

Nitrate Removal from Groundwater by Nanoscale Zero-Valent Iron (NZVI) Coupling Autohydrogenotrophic Denitrification

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Abstract—In this work, the denitrification performance of a bio-reactor based on nanoscale zero-valent iron (NZVI) coupling autohydrogenotrophic denitrification was investigated. A series of bio-reactors were configured by inoculating and acclimating pure culture capable of denitrification. Effects of various parameters including nitrate ($\text{NO}_3\text{-N}$) loading, NZVI to nitrogen ratio (Fe/N), pH and atmosphere on denitrification were evaluated by batch tests. The results showed that the optimum Fe/N and $\text{NO}_3\text{-N}$ loading were 2.8 and 105 mg/L, respectively. Denitrification process remained unaffected by pH ranging from 6.0 to 9.0, while sharp accumulation of nitrite ($\text{NO}_2\text{-N}$) occurred at pH 9.0. Complete $\text{NO}_3\text{-N}$ removal was obtained by providing both nitrogen (N_2) and hydrogen gas (H_2). In general, excellent nitrogen removal efficiency was always achieved in the chemical-biological coupling system, indicating that the system had strong stability and adaptability for practical application, which offered both theoretic and technical supports to a new efficient and cost-effective method to eliminate $\text{NO}_3\text{-N}$ from water.

Keywords—Nitrate removal; NZVI; chemical denitrification; autohydrogenotrophic denitrification; coupling system.

I. INTRODUCTION

With the rapid development of industrialization and overuse of synthetic fertilizers, nitrate ($\text{NO}_3\text{-N}$) has contaminated groundwater in many countries over years [1]. Nowadays, scientific approaches for removing $\text{NO}_3\text{-N}$ have gained great attention due to the fact that high level of $\text{NO}_3\text{-N}$ may cause diseases such as methemoglobinemia and cancer [2]. Many countries thus promulgate specific regulation to set the upper limit of $\text{NO}_3\text{-N}$ in groundwater. The maximum value of $\text{NO}_3\text{-N}$ nitrogen in groundwater proposed by China is 10 mg/L [3], which is in accord with World Health Organization (WHO) standard value [4].

Currently, traditional technologies for eliminating $\text{NO}_3\text{-N}$ from groundwater include abiotic and biological methods. Abiotic treatments include reverse osmosis, electrodialysis, ion exchange, distillation and catalytic reduction etc [5]. However, there are still some feedbacks of physicochemical methods, such as the high operating cost [6;7], low selectivity, and the generation of byproduct brine [4]. Biological denitrification has been considered one of the most common and effective approaches [8]. Although being environmental-friendly

and economical, it has some apparent disadvantages: residue of bacteria and organic matter, high yield of surplus sludge, and managerial difficulties.

Traditional technologies can no longer match the requirements of wastewater discharge for the increasing sewage discharge and high cost. It is essential to develop an alternative approach. In recent years, with the development of nanotechnology, nanoscale zero-valent iron (NZVI) has raised concern due to its huge surface area, excellent surface adsorption and chemical reaction activity [9;10]. Previous studies on NZVI denitrification were pretty rare. The high cost and requirement for pH also limit its further application. NZVI-based microbial hydrogen-utilizing denitrification for $\text{NO}_3\text{-N}$ removal has been proposed and verified as a promising approach [11;12]. Therefore, a couple system by combining chemical denitrification with biological denitrification was constructed for potential $\text{NO}_3\text{-N}$ removal.

In this work, a bio-reactor by coupling chemical and biological denitrification was developed. The purpose of this work was to investigate the effects of various factors including $\text{NO}_3\text{-N}$ loading, pH, iron to nitrogen ratio (Fe/N) and atmosphere on denitrification performance, aiming to add some novel insight into $\text{NO}_3\text{-N}$ removal by chemical-biological denitrification.

II. MATERIALS AND METHODS

A. Experiment set-up

Four airtight flask with a working volume of 250 mL were used for batch tests in present study. Prior to batch experiments, domesticated anaerobic sludge 100mL (mixed liquor suspended solids (MLSS) 77.9 g/L, mixed liquor volatile suspended solids (MLVSS) 35.1 g/L), fresh NZVI (10 ml) and bacterial culture media were inoculated into each flask. Continuous H_2 (0.05 MPa) was introduced to the flasks to keep out oxygen. All flasks were placed into an Oven Controlled Crystal Oscillator.

