FeS-based autotrophic denitrification for removal of nutrients and emerging contaminants

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Introduction:

FeS-based autotrophic denitrification (IAD) is a promising technology for nitrate (NO_3^-) and phosphorus (PO_4^{3-}) removal from low C:N ratio wastewater due to its cost-effectiveness and low sludge production. The reactions of IAD can be expressed as Eqs. (1) (Hu et al. 2020).

$$10FeS + 18NO_3^- + 16H_2O \rightarrow 10SO_4^{2-} + 9N_2 \uparrow + 2H^+ + 10Fe(OH)_3 \downarrow \qquad (1)$$

However, the slow kinetics of IAD, compared to other sulfur-based autotrophic denitrification (SAD) processes, limits its engineering application. How to further improve the nitrate removal kinetics of IAD is worth exploring.

Tetracycline antibiotic (TC), a refractory contaminant in wastewater, commonly coexists with nutrients (NO_3^- and PO_4^{3-}) and inhibits biological nutrient removal. It has been found that FeS can effectively remove tetracycline from water (Xie et al. 2019). The adsorption and redox reactions are considered as the two removal pathways in the FeS-TC system. Therefore, simultaneous biological nitrate removal and chemical TC removal might be achieved theoretically in IAD. Up to date, no related studies have been reported.

In this study, column experiments were conducted to explore the enhanced nitrate removal in a FeS and elemental sulfur (S^0) coupled system through the long-term operation. Batch tests were conducted to investigate the feasibility of simultaneous nutrients and tetracycline removal in IAD system.

Material and methods:

One glass column (internal diameter, 30 mm; height, 330 mm) was constructed in the laboratory. A mixture of FeS and elemental sulfur (S^0), with a volume ratio of 2:1, was added into the biofilter as biofilm substrate. The biofilter was operated under different nitrate loading rates (100-960 mg/L/d) for six phases. The medium consisted of $NaHCO_3$, $MgCl_2$, $NaNO_3$, and KH_2PO_4. Effluent samples were collected every two days and filtered with 0.45 μm nylon syringe filters before analysis. Concentrations of NO_3^--N, NO_2^--N, SO_4^{2-}, and PO_4^{3-} of the effluent were measured by the Konelab nutrient analyzer (Konelab 20, Thermo, USA).

In the batch tests, three experiments were applied, i.e., G1, G2, and G3. 0.5 g FeS and 10.0 mL inoculum were added in G1. In G2, 0.5g FeS and 10 or 50 mg/L TC were added. 0.5 g FeS, 10.0 mL inoculum, and 10 or 50 mg/L TC were added in G3. For the control (G2) without the inoculum, 10.0 mL of deionized water was added instead of the inoculum. For the control without TC (G1), the same volume of ultrapure water was added. Water samples were collected every 48 hours and then analyzed for NO_3^--N, NO_2^--N, SO_4^{2-}, PO_4^{3-} and TC.

Results and discussion:

Enhanced nutrients removal in the FeS-S^0 coupled biofilter

The variation of NO_3^--N, NO_2^--N, NH_4^+-N concentrations, and TN (NO_3^--N+NO_2^--N+NH_4^+-N) removal efficiency in the effluent of the coupled system over the whole operational period (281 days) is presented in Fig.1 (a). During Phase I, NO_3^--N concentrations were kept below 0.2 mg/L, and no NO_2^--N was detected. TN removal efficiency was around 90% in this period. It indicated that autotrophic denitrifiers were successfully colonized in the biofilter after the inoculation period. In Phase II, the influent N loading rate was increased to 160 mg/L/d when HRT was decreased to 6 h. The sudden change of HRT resulted in the increase of effluent NO_3^--N and NO_2^--N concentrations in the first several days of this period because of the acclimation of microorganisms. And then, effluent NO_3^--N and NO_2^--N concentrations were decreased to be as low as those in Phase I. In Phase III, the N loading rate was further increased to 320 mg/L/d. The overall TN removal efficiency was around 100% during this period. In Phases IV and V, the N loading rate was further increased to 480 and 960 mg/L/d, respectively, and effluent NO_3^--N and NO_2^--N concentrations were below 0.5 mg/L.

Effluent phosphate concentrations and removal efficiencies of the biofilter over the 281-day trial are shown in Fig. 1(b). As the influent PO_4^{3-}-P was 10 mg/L in Phase I, the average effluent PO_4^{3-}-P of the ISAD biofilter was 1.51 ± 0.34 mg/L during the first 83 days at HRT of 12 h, with the PO_4^{3-}-P removal efficiency between 79.3% to 91.3%. From day 84 to day 119, the averaged effluent P concentrations were 0.29 ± 0.09 mg/L. In the subsequent phases, the biofilter showed excellent P removal performance, with averaged effluent P concentrations below 0.05 mg/L. Precipitation of PO_4^{3-} by Fe^{2+}/Fe^{3+} is the primary P removal mechanism in FeS-based biofilter (Li et al. 2016). The dissolution of FeS released Fe^{2+} to the solution, and Fe^{2+} was oxidized to Fe^{3+} by autotrophic microorganisms through the denitrification process.

