scale reactors.

The ceramsites (diameter 5–10 mm) were used as the carrier for both lab-scale and pilot-scale reactors, yet when using the elemental sulfur as electron donor, the sulfur-limestone (diameter 5–8 mm) was used as the carrier and alkali at the same time. The reactors were seeded with digested sludge from the municipal wastewater treatment plant. No temperature controller was installed in order to simulate the natural temperature