B. Synthetic wastewater

The compositions of synthetic wastewater contained (per liter): NaNO_3 25-150 mg, NaHCO_3 750 mg, KH_2PO_4 97.5 mg, ZnCl_2 0.68 mg, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 0.19 mg, $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ 0.12 mg, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 0.27 mg, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ 0.36 mg, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 0.32 mg,

MgCl₂·6H₂O 0.28 mg, and H₃BO₃ 0.35 mg. NaHCO₃ was used as the only inorganic carbon source.

C. Domestication of denitrifying bacteria

Denitrifying bacteria was collected from the anaerobic tank of Erlangmiao Municipal Wastewater Treatment Plant (WWTP) in Wuhan, China. The collected sludge was cultured for 30 days. About 2L of anaerobic sludge (mixed liquor supernatant) was added into a bottle with nutritive material at 25°C. The compositions of the nutritive solution were (mg/L): NaNO₃ 42.5, NaHCO₃ (inorganic carbon source) 750, KH₂PO₄ 97.5 and some trace element solution. Fresh nutritive solution was cycled every 7 days. Meanwhile, sufficient H₂ was supplied over process. The domestication of bacteria was accomplished when the NO₃-N degradation rate was jarless. The MLSS and MLVSS were 77.9 and 35.1 mg/L, respectively.

D. Analytical methods

NO₃-N, NO₂-N, ammonia (NH₄⁺-N), total nitrogen (TN), ferrous ion (Fe²⁺), iron (Fe), MLSS, and MLVSS were measured according to the standard methods [12], the pH was measured by pH meter, dissolved oxygen (DO) was measured by YSI550A DO meter and temperature was measured by thermometer.

III. RESULT AND DISCUSSION

A. Effect of Fe/N

Effect of Fe/N on denitrification was shown in Figs. 1 and 2. A volume of 5ml, 10ml, 20ml and 30ml of NZVI solution was injected to the bioreactor to keep a Fe/N ratio of 1.4 to 8.4. The concentration of NO₃-N and NH₄⁺-N via operation time were monitored.

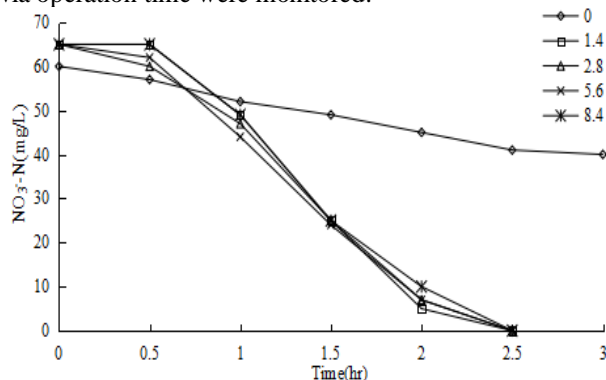


Figure 1. NO₃-N removal at different Fe/N (pH 7.0, NO₃-N loading 65 mg/L, H₂ pressure 0.05 MPa, temperature 30°C)

As shown in Fig. 1, Fe/N had little effect on NO₃-N removal since NO₃-N was completely removed within 2.5 h with Fe/N of 1.4-8.4. Introduction of NZVI greatly enhanced the reduction rate as the average NO₃-N degradation rate for bioreactor with or without NZVI were 26 and 6.7 mg NO₃-N/L/h. It's apparently that introduction of NZVI can significantly improve the reactivity of the system, due to the high surface adsorption and chemical reaction activity of NZVI [9].

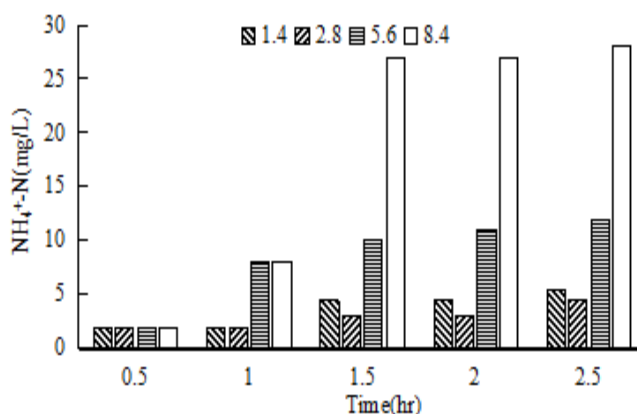


Figure 2. Effect of Fe/N on NH₄⁺-N (pH 7.0, NO₃-N loading 65 mg/L, H₂ pressure 0.05 MPa, temperature 30°C)

However, the introduction of NZVI would increase NH₄⁺-N concentration (Fig. 2). This was because NZVI had strong reduction and excellent surface adsorption, which was active to reduce NO₃-N with NH₄⁺-N as the main product [13]. In addition, it may also adsorb reactant or the intermediate section. Therefore, considering the denitrification rate and denitrification product, the optimum Fe/N was 2.8.

