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Characteristics of nitrophenol wastewater treatment via a NZVI/microorganism coupling system

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ABSTRACT

Nitrophenol was selected as the target pollutant for an intermittent test and was mixed with anaerobic microorganisms to inspect the degradation of the nitrophenol at different dosages of nanoscale zero-valent iron (NZVI), initial pH levels, and initial nitrophenol concentrations, using glucose as a co-substrate. The research results indicated that the degradation effect of nitrophenol with the NZVI/microorganism coupling system was obviously higher than that of a single-NZVI/single-microorganism system. There was a noticeable synergistic effect between the NZVI and anaerobic microorganisms, and the motivational effect of the coupling system on the target pollutant with a neutral or acidic environment was more overt than that with an alkaline environment. The degradation of nitrophenol was enhanced as the dosage of NZVI increased.

Keywords: Nanoscale zero-valent iron; Nitrophenol; Anaerobic microorganism

1. Introduction

Nitrophenol is a long-lasting organic pollutant that is harmful to the human body, covers a wide pollution range, and is hard to biodegrade [1,2]. The United States Environmental Protection Agency has included nitrophenols in the list of "prioritized controlled pollutants" and set strict standards for the concentration of this compound that can be released into the natural environment [3]. Biological methods are inexpensive, do not lead to secondary pollution, and have been widely applied in sewage treatment; thus, they remain an important direction of study regarding environmental remediation technology. However, owing to the high toxicity and anti-biodegradability of nitrophenol wastewater, traditional biological methods fail to deal with it in an effective way [4]. Since nanoscale zero-valent iron (NZVI) has high specific surface area and surface activity, and show excellent magnetic, optical absorption, and biological applications [5,6], it has become a hot topic in the field of environmental pollution remediation. For example, NZVI has been applied to groundwater and soil in order to deal with the organic chlorinated materials in situ as well as to industrial water in the paper and electroplating industries to remove chlorinated aromatics and other refractory pollutants. Good results have been achieved for all the applications [7,8].

The coupling of NZVI reduction and degradation technology [9] with less costly anaerobic microorganisms to deal with nitrophenol wastewater was explored in this study, and the influences of NZVI dosage, initial pH, and initial phenol concentration on this treatment were investigated. The aim was to provide a basis for further study on the degradation characteristics of toxic and refractory pollutants of the NZVI/anaerobic microorganism coupling system.

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2. Material and methods

2.1. Inoculation of microorganisms

Anaerobic sludge from a citric acid wastewater treatment internal circulation reactor was used as the source of inoculation microorganisms. Glucose was co-cultured continuously for 2 months to obtain an anaerobic mixed bacterium.

2.2. Experimental method

The shake flask test was adopted, and the reaction was conducted in a 250-mL medical serum bottle. The NZVI was added together with simulated wastewater according to its dosage at the initial reaction time. The dosages of nutrients in the simulated wastewater are shown in Tables 1 and 2 below. The pH was adjusted with 1:6 H_2SO_4 and 0.01 mol/L NaOH. After the reaction flask was purged with nitrogen, it was sealed with a rubber stopper and incubated in a thermostatic shaker 35°C ± 1°C. The sample was timely obtained with a syringe from the stopper to analyze the concentration of nitrophenol.

2.3. Items and methods of analysis

The filter paper quick-drying standard weighing method was used for measuring volatile suspension solid (VSS) levels, and a pH meter was employed to measure the pH of the solution. Nitrophenol concentration was determined via UV spectrophotometry. Volatile fatty acid (VFA) concentration was measured using steam distillation [10].

3. Results and discussion

3.1. Comparison of the different systems

The degradation effects of an NZVI/microbial combination system, a NZVI only system, and a microorganism-only system on nitrophenol are shown in Fig. 1, wherein the NZVI dosage is 500 mg/L, the inoculum microbial biomass is 1,000 mg VSS/L, and the initial pH is 7.0 for each system.

