The removal of 2,4,6-trichlorophenol in water by Ni/Fe nanoparticles

Zining Wang, Junyi Chen, Zihao Pan, Hui Bai, Yan Zhang, and Zhen Zhang*

Zhejiang Provincial Key Laboratory of Evolutionary Ecology and Conservation, Taizhou University, 318000 Taizhou, China.

Abstract. In this paper, the removal of 2,4,6-trichlorophenol (2,4,6-TCP) by synthesized Ni/Fe nanoparticles were investigated. At the same time, the factors, such as the dosage of Ni/Fe, Ni content in Ni/Fe nanoparticles, sulfate ion, HA, coexisting substances in water which affected the removal of 2,4,6-TCP by synthesized Ni/Fe nanoparticles were also investigated. Under the experimental conditions, the removal efficiency of 2,4,6-TCP by Ni/Fe nanoparticles in water was about 72% for 2 h. The dosage of Ni/Fe, Ni content in Ni/Fe nanoparticles, and Fe^{3+} all promoted the dechlorination reaction of 2,4,6-TCP by Ni/Fe nanoparticles. Sulfate, oxalic acid and citric acid played an inhibitory role on the removal of 2,4,6-TCP by Ni/Fe nanoparticles in water. Fe^{2+} had no obvious affect to the removal of 2,4,6-TCP by Ni/Fe nanoparticles in water. In addition, low initial HA concentration was favorable for the removal of 2,4,6-TCP by Ni/Fe nanoparticles, while high concentrations of HA played an inhibitory role.

1. Introduction

Chlorophenol compounds are a class of widely used organic substances that are toxic to the environment and difficult to degrade. In recent years, a large number of chlorophenol-based organic compounds have entered our life circle through various channels. Many studies have pointed out that some of the chlorophenol compounds contain similar natural hormones to the human body, which would result in genetic diseases and cancer [1, 2]. 2,4-dichlorophenol, 2,4,6-TCP and pentachlorophenol, which are chlorophenol compounds, have been listed as priority pollutants in China due to their potential danger. 2,4,6-TCP is one of the phenol derivatives, and its molecular formula is C_{6}H_{3}Cl_{3}O. 2,4,6-TCP can be used for antiseptic and sterilization, and it is also widely used in organic synthesis in paper mills, printing and dyeing industries [3]. It has a damaging effect on the skin and mucous membranes, it can stay in the organism for a long time and is difficult to eliminate, thus having a certain impact on the growth and development of the organism. Therefore, it has been identified as an environmental hormone substance that can cause great harm to the human body and environment as a persistent pollutant [4].

Therefore, the removal of chlorophenol compounds in water or soil is an urgent problem to be solved urgently in today's environment.

Since the 1960s, many researchers have used zero valent metallic iron to dechlorinate chlorine-containing organic compounds, thereby improving their biodegradability. However, the disadvantage of this method is that the removal efficiency of low-chlorine organics and chlorinated organics with benzene rings by zero-valent iron is not high [5]. Therefore, zero-valent iron nanoparticles was proceeded for the remediation of chlorinated organic compounds due to its strong reducibility, low cost, non-toxic to the environment and abundant in nature, etc. The mechanism for the degradation of chlorine-containing organic compounds by zero-valent iron nanoparticles is to remove the chlorine element in the organic chloride through the reduction of iron, so that the organic chloride becomes the parent hydrocarbon, thereby reducing its toxicity and improving its biodegradability [6, 7]. However, there are still some problems: the degradation of some chlorine-containing organic compounds by zero-valent iron nanoparticles is slow, and the dechlorinating is incomplete. After the reaction, other chlorine-containing intermediate products may be generated; Fe(OH)_{3}, Fe(OH)_{2}, precipitation or insoluble carbonates may be formed on the surface of the nanoparticles and these substances will form a passivation layer on the surface of iron nanoparticles to prevent the further dechlorinating reaction [8]. In response to the above problems, nanoscale iron-based zero-valent bimetallic metals came into being. The nanoscale bimetallic metals composed of iron and other transition metals (such as Pd, Mg, Ni), which is used to dechlorinate and degrade chlorine-containing organic compounds, and their dechlorination degradation rate are much higher than that of nano-zero-valent iron [9-11]. Ni/Fe bimetallic nanoparticles are more widely used for the degradation of chlorine-containing organic compounds than other bimetallic systems. Because of their lower cost, easy to preparation, and can accelerate the reductive dechlorinating reaction of chlorine-containing organic compounds, they have received increasing attention. Therefore, the removal of
2.4,6-TCP by Ni/Fe bimetallic nanoparticles was studied in this paper.