B. Effect of pH

Effect of pH on denitrification was present in Figs. 3 and 4. For NZVI, acidic conditions were conducive to NO₃-N removal [14], while for autotrophic denitrifying microbes, neutral or slightly alkaline environment were more advantageous [15].

It could be seen from Fig. 3 that there was no distinct discrepancy at different initial pH from 6.0 to 9.0, for 100% of influent NO₃-N was eliminated within 2.5 h. According to Xia et al [7], the optimum pH for autotrophic denitrification was 7.2-8.2, with the maximum efficiency at pH 7.7, since the over-high pH would affect the enzyme activity of denitrifying bacteria and lead to the deposit of iron oxides and hydroxides on the surface of NZVI thus preventing the reaction [9]. Rezania et al.[16;17] reported that when pH>8.6, denitrification was unable to continue. In this experiment, coupling system could still remove NO₃-N completely even when PH at 9. This may because the domesticated activated sludge had a strong adaptive ability to alkaline environments, and NZVI improved system's activity.

NO₂-N accumulation over pH was present in Fig. 4. No obvious accumulation was found under pH 6.0-8.0. However, a maximal of 1.9 mg/L of NO₂-N was detected at pH of 9.0. Moreover, the concentration of NH₄⁺-N (data not shown) fluctuated slightly (below 1.0 mg). This differed from the previous researches, which might because biological denitrification by autohydrogenotrophic denitrifiers dominated in coupling system, while NZVI contributed less. NH₄⁺-N generation mainly depended on the amount of adsorbed NO₃-N on the surface of iron [9], thus resulting in slight changes of NH₄⁺-N.

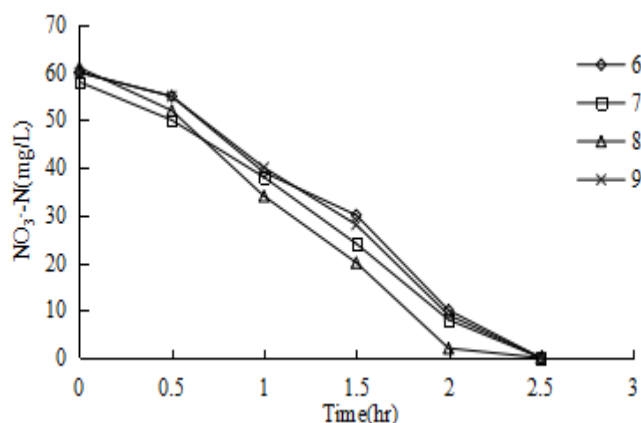


Figure 3. NO_3^- -N removal at different pH (NZVI 10 ml, activated sludge 100 ml, NO_3^- -N loading 65 mg/L, H_2 pressure 0.05 MPa, temperature 30°C)

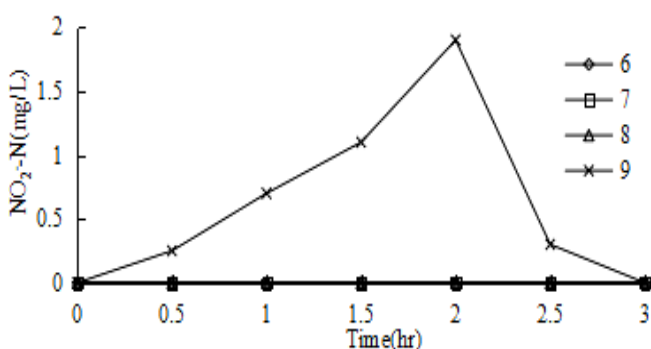


Figure 4. NO_2^- -N accumulation at different pH (NZVI 10 ml, activated sludge 100 ml, NO_3^- -N loading 65 mg/L, H_2 pressure 0.05 MPa, temperature 30°C)

C. Effect of nitrate loading

Fig. 5 revealed the NO_3^- -N degradation performance with different initial NO_3^- -N concentration. It's obvious that an average NO_3^- -N degradation rate of 20-30 mg NO_3^- -N/L/h was obtained at initial concentration varying from 25 to 150 mg/L. A higher NO_3^- -N loading required more time for complete reduction (1 h for 25 mg/L to 6 h for 150 mg/L). The highest removal rate (30 mg NO_3^- -N/L/h) was observed at 105 mg/L. In addition, effluent NH_4^+ -N fluctuated slightly and was always below 1.0 mg/L.

