

Influence Factors on Removal of 2,4-DCP by Sulfided Nanoscale Zerovalent Iron

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Abstract. 2,4-Dichlorophenol (2,4-DCP) has been extensively applied for chemical and pharmaceutical production, resulting in severe environmental pollution. In this paper, the sulfided nanometer zero-valent iron (S-nZVI) was synthesized and applied to remove 2,4-DCP. The experimental tests displayed that when the sulfur iron mole ratio was 0.129, the elimination rate for 2,4-DCP was 91.9%, and the removal rate declined when the sulfur-to-iron proportion increased. As the initial concentration of 2, 4-DCP improved from 10 to 40mgL⁻¹, the elimination rate of 2,4-DCP declined from 92.6% to 65.3%. The elimination effect of S-nZVI on 2,4-DCP increased with rising temperature. The removal rate of 2,4-DCP varied under various pH conditions. The removal efficiencies were reduced from 75.5% to 48.8% when the initial pH ranged from 5 to 3. When pH is 11, the removal rate is 97.9%. Kinetics of degradation reaction of 2,4-DCP under different conditions were conducted. The process for removing 2,4-DCP was in accord with the pseudo-first-order kinetics model. The initial pH and sulfur mole ratio played a decisive role, which determined the removing rate of 2,4-DCP. The findings can guide more efficient S-nZVI reactivity towards the target contaminants in water remediation.

1 Introduction

2,4-dichlorophenol (2,4-DCP) drew much attention because of its high toxicity and non-biodegradability, causing considerable harm to humans and the environment[1,2]. Therefore, it is necessary to develop remedial technology. Methods for eliminating 2,4-DCP contaminants include the microorganism method and chemical oxidation methods[3,4]. However, the different solutions to the problem have some disadvantages, such as toxic intermediate products and the requirement of microbial domestication. Hence, the development of an efficient chemical reduction technology is desired.

Nowadays, nanoscale zero-valent iron particles (nZVI) have become a better repair material for removing organic pollutants [5,6]. However, there are still many technical challenges in water remediation with the implementation of nZVI. The main issue restricting broad-scale nZVI use is that nZVI particles can react with water to form iron oxide layers outside the nZVI particles and inhibit the reaction between nZVI and contaminants[7,8]. Increasing its selectance for objective contaminants rather than water is necessary to increase efficiency. Sulfidation is an emerging method to stabilize nano zero-valent iron particles. Recently, nanometer zero-valent iron sulfide (S-nZVI) has attracted extensive attention from researchers due to its favourable properties in water remediation[9]. Researchers found that sulfur can form sulfide layers clinging to nano zero-valent iron, avoid contact with oxygen and decrease the

passivation of the materials, to result in the decrease of reactivity[10]. In addition, the hydrophobicity and the electron transfer efficiency of sulfide layers were superior to oxide layers. Thus the removal efficiency of pollutants is higher[11].

In this work, S-nZVIs were synthesized and used to remove 2,4-DCP. The influences of reaction factors (temperature, initial concentration, dosage, and sulfur iron mole ratios) on the treatment efficiency of 2,4-DCP pollutants were studied. According to the experimental results, the sulfur mole ratio significantly influences the 2,4-DCP removal.

2 Materials and Methods

2.1 Material

2,4-dichlorophenol (C₆H₄Cl₂O), o-chlorophenol (C₆H₅ClO), p-chlorophenol (C₆H₅ClO), and phenol (C₆H₆O) was acquired from Shanghai Maclin Biochemical Technology Co., LTD (Shanghai, China). The experimental medicines were obtained from Tianjin Fuchen Chemical Factory (Tianjin, China) included potassium borohydride (KBH₄), hydrochloric acid (HCl), ferrous sulfate (FeSO₄•7H₂O), sodium dithionite (Na₂S₂O₄), and sodium hydroxide (NaOH). All chemicals were analytical grade. Nitrogen (N₂) was purchased from Beijing Shunchi East ring dry ice

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operation Center (Beijing, China). All Ultrapure water was used to prepare the chemical solutions.

2.2 Preparation of Sulfided nanometer zero-valent iron

S-nZVI particles were prepared based on the one-step method. Firstly, the solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was formed by adding $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ into three-necked flasks. Then, the mixed NaBH_4 and $\text{Na}_2\text{S}_2\text{O}_4$ solutions were slowly poured into $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solutions, constantly stirring, where the ratio of $\text{BH}_4^-/\text{Fe}^{2+}$ was 2.2. After reduction, it continues stirring for 30 minutes. The entire process referred to above was carried out under the N_2 atmosphere. The resulting SNZVI suspensions were extracted through vacuum filtration, and the solid was collected and cleaned with deoxygenated ultrapure water three times. The as-prepared S-nZVI particles were vacuum-dried before use.