It can be seen from Fig. 1 that the nitrophenol degradation efficiency of the NZVI/microorganism combination system was significantly better than that of the NZVI only and microorganism-only systems. The removal rate of nitrophenol with the combination system was as high as 97.5% at 5 h and was 40% higher compared with that of the microorganism-only system, indicating that the engagement of NZVI greatly promoted the degradation of nitrophenol. The removal rate of nitrophenol with the NZVI only system reached 66.7% at 6 h, showing that the NZVI still had chemical reduction function for the nitrophenol. However, after a certain period of reaction (4 h), almost no nitrophenol was degraded in this system. In the NZVI/microorganism combination system, organic acids and biogas produced through anaerobic biodegradation processes may activate the NZVI surface, which leads to the long-lasting effect of NZVI [11].

Table 1
Major nutrients in the simulated wastewater (mg/L)

Category	Dosage
$C_6H_{12}O_6{\cdot}H_2O$	1,000
NH_4Cl	220
KH_2PO_4	44
$CaCl_2$	75
$MgSO_4{\cdot}7H_2O$	200

Table 2
Trace elements in the simulated wastewater (mg/L)

Category	Dosage
$CoCl_2{\cdot}6H_2O$	90
$NiSO_4$	50
$ZnCl_2$	50
$CuSO_4{\cdot}5H_2O$	30
$FeSO_4{\cdot}7H_2O$	80
$MnSO_4{\cdot}H_2O$	0.07
$(NH_4)_6MoO_{24}{\cdot}H_2O$	70

3.2. Influence of NZVI dosage

Reaction flasks started with 1000 mg VSS/L of microbial inoculum and a pH of 7.0, and then a dosage of 0, 60, 120, 180, or 240 mg/L NZVI was added to evaluate the effect of NZVI dosage on the degradation of nitrophenol.

It can be seen from Fig. 2 that the nitrophenol degradation efficiency increased with the increase in NZVI dosage. When the dosage was 240 mg/L, the nitrophenol was almost completely degraded, with a removal rate of 98.3%, whereas the removal rate of the microorganism-only system (without NZVI) was only 66.7%. The NZVI/microorganism combination system and microorganism-only system both experienced the process of adsorption, analyzing and

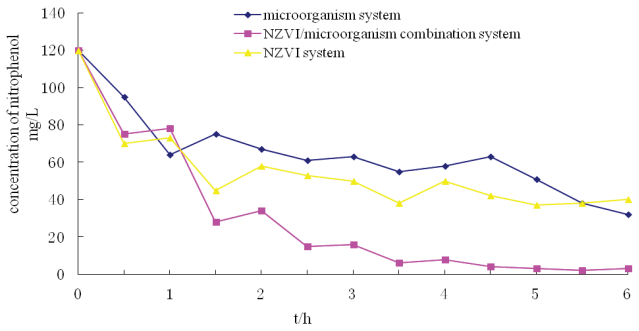

Fig. 1. Degradation effect of different systems on nitrophenol.

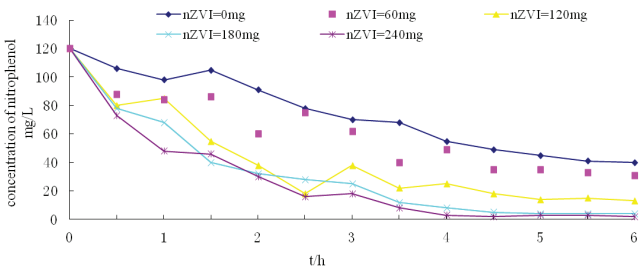

Fig. 2. Influence of NZVI dosage on the degradation of nitrophenol.

biodegradation in the degradation of nitrophenol. The early reaction was mainly characterized by adsorption. After analysis, the NZVI/microorganism combination system and microorganism-only system took a long time to degrade the target pollutant. Because nitrophenol can be easily reduced but is hard to oxidize, it may have been directly reduced and degraded by the NZVI. Another possibility is that the NZVI might lower the toxicity of NZVI, which benefits the functions of the microorganisms in the combination system.