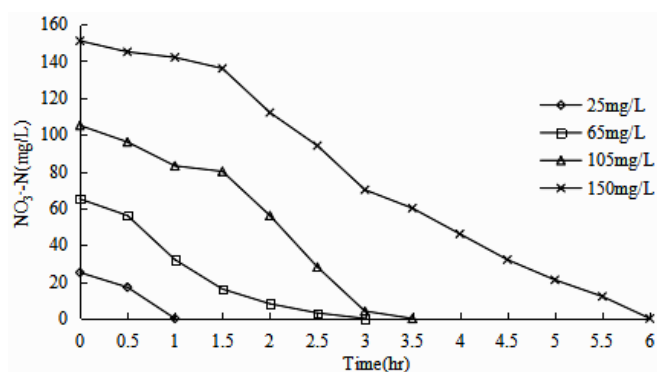


Figure 5. NO_3^- -N degradation at different NO_3^- -N loading (NZVI 10 ml, activated sludge 100 ml, pH 7.0, H_2 pressure 0.05 MPa, temperature 35°C)

The results were consistent with those by Yang et al [9], confirming the effective reduction power of NZVI in treating highly concentrated mg NO_3^- -N. High level of NO_3^- -N could result in NO_2^- -N accumulation of during the NO_3^- -N reduction [18]. However, no accumulated NO_2^- -N was seen over operation. This might be explained by the different reaction route as (1) and (2), for the intermediate NO_2^- -N could be timeously converted into N_2 :

Effect of atmospheres

Fig. 6 showed the effect of different filling atmosphere on NO_3^- -N reduction. It was apparent that NO_3^- -N degradation rate of coupling system with sufficient H_2 was 22 mg NO_3^- -N/L/h, which was much higher than that with N_2 (11 mg NO_3^- -N/L/h). During the operation, there was no NO_2^- -N accumulated and the NH_4^+ -N was below 1.0 mg/L.

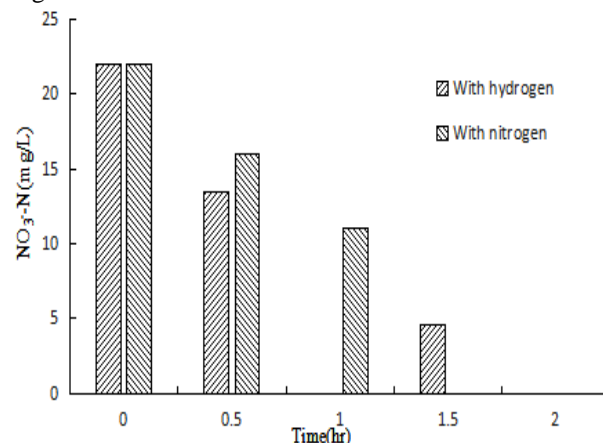


Figure 6. NO_3^- -N degradation performance at H_2/N_2 atmosphere (NZVI 10 ml, activated sludge 100 ml, pH 7.0, NO_3^- -N loading 22 mg/L, temperature 30°C)

Previous studies by Mousavi et al.[19] showed that biological denitrification failed to operate without injecting H_2 as electron donor in an activated sludge reactor. Therefore, there might be two reasons: chemical denitrification process of NZVI in coupling system reduced NO_3^- -N, which remained unaffected by the presence of H_2 [20]; H_2 produced by micro-electrolysis of NZVI [21] served as electron donor for denitrification, thus aiding the denitrification process.

IV. CONCLUSIONS

The aim of this work was to investigate the effects of important parameters including Fe/N, pH, nitrate loading, and atmosphere on NO_3^- -N in a combination of chemical denitrification by NZVI with autohydrogenotrophic denitrification system.

NZVI could greatly strengthen the reaction rate of couple system compared with individual biological denitrification. The optimum Fe/N was 2.8 for present study. Denitrification efficiency changed slightly when pH varied from 6.0 to 9.0, but nitrite would accumulate when pH was 9.0. This coupling system could cope with nitrate ranging from 25 to 155 mg. The highest denitrification rate reached 30 mg NO_3^- -N/L/h at initial NO_3^- -N loading of 105 mg/L. In addition, the supply of H_2 could aid denitrification of couple system for both chemical and biological mechanisms.

Given the complete NO₃-N removal at various conditions, that coupling system had strong stability and adaptability for further practical application.

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