Effect of current on biofilm-electrode reactor coupled with sulfur autotrophic denitrification process (BER-SAD) for nitrate removal from wastewater

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Abstract. The biofilm-electrode reactor coupled with sulfur autotrophic denitrification process (BER-SAD) was used to remove nitrate in groundwater, and the effect of current intensity on the denitrification characteristics of the coupled process was explored. Current intensity had a great influence on the denitrification effect of the coupled process, the maximum nitrate removal efficiency of 99.9% and lowest nitrite production were gained under the optimum current density of 100 mA. Moreover, the accumulation concentration of SO_4^{2-} increased gradually with the increase of current intensity. With the increase of current intensity, the proportion of hydrogen autotrophic denitrification decreased, while the proportion of sulfur autotrophic denitrification increased.

1 Introduction

Nitrate was considered to be a ubiquitous contaminant of natural water resources and has several sources, such as synthetic and natural fertilization, bacterial production, atmospheric deposition, and leaking septic systems. This worldwide pollution not only affected aquatic ecosystems, but could also pose threat to human health[1]. High levels of nitrate in drinking water, which was converted to nitrite in the human gut, could cause blue baby syndrome in infants and gastrointestinal cancer in adults[2]. Therefore, the maximum contaminant level (MCL) for nitrate stipulated by the World Health Organization (WHO, 2008) is at 11.29 mg-N/L in drinking water, and the value proposed by China is 10 mg-N/L (Standards for Drinking Water Quality, China: GB5749-2006). Various conventional methods have been used for nitrate removal, such as chemical processes and physicochemical approaches, but some of the methods still need further treatment and could incur high costs[3]. Compared with other methods, biological method has the characteristics of high efficiency and low energy consumption, so the method of removing nitrate in water by biological denitrification has been more and more applied[4].

The biofilm-electrode reactor (BER), which combined electrochemistry and biological denitrification, has become a promising technology due to high efficiency and low investment costs[5]. However, traditional BERs consumed a lot of electrical energy to produce sufficient H_2 , nitrate removal capacity might be restricted by the surface area of cathode, and denitrification process was easily affected by current[6]. In order to further improve

denitrification efficiency and reduce the consumption of electric energy in BER, the BER coupled with sulfur autotrophic denitrification process (BER-SAD) has been developed to treat nitrate polluted water. In the coupling system, the sulfur autotrophic microorganism can use the sulfur element as electron donor, and autotrophic microorganisms can utilize the hydrogen produced by cathode as electron donor.

The current intensity is a key factor affecting the nitrogen removal efficiency of BER-SAD, which directly determines the hydrogen production rate on the cathode surface. At the same time, microorganisms played a vital role in the bio-electrochemical reactors, which in turn were affected by some environmental parameters. The change of current intensity can also cause the change of nitrate reductase activity in autotrophic denitrifying bacteria, suitable electro-stimulation has a positive effect on bacteria by promoting their metabolism and activity[7]. On the other hand, high electro-stimulation could also have negative effects on bacteria, thus affecting the nitrogen removal efficiency of the coupling system[8].

Therefore, in this study, a biofilm-electrode reactor coupled with sulfur autotrophic denitrification process (BER-SAD) was developed: (1) determine the optimum current density by investigating nitrate removal efficiency under different current intensities, and (2) investigate the proportion of hydrogen autotrophic denitrification and sulfur autotrophic denitrification in the coupled system.

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2 Materials and Methods

2.1. Experimental apparatus

The experimental apparatus consisted of a BER-SAD reactor (a cylinder reactor, an anode and a cathode) and a DC regulated power supply. The hydraulic retention time (HRT) was set at 8 h and the temperature of BER-SAD was maintained at 30 °C.

2.2. Synthetic wastewater preparation

Synthetic wastewater was prepared by dissolving NaNO_3 , KH_2PO_4 and NaHCO_3 in a liter of tap water. Then sulfur particles (2-3 mm) were added to the reactor as electron donors. The concentration of NO_3^- -N was prepared as 50.00 mg/L. The original pH was around the range of 7.25 ± 0.02 and needed no further adjustment.

2.3. Analytical methods

Nitrate-N and Nitrite-N was determined using an ultraviolet spectrophotometer according to the Water and Wastewater Monitoring Analysis Method (SEPA, 2002). The SO_4^{2-} was determined by ionic chromatography.