2. Materials and methods

2.1 Chemicals

The chemical reagents used in the experiments are analytical reagents, and were used directly without any chemical treatment. All deionized water, which were used in the experiments, was purged with nitrogen for 1 hour to remove the small amount of dissolved oxygen.

2.2 Analysis

2,4,6-TCP was analysed by Fuli GC9790 gas chromatograph with an µECD detector. The detector and inlet temperature were 260 °C, the injection volume is 1 µL, and the temperature was programmed: 80 °C maintained for 0.1 min, then increased to 180 °C at a rate of 10 °C / min, maintain 0.1 min, then increased to 260 °C at a rate of 20 °C / min, and maintained for 2 minutes.

2.3 The preparation of Ni/Fe nanoparticles

Ni/Fe bimetallic nanoparticles were prepared in a 1000 mL three-necked flask under nitrogen gas. The preparation method of Ni/Fe bimetallic nanoparticles was exactly the same as the preparation method of literature [12].

2.4 Batch experiments

Batch experiments for 2,4,6-TCP dechlorinating were performed in the same three-necked flask by addition of a certain volume of 2,4,6-TCP from the stock solution and a certain amount of deoxygenated deionized water were added into the same three-necked flask containing freshly prepared Ni/Fe nanoparticles. At a certain time interval, 5 ml sample was sampled with an all-glass syringe, and then extracted with 10 ml n-hexane. The extract was passed through a 0.22 µm filter membrane and placed in a refrigerator to be stored at -4 °C before analysis.

3. Result and discussion

3.1 The removal of 2,4,6-TCP in water by Ni/Fe nanoparticles

In benchmark experiment, the removal efficiencies of 2,4,6-TCP by Ni/Fe nanoparticles were about 57%, 61%, 64%, 68%, 72%, at 5min, 10min, 30min, 1h and 2h, respectively (Figure 1). It can be seen that with the increase of the reaction time, the removal efficiency of 2,4,6-TCP by Ni/Fe nanoparticles in water gradually increased. The growth rate of 2,4,6-TCP removal efficiency by Ni/Fe nanoparticles slowed down with the increase of reaction time, and the removal rate tended to be flat at 2h. The main reason is that after a period of reaction, the Fe(OH)₃ and Fe(OH)₂ film formed on the surface of Ni/Fe nanoparticles, that will reduce the activity of the catalyst, leading the reductive reaction rate slowed down [13].

3.2 Effect of Ni/Fe dosage on the degradation of 2,4,6-TCP in water by Ni/Fe nanoparticles

Since the degradation of 2,4,6-TCP by Ni/Fe nanoparticles takes place on the surface of nanoparticles, the Ni/Fe to 2,4,6-TCP ratio (g Ni/Fe to mg 2,4,6-TCP) is a significant variable parameter. The effect of Ni/Fe nanoparticles dosage on the degradation of 2,4,6-TCP by Ni/Fe nanoparticles was investigated with only Ni/Fe nanoparticles dosage changed (Figure 2). After 2 hours of reaction, when the dosages of Ni/Fe nanoparticles were 2 g/L, 3 g/L, 4 g/L, 5 g/L, the removal efficiencies of 2,4,6-TCP in water by Ni/Fe nanoparticles were about 59 %, 63 %, 72 % and 66 %, respectively. The increase of Ni/Fe nanoparticles’ dosage often means an increase in the concentration of the catalyst surface area, which would lead to an increase in the removal efficiency of pollutants. However, the excessive amount of Ni/Fe nanoparticles’ dosage will increase the chance of collision between particles, which would lead to the decrease of the removal efficiency of pollutants [14]. In summary, under the experimental conditions, the appropriate dosage of Ni/Fe nanoparticles is 4 g/L.

3.3 Effect of Ni content in Ni/Fe on the degradation of 2,4,6-TCP by Ni/Fe nanoparticles

Nickel is a well-known catalyst for the degradation of 2,4,6-TCP by nanoscale zero-valent Ni/Fe particles.
Coexistence of Ni and Fe in the particles has been proved to be highly effective to accelerate the dechlorinating reaction. Figure 3 shows the effect of Ni content in Ni/Fe nanoparticles on the degradation of 2,4,6-TCP by Ni/Fe with only Ni content in Ni/Fe nanoparticles changed. With Ni content increased from 1.0 % to 1.5 %, 2.0 % and 2.5%, the removal efficiency of 2,4,6-TCP by Ni/Fe nanoparticles first increased from 48% to 54%, and then to 72% in 2h, at last reduced to 58%. It can be seen that the removal efficiency of 2,4,6-TCP by Ni/Fe nanoparticles reached the maximum when Ni content was 2.0 %. Ni is a transition metal and has a catalytic hydrogenation role during the reaction, so it can promote the dechlorinating reaction to some extent. Therefore, the removal efficiency of 2,4,6-TCP by Ni/Fe nanoparticles increased with the increase of Ni content in Ni/Fe nanoparticles within a certain range. However, addition too much nickel, such as 2.5 % Ni content in the experiment, would increase the Ni area on the catalyst surface and decrease the Fe area, thereby reducing the removal efficiency of 2,4,6-TCP by Ni/Fe nanoparticles.