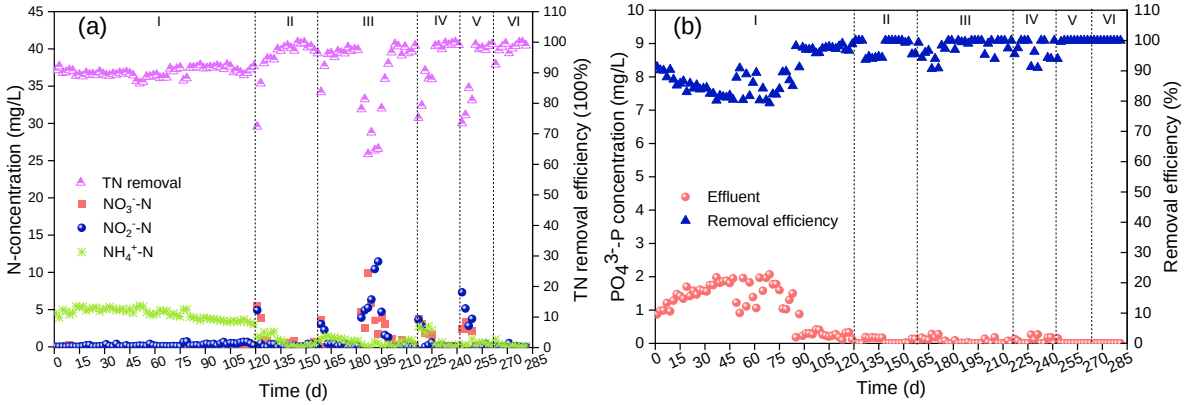

Fig.1 Dynamics of effluent NO_3^--N, NO_2^--N, NH_4^+-N concentrations, total nitrogen removal efficiency (a) and PO_4^{3-} concentrations and removal efficiencies (b) during the long-term operation of the coupled biofilter.

Simultaneous nutrients and TC removal in IAD

As shown in Fig. 2, NO_3^- removal in the IAD system was not inhibited as much with the addition of TC. During the first two days, the removal efficiencies of NO_3^--N in the control group was 80.50±7.0 %, and it was 73.8 ±6.1 % and 49.8±1.8 % in the two TC groups with TC concentrations of 10 mg/L and 50 mg/L, respectively. Finally, the NO_3^--N removal efficiencies exceeded 98% in all the three groups. The total nitrogen (TN) removal efficiency reached the same level as the control group when the TC concentration was 10 mg/L in the IAD system, which suggested the effective detoxification effect of FeS. The highest TC removal efficiency was obtained in the IAD system with the initial TC concentration of 10 mg/L, which was due to the combined adsorption by FeS and biomass. Besides, the highest and continuous PO_4^{3-}-P removal was shown when the initial TC concentration was 50 mg/L, with a removal efficiency of 83.3% within 8 days.

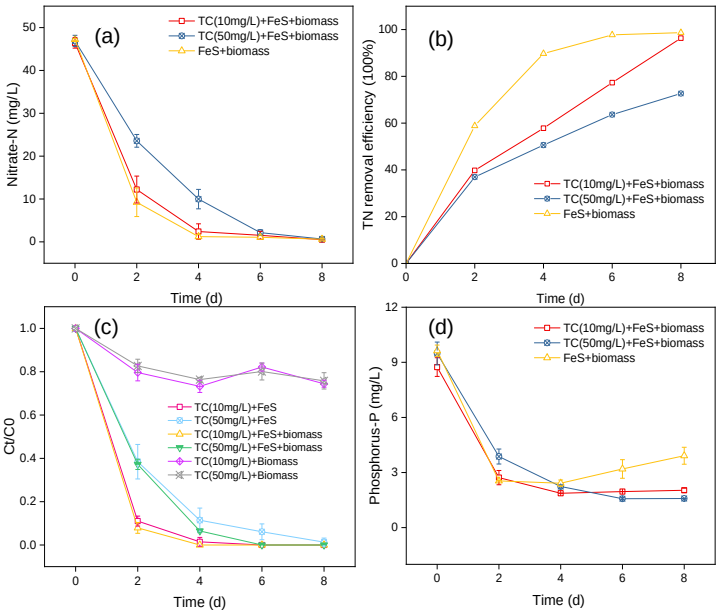

Fig. 2. Nutrients and TC removal patterns in the IAD system during the batch test.

Conclusions:

The enhanced nitrate and phosphate removal was achieved in the FeS and S^0 coupled system, with the highest nitrate removal rate of 960 mg/L/d and the phosphate removal efficiency of 100% at 1 h HRT. The simultaneous nutrients and TC removal was also confirmed in IAD. This study highlights that the IAD system is promising for the sustainable wastewater treatment towards energy and P recovery, nitrogen and antibiotics removal.

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References:

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