3.3. Influence of initial pH

Reaction flasks started with 1,000 mg VSS/L of microbial inoculum and a dosage of 200 mg/L NZVI, and then the initial pH was set to 5.5, 6.5, 7.2, 8.5, or 9.5 to study the effect of pH on the degradation of nitrophenol by the NZVI/microorganism combination system.

It can be seen from Fig. 3 that the pH of the solution had a significant effect on the capability of the NZVI/microorganism system to degrade nitrophenol. With the pH decreased, the degradation rate of nitrophenol obviously increased. Under the initial pH values of 5.5 and 6.5 (acidic environment), the degradation rate of nitrophenol was high, reaching 97.5% and 96.7%, respectively, at 6 h, whereas the degradation rate of nitrophenol for the initial pH values of 7.2, 8.5, and 9.5 were 90%, 76.7%, and 64%, respectively. Nitrophenol degraded slowly under alkaline conditions (pH = 8.5 and 9.5) because such conditions affect not only the activity of microbial enzymes but also the charge properties of cell membranes, thus affecting metabolic processes. In addition, high pH can cause ionization of nitrophenol, affecting microbial absorption. For the neutral condition (pH = 7.2), although the degradation rate of nitrophenol was slower than that under mildly acidic conditions, the final degradation rates for the two types of conditions were similar, which indicated that the NZVI could better promote the degradation of nitrophenol by anaerobic microorganisms under mild experimental conditions.

3.4. Influence of initial nitrophenol concentration

Reaction flasks started with 1,000 mg VSS/L of microbial inoculum and a pH of 7.0, and then the initial concentration of nitrophenol was set to 100, 200, 300, or 500 mg/L to determine the effect of initial nitrophenol concentration on degradation of the nitrophenol. The results are shown in Fig. 4.

Nitrophenol is toxic to microbes; therefore, its initial concentration in wastewater will affect its degradation. As can be seen from Fig. 4, after 6 h of reaction, the degradation rate of nitrophenol was 97.5% with an initial concentration of 100 mg/L, 57% with an initial concentration of 200 mg/L, and only 7.6% with an initial concentration of 500 mg/L. This shows that a high concentration of nitrophenol can significantly inhibit the degradation ability of microorganisms, resulting in a greatly reduced effect with the combination treatment.

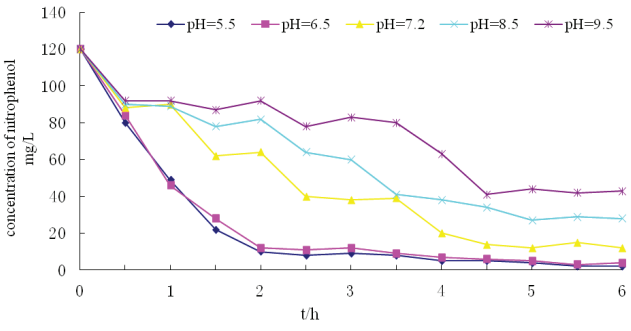

Fig. 3. Influence of pH on the degradation of nitrophenol.

3.5. Changes in pH value during the NZVI/microorganism combination system reaction

Reaction flasks contained 1,000 mg VSS/L of microbial inoculum, 200 mg/L NZVI, and 100 mg/L nitrophenol. Three different initial pH levels, that is, 6.5, 7.2, and 8.5, were examined to analyze the changes in pH during the degradation of nitrophenol via the NZVI/microorganism combination system, as shown in Fig. 5.