**Figure 3.** Effect of Ni content in Ni/Fe nanoparticles on the degradation of 2,4,6-TCP by Ni/Fe nanoparticles

### 3.4 Effect of SO$_4^{2-}$ on the degradation of 2,4,6-TCP by Ni/Fe nanoparticles

The change of SO$_4^{2-}$ concentration was achieved by addition of different concentrations of sodium sulfate solution. It can be seen from Figure 4 that after 2 hours of reaction, the removal efficiency of 2,4,6-TCP in water by Ni/Fe nanoparticles was about 58% when 1 mmol/L of SO$_4^{2-}$ appeared. And it continue decreased to 53% and 46% when 2 mmol/L and 3 mmol/L of SO$_4^{2-}$ appeared in the reaction solution. Sulfate inhibited the degradation of 2,4,6-TCP in water by Ni/Fe nanoparticles, and as the concentration of sulfate increased, the inhibitory effect was more obviously. The reasons are on one hand sulfate would form a passivation layer on the surface of metal iron, reducing the specific surface area of the reaction, thereby inhibiting the progress of the reaction. On the other hand, the sulfur in the sulfate would poison the catalyst and reduce the activity of the catalyst [15].

**Figure 4.** Effect of SO$_4^{2-}$ on the degradation of 2,4,6-TCP by Ni/Fe nanoparticles

### 3.5 Effect of HA on the degradation of 2,4,6-TCP by Ni/Fe nanoparticles

In subsurface environment, natural humic substances such as humic acid (HA) are abundant, there is no doubt that HA would affect the dechlorinating reaction of 2,4,6-TCP in water by Ni/Fe nanoparticles. It can be seen from Figure 5, when HA initial concentration increased from 0 to 10, 20, 30mg/L, the removal efficiency of 2,4,6-TCP by Ni/Fe nanoparticles in 2h increased from 72 % to 74 %, 75 % and 77 %. Continue increasing the HA initial concentration to 40mg/L, it decreased by 7 % to 70 % in 2h. It can be seen that in low initial HA concentration (less than 30mg/L), the higher the initial HA concentrations were, the higher the removal efficiencies of 2,4,6-TCP by Ni/Fe nanoparticles were. While high HA initial concentration (40 mg/L) would inhibit the degradation 2,4,6-TCP by Ni/Fe nanoparticles. Mainly for the active groups in HA would promote the degradation reaction with low initial HA concentration, but excessively high HA concentration would cause the adsorption of HA on the surface of Ni/Fe catalyst, resulting in the reduce of the reaction rate [9, 12].

**Figure 5.** Effect of HA on the degradation of 2,4,6-TCP in water by Ni/Fe nanoparticles

### 3.6 Effect of coexisting substances on the degradation of 2,4,6-TCP in water by Ni/Fe nanoparticles

Actual wastewater often has complex components and multiple substances coexist. Therefore, we investigated the effect of coexisting substances on the degradation of 2,4,6-TCP in water by Ni/Fe nanoparticles (Figure 6). For ferrous iron and ferric iron ions, we used the
corresponding sulfate salts, when considering the influence of ferrous iron and ferric iron ions, the effect of sulfate should be considered. When 1 mmol/L Fe²⁺, Fe³⁺, citric acid and oxalic acid appeared in the reaction solution respectively, the removal efficiency of 2,4,6-TCP by Ni/Fe nanoparticles in 2h were 56%, 70%, 49% and 46%. Because the removal efficiency of 2,4,6-TCP by Ni/Fe nanoparticles was 58% when 1 mmol/L of sulfate appeared, the effect of Fe²⁺ on the degradation of 2,4,6-TCP in water by Ni/Fe nanoparticles was not obvious. However, Fe³⁺ obviously promoted the degradation of 2,4,6-TCP by Ni/Fe nanoparticles due to its strong oxidation, it could react with zero-valent iron and maintain the surface of zero-valent iron nanoparticles at high reactivity. Obviously, oxalic acid and citric acid inhibited the catalytic reductive dechlorinating reaction of 2,4,6-TCP by Ni/Fe nanoparticles.