2.3 Batch experiments

S-nZVI was evaluated using batch-type experiments of 2,4-DCP degradation at different sulfur iron mole ratios (0.026, 0.064, 0.129, 0.257), pH values (3, 5, 7, 9, 11), initial concentration of 2,4-DCP (10, 20, 30, 40 mg/L) and reaction temperature (15, 25, 30, 40 °C). 0.4 g S-nZVI was dispersed in 200 mL 2,4-DCP solutions (20mg/L), located in a constant temperature shaking table (200 rpm) at 25 ± 1 °C. At a given time interval, a 5ml sample was extracted with an injection syringe and filtered by a 0.45 μm filter membrane before use. All experiments were carried out in triplicate. The concentration of 2,4-DCP was analyzed by high-performance liquid chromatography (HPLC, LC-2030) equipped with a C18 column, and the UV detector wavelength was 284 nm.

3 Results & Discussion

3.1 Effect of Sulfur mole ratio

Fig 1(a) depicts the removal efficiency at different sulfur molar ratios. The results showed that when the sulfur molar ratio was 0.129, the highest removal rate was 91.9%. However, the removal rate decreased with the sulfur molar ratio increased to 0.257. Table (1) displays the pseudo-first-order rate constant for 2,4-DCP removal versus S-nZVI sulfur molar ratio. At the low sulfur molar ratio, as the sulfur molar ratio increase to 0.129, the K_{obs} is up to 0.02339 h^{-1} , which indicates that the removal rate continues to accelerate. When the sulfur molar ratio is more than 0.257, the K_{obs} decrease when the sulfur molar ratio is low because the surface of nZVI is not completely coated by the sulfide layer. Exposed nZVI could directly react with 2, 4-DCP. When the sulfur molar ratio was 0.064, the surface of nZVI was entirely covered with sulfide layer; the sulfur content was too low for removal efficiency to slow. With the increase of sulfur content, the removal efficiency and

reaction duration are the best. The removal efficiency decreases when the sulfur molar ratio is more than 0.129. This is because too much FeS and FeS_2 on the surface of nZVI could plug the active surface sites, thus decreasing the results. Furthermore, the higher bandgap (0.95eV) could slow down electron transfer [12].

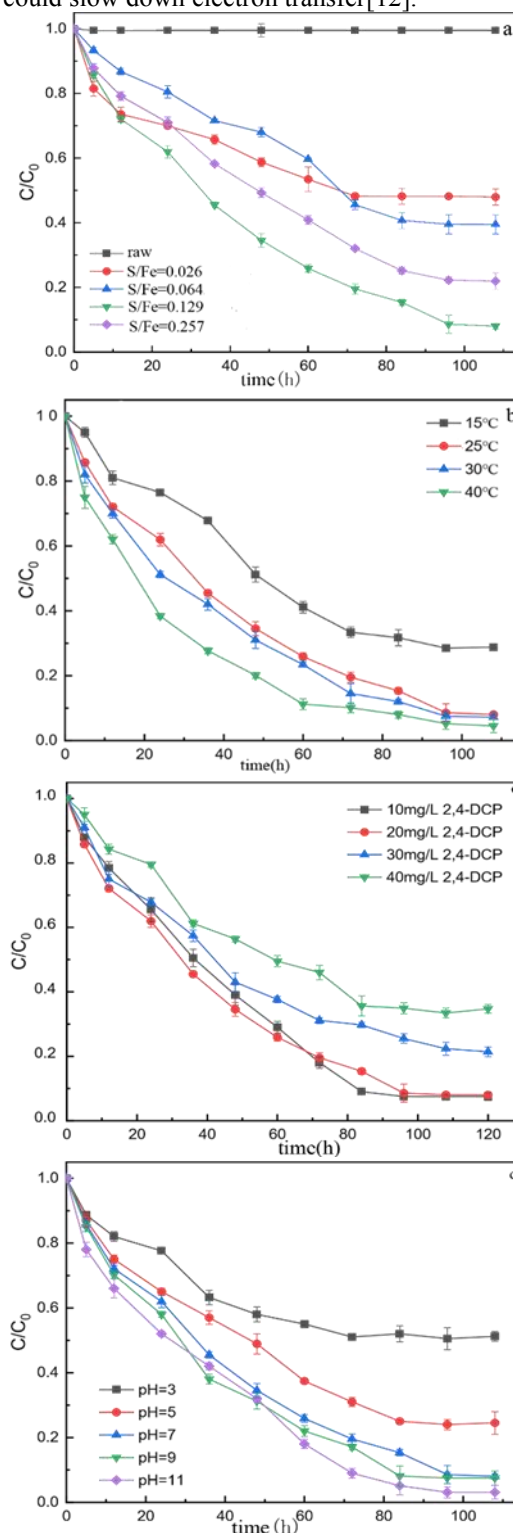


Fig.1 (a) The removal effect of 2,4-DCP at different sulfur molar ratios, (b) The removal effect of 2,4-DCP at different reaction temperatures, (c) The removal rate of 2,4-DCP at different initial concentrations, (d) The removal effect of 2,4-DCP at different initial pH.