When the initial pH was 6.5, the pH of the combination system gradually increased during the reaction, and the final pH remained stable at about 6.8. When the initial pH was 7.2, the pH was more stable. When the initial pH was 8.5, the pH during the reaction decreased at first, then increased, and eventually stabilized, with the final pH remaining at about 7.6. This is because the OH^- produced through NZVI corrosion could balance the H^+ in acidic environments.

3.6. Changes in VFAs during the NZVI/microorganism combination system reaction

Reaction flasks comprised 1,000 mg VSS/L microbial inoculum, 200 mg/L NZVI, and 100 mg/L nitrophenol, with an initial pH of 7.2. The changes in VFAs of the microorganism-only system and NZVI/microorganism combination system are shown in Fig. 6.

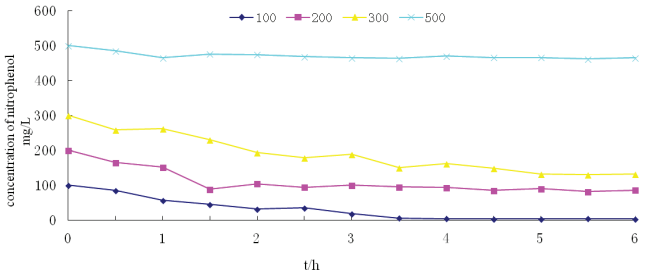

Fig. 4. Influence of initial nitrophenol concentration on degradation of the nitrophenol.

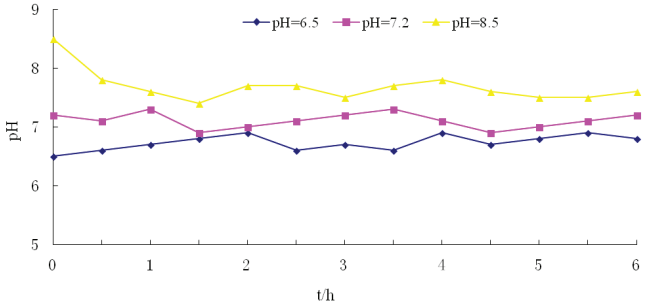

Fig. 5. Changes in pH during the NZVI/microorganism combination system reaction.

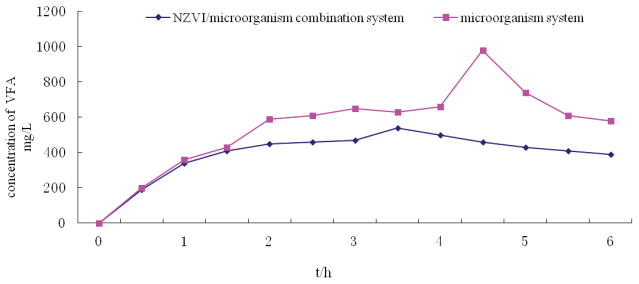

Fig. 6. Changes in VFAs during the NZVI/microorganism combination system reaction.

The VFA concentration in the microorganism-only system during the reaction was always higher than that of the NZVI/microorganism combination system. With the microorganism-only system, glucose was fermented in a short period and a large amount of organic acids was produced to maintain the VFA concentration of the system at a high level. In the NZVI/microorganism combination system, the NZVI corroded quickly and the produced OH^- effectively balanced the organic acids produced through glucose fermentation and kept the VFA concentration at a relatively low level [12]. Meanwhile, the pH of the combination system increased and then stabilized.

4. Conclusion

- The NZVI/anaerobic microorganism coupling system can significantly improve the degradation of nitrophenol. The system performs better degradation with acidic and neutral environments than with mild alkaline environments.
- Higher dosages of NZVI can obviously promote the degradation of nitrophenol, as the rate of this degradation increases with increasing NZVI dosage.
- OH^- generated by the NZVI can effectively balance the organic acids produced through glucose fermentation and maintain the VFA concentration of the NZVI/microorganism coupling system at a low level. The pH of the coupling system increases and then stabilizes, which is conducive for anaerobic microbial degradation of nitrophenol.

Acknowledgements

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