3 Results & Discussion

3.1. Nitrate removal

Figure 1. Effect of current intensity on NO_3^- -N removal, NO_2^- -N and SO_4^{2-} concentration

3.2. Nitrite and sulfate accumulation

NO_2^- -N change could attribute to the denitrification processes (i.e. $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$), in which nitrite was the intermediate byproduct[10]. Variation of NO_2^- -N concentrations in different applied current intensities was also tested and showed in Figure 1. The initial NO_2^- -N concentration in influent was less than 0.02 mg/L in all set-ups. When no current applied, the NO_2^- -N concentration accumulations of 2.01 mg/L. When the current intensity was 50, 100, 150 and 200 mA, NO_2^- -N average concentration in effluent was 0.60, 0.29 0.52 and 1.75 mg/L, respectively. The NO_2^- -N accumulations

As shown in Figure 1, NO_3^- -N could be reduced under different current intensities. The NO_3^- -N concentrations in influent were 50 ± 0.90 mg/L at all current intensities. When the applied current intensity was increased incrementally up to 100 mA, NO_3^- -N concentration in effluent was decreased accordingly. The average concentration of NO_3^- -N in effluent were 5.31, 3.02 and 0.24 mg/L at 0, 50 and 100mA, respectively. The maximum nitrate reduction efficiency was 99.9% at 100 mA. When the applied current intensity was further raised to higher than 100 mA, the average NO_3^- -N concentration in effluent increased, especially when the current intensity increased to 200 mA, the concentration of NO_3^- -N was raised rapidly. The average concentration of NO_3^- -N in effluent were 1.82 and 3.60 mg/L at 150 and 200 mA, respectively.

The NO_3^- -N concentration in the reactor might be due to the following reasons: (1) the increase of current intensity can promote the formation of more hydrogen on the cathode surface and accelerate the formation of more CO_2 by anode graphite rod electrolysis, thus providing more electron donors and inorganic carbon sources for autotrophic microorganisms; (2) the increase of current intensity can stimulate the activity of nitrate reductase in autotrophic microorganism, thus promoting the utilization of electronic donor H_2 and S, and improving denitrification efficiency of the system; (3) while higher current intensity has a lethal influence on denitrifying bacteria, which finally decreased the denitrification performance[9].

were higher at 50 mA than 100 and 150 mA, it might be explained by the sensitivity of the enzyme nitrate reductase to such current levels, affecting their activity leading to the large amount of NO_3^- -N to be reduced to NO_2^- -N. The terminal NO_2^- -N concentrations under 100 mA was also significantly lower than the other current intensities. These indicated that optimum current intensity into the reactor not only accelerated the nitrate reduction but also led to the significant increases in nitrite reduction. Results also showed that without electrical stimulation, both rates of increase or decrease of nitrite were generally lower than other conditions that were applied with current. This suggests that the current had a stimulating effect on both nitrate reductase and nitrite reductase. In addition, no

nitrite was detected in the electrochemical reduction without bacteria, further implying that the microorganisms were the main reason for $\text{NO}_2\text{-N}$ accumulation. Except for the direct influence of current, nitrite reductase might be inhibited by higher concentration of hydrogen gas.

Sulfate concentrations was also showed in Figure 1, with the increase of current, the concentration of sulfate increases. When the applied current intensity was increased incrementally from 0 to 200 mA, the average concentration of sulfate values were 110, 225, 331, 422 and 507 mg/L, respectively. The maximum sulfate concentration at current intensity was 200 mA. According to previous study, when nitrate was reduced, sulfate production by elemental sulfur based denitrification, this results in a large amount of sulfate accumulation[11].

3.3. The proportion of hydrogen autotrophic denitrification and sulfur autotrophic denitrification

Substituting the test data into the above formula, the effect

Figure 2. Effect of current intensity on proportion of hydrogen autotrophic denitrification and sulfur autotrophic denitrification

4 Conclusions

The biofilm-electrode reactor coupled with sulfur autotrophic denitrification process (BER-SAD) was used to remove nitrate in groundwater, and the effect of current intensity on the denitrification characteristics of the coupled process was explored. Current intensity had a great influence on the denitrification effect of the coupled process. The maximum nitrate removal efficiency 99.9% were obtained when temperature was 30 °C, influent nitrate concentration was about 50 mg /L, influent NaHCO_3 concentration was 1 g/L, influent pH was 7.25, HRT was 8 h at the optimum current intensity of 100 mA in a BER-SAD, at which low nitrite production was obtained. The increase of current intensity can promote the utilization of S by sulfur autotrophic bacteria, resulting in the increase of SO_4^{2-} accumulation with the increase of current intensity in the coupled reactor. With the increase

of current intensity on proportion of hydrogen autotrophic denitrification and sulfur autotrophic denitrification are shown in Figure 2. When no current applied, proportion of sulfur autotrophic denitrification was 47%. When the applied current intensity was increased, the proportion of hydrogen autotrophic denitrification decreased, and the two proportions have almost the same level at 150 and 200 mA. The reason may be that the increase of current intensity has a greater promoting effect on nitrate reductase activity in sulfur autotrophic microorganisms, so more elemental S in the system is used by sulfur autotrophic microorganisms. At the same time, when the current intensity increases to a certain extent, it has a "hydrogen inhibition" effect on hydrogen autotrophic bacteria.

of current intensity, the proportion of hydrogen autotrophic denitrification decreased, while the proportion of sulfur autotrophic denitrification increased.

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