3.2 Effect of reaction temperatures

As shown in fig1 (b), the results indicated that the reaction rate remarkably increased with the reaction temperatures build-up. The degradation efficiencies were only up to 71.2% when initial reaction temperatures of 15 °C. With the reaction temperatures ranging from 15 to 40 °C, the removal efficiencies are up to 95.5%. As shown in Table 2, the observed rate constants were 0.01627–0.03217 h⁻¹, respectively, at reaction temperatures 15-40 °C. This effect was ascribed to the fact the number of activated molecules increases with the reaction temperatures increase, the mass transfer velocity of 2,4-DCP increases, thus accelerating the reaction process. However, low temperature inhibits the reaction process.

Table 1. The fitting parameters at different ferrite molar ratios

ferrite molar ratios	reaction rate constant k_{obs} (h ⁻¹)	R ²
0.026	0.0937	0.94553
0.064	0.0986	0.98984
0.129	0.2339	0.99487
0.257	0.1568	0.99774

Table 2. The fitting parameters at different reaction temperatures

reaction temperatures	reaction rate constant k_{obs} (h ⁻¹)	R ²
15	0.01627	0.98157
25	0.02339	0.99487
30	0.02591	0.99321
40	0.03217	0.97928

3.3 Effect of the initial concentration of 2,4-DCP

Fig 1(c) studied the relationship between the initial concentration of 2,4-DCP and removal efficiency that with the 2,4-DCP concentration in the initial solution of 10, 20, 30, and 40 mg L⁻¹, the removal efficiency of 2,4-DCP were 92.5%,91.9%, 78.6%, 65.3%, respectively. With an increase in the initial concentration of 2,4-DCP, the equilibrium time is prolonged. As shown in table 3, k_{obs} decreased with an initial concentration of pollutants. In theory, a high concentration of 2,4-DCP can increase the probability of practical collision between 2,4-DCP and nanoparticles. However, the dosage of S-nZVI was

constant when it increased the concentration, and the reactive sites were limited, decreasing the degradation rate.

Table 3. The fitting parameters at different original concentrations of 2,4-DCP

initial concentrations of 2,4-DCP	reaction rate constant k_{obs} (h ⁻¹)	R ²
10	0.02493	0.97878
20	0.02339	0.99487
30	0.0153	0.99243
40	0.01153	0.99447

3.4 Effect of initial pH

Fig2 showed the zeta potentials of nZVI and S-nZVI at various pH values. The zeta potentials value of nZVI and S-nZVI first decreases and increases as the pH increases. The isoelectric point of nZVI($pH_{ZPC}=6.40$) is less than S-nZVI ($pH_{ZPC}=7.23$), which also confirmed that sulfur could change the surface properties of nZVI. Furthermore, S-nZVI is more stable at high pH combined with Zeta potential measurement results. As shown in Fig 1 (d), the pH value significantly affects the elimination process of 2,4-DCP by S-nZVI. The removal efficiencies were reduced from 75.5% to 48.8% when the initial pH ranged from 5 to 3. At low pH, the corrosion rate of Fe⁰ and a large amount of hydrogen are produced to decrease the removal rate because of the dissolution of the sulfide layer.

On the contrary, the degradation efficiencies were up to 97.9% on the alkaline condition at an initial pH of 11. This result is consistent with previously reported sulfided nanoscale zero-valent iron[13]. Table 4 indicated that the pseudo-first-order model had a good correlation($R^2=0.95$). Alkaline conditions are favourable for the reaction, and removal efficiency for S-nZVI is highest (97.9 %) at pH = 11.

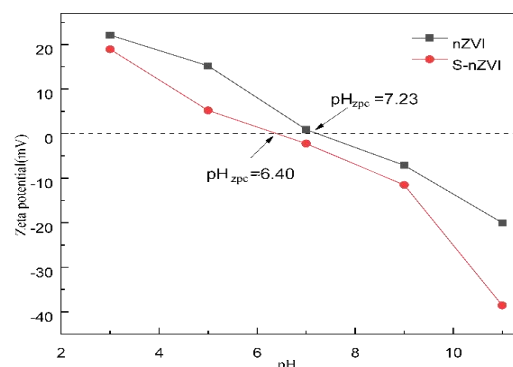


Fig.2 The Zeta potential plots of nZVI and S-nZVI

Table 4. The fitting parameters at different different initial pH

initial concentrations of 2,4-DCP	reaction rate constant k_{obs} (h^{-1})	R^2
3	0.00873	0.95661
5	0.01584	0.98657
7	0.02339	0.99487
9	0.02676	0.98323
11	0.03291	0.95921

4 Conclusions

This study investigated the effect of diverse experimental conditions for removing 2,4-DCP. The initial pH and sulfur mole ratio played a significant role, which determined the removal rate of 2,4-DCP. The findings of the experiment can guide more efficient S-nZVI reactivity towards the objective contaminants in water remediation.

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