In this paper, the reductive dechlorination of 2,4,6-TCP in water by Ni/Fe bimetallic nanoparticles was investigated, and the factors which affected the reaction, such as the dosage of Ni/Fe nanoparticles, Ni content in Ni/Fe nanoparticles, sulfate ion, HA, coexisting substances in water, were also investigated. The main conclusions are as follows:

Ni/Fe bimetallic nanoparticles had a higher efficiency of degrading and/or reducing 2,4,6-TCP. When the reaction time was 5min, 10min, 30min, 1h and 2h, the removal efficiencies of 2,4,6-TCP by Ni/Fe nanoparticles were about 57%, 61%, 64%, 68% and 72%, respectively. The removal efficiency of 2,4,6-TCP by Ni/Fe nanoparticles increased with the increase of reaction time, but the growth rate of removal efficiency gradually slowed down and became stable.

Under the experimental conditions, when Ni/Fe nanoparticles dosage was 4 g/L, the Ni content in Ni/Fe nanoparticles was 2.0 %, Ni/Fe nanoparticles had the highest removal efficiency for 2,4,6-TCP.

Low initial HA concentration promoted the catalytic reductive dechlorination of 2,4,6-TCP by Ni/Fe nanoparticles. But excessive high concentration of HA inhibited the catalytic reductive dechlorination of 2,4,6-TCP by Ni/Fe nanoparticles. Mainly because the active groups contained in HA could promote the degradation reaction with low HA concentration, but excessive high HA concentration caused the adsorption of HA on the surface of Ni/Fe nanoparticles, resulting in the decrease of 2,4,6-TCP removal efficiency.

The effect of Fe³⁺ on the degradation of 2,4,6-TCP in water by Ni/Fe nanoparticles was not obvious. Fe³⁺ obviously promoted the degradation of 2,4,6-TCP by Ni/Fe nanoparticles due to its strong oxidation. Oxalic acid and citric acid inhibited the catalytic reductive dechlorinating reaction of 2,4,6-TCP by Ni/Fe bimetallic nanoparticles.

At present, for the study of zero-valent iron remediation technology, there have been many studies focusing on the improvement of the reductive dechlorinating technology of nanoscale bimetallic systems. Xing et al added vitamin B12 to nanoscale Fe/Cu bimetallic system to effectively dechlorinate of pentachlorophenol. Their research showed that vitamin B12 could enhance the reductive reaction activity of the system and could increase the reaction rate [5]. Zhou et al used a complexing agent EDTA to optimize the degradation of organic chloride in water by Pd/Fe bimetallic nanoparticles. Their results showed that EDTA could complex iron ions and prevent the formation of a passivation layer on the catalyst surface, thereby improving the degradation efficiency [11]. Zhao et al used activated carbon particles to increase the stable specific surface area of the prepared Pd/Fe bimetallic nanoparticles, thereby effectively improving their removal efficiency of PCBs [10, 16]. In the future, we will focus on the study of stabilized bimetallic nanoparticles for the dechlorinating of chlorophenol in wastewater.

4. Conclusion

In this paper, the reductive dechlorination of 2,4,6-TCP in water by Ni/Fe bimetallic nanoparticles was investigated, and the factors which affected the reaction, such as the dosage of Ni/Fe nanoparticles, Ni content in Ni/Fe nanoparticles, sulfate ion, HA, coexisting substances in water, were also investigated. The main conclusions are as follows:

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Under the experimental conditions, when Ni/Fe nanoparticles dosage was 4 g/L, the Ni content in Ni/Fe nanoparticles was 2.0 %, Ni/Fe nanoparticles had the highest removal efficiency for 2,4,6-TCP.

Low initial HA concentration promoted the catalytic reductive dechlorination of 2,4,6-TCP by Ni/Fe nanoparticles. But excessive high concentration of HA inhibited the catalytic reductive dechlorination of 2,4,6-TCP by Ni/Fe nanoparticles. Mainly because the active groups contained in HA could promote the degradation reaction with low HA concentration, but excessive high HA concentration caused the adsorption of HA on the surface of Ni/Fe nanoparticles, resulting in the decrease of 2,4,6-TCP removal efficiency.

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Acknowledgements

This study was supported by Zhejiang Province National Science Foundation of China (No. LY20E080013), by Taizhou science and Technology Bureau (1902gy17), and by Zhejiang Province undergraduate Science and Technology Innovation Project (2018R436011).

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