Effect of Ni morphology on removal of pentachlorophenol with Fe/Ni nanomaterials
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ABSTRACT
Chlorinated phenols are a kind of environmental priority pollutant that attract much attention. Nanosized Fe and Fe/Ni materials are considered as promising options for chlorinated phenol removal. The effect of Ni morphology on the removal of pentachlorophenol (PCP) with Fe/Ni nanomaterials was investigated in this study. Iron nanoparticles and nickel nanomaterials with different shapes were synthesized using a chemical reduction method and wet chemical techniques, respectively. The concentrations of PCP and chloride in solutions were measured with and without Ni present. The intermediates of PCP were also analyzed. The results showed that the dechlorination of PCP was promoted by Ni nanomaterials, among which the tubular porous Ni nanomaterials expressed the most promotion, then those with net shape and nanochains. However, the tubular porous Ni nanomaterials inhibited the removal of PCP, and the other two expressed a certain promotion. In the Fe/Ni system, Fe nanoparticles transformed into magnetite (Fe₃O₄) and/or maghemite (Fe₂O₃), and Ni nanomaterials were still pure Ni after reaction. The introduction of Ni nanomaterials would improve dechlorination of PCP, but the removal of PCP might be inhibited or improved as the morphology of Ni changed.

Key words | dechlorination, iron nanoparticles, morphology, nickel nanomaterials, pentachlorophenol (PCP)

INTRODUCTION
Chlorophenols, which are bioaccumulative, refractory and carcinogenic, are recognized as environmental priority control pollutants (Squillace et al. 1999). Because of extensive bactericidal and insecticidal effects, chlorophenols have been widely used as insecticides, disinfectants and preservatives. In addition, chlorophenols are a class of aromatic compounds with high water solubility, and the adsorption and fixation of chlorophenols in soil is weak, so chlorophenols can spread widely into the environment with water as the carrier (Droste et al. 1998). The effective treatment of chlorophenols is an important issue to be solved.

Because of the special interface, physical and chemical properties, zero-valent iron nanoparticles (ZVI NPs) can transform a variety of environmental pollutants effectively. As a result, ZVI NPs can be used for in situ or ex situ remediation of groundwater pollution. In recent years, ZVI NPs have been extensively studied and applied in the field of environmental remediation and pollution control. Based on the current study, various pollutants including chlorinated organic compounds, heavy metals, nitrate, dyes, radionuclides, phosphate, and sulphion can be removed by ZVI NPs (Cheng et al. 2007; Zhang & Fang 2010; Suzuki et al. 2012; Huang et al. 2013; Nakatsuji et al. 2015). In addition, ZVI NPs can also remove the disinfection byproducts of drinking water including bromate effectively (Lim et al. 2007).

However, ZVI NPs still have some disadvantages. For example, ZVI NPs can be easily oxidized, which will decrease the reactivity of ZVI NPs. The dechlorination process of some chlorinated organic compounds is slow, and other toxic chlorinated byproducts will be produced. Studies have shown that the degradation rate of pollutants can be
improved when a second metal (usually an inert metal) is introduced into the ZVI NP system, and some organic pollutants which are refractory in the ZVI NP system can be degraded effectively (Smuleac et al. 2011). Subsequently, bimetal systems have been widely studied to achieve rapid and complete dechlorination including Fe/Ni, Fe/Pd, Fe/Cu, etc. (Zhang et al. 2010; Han & Yan 2014; Lai et al. 2014).

As a widely used catalyst, Ni nanomaterials show high activity and selectivity in reactions such as catalytic hydrogenation, oxidation and cracking (Park et al. 2005; Busca et al. 2014; Zhou et al. 2014). However, few studies have focused on the effect of the morphology of the catalyst (Mahjoub et al. 2012). In this research, pentachlorophenol (PCP) was selected as the model pollutant, and Ni nanomaterials with different morphology were introduced into the ZVI NP system. The effect of Ni morphology on the removal of PCP in the nano-Fe/Ni system was investigated, and the role of nano-Ni in the system was also analyzed.

**METHODS**

**Preparation and characterization of nanomaterials**

The ZVI NPs were prepared with a chemical reduction method. One hundred millilitre FeSO4·7H2O (99.0%–101.0%, Shenyang Reagent Factory, China, AR) solutions of 40 mmol·L−1 were added into the four-necked flask at room temperature, then 100 mL KBH4 (96%, Nankai Fine Chemical Factory, Tianjin, China, AR) solutions of 0.2 mol·L−1 were added into the flask dropwise under intense mixing. The whole process was conducted in Ar (99.99%, Beijing Aolin Gas Company, Beijing, China, AR) atmosphere. The chemical reaction is shown as follows:

\[
\text{Fe(H}_2\text{O)}_6^{2+} + 2\text{BH}_4^- \rightarrow \text{Fe}^0 + 2\text{B(OH)}_3 + 7\text{H}_2 \uparrow \quad (1)
\]

The prepared ZVI NPs were rinsed with deionized water, and were then dried in a vacuum drying oven (DZ-1 BC, Tianjin Taisite Instrument Co. Ltd).

Ni nanomaterials were synthesized using polyvinyl pyrrolidone (PVP, K30, Sigma-Aldrich Chemical Co. Ltd) as the template and wet chemical techniques were adopted (Liu et al. 2004). The specific preparation method was as follows: 15 mL NiSO4 (Shanghai Hengxin Chemical Reagent Co. Ltd, AR) solutions of 0.025 mol·L−1 and 30 mL PVP of 0.3 mol·L−1 were dissolved in 60 mL ethylene glycol (EG, Shanghai Chemical Reagent Company, AR), and ultrasonic treatment was then used for 15 min in order to make sure the Ni2+ was evenly dispersed in the solution. Then 0.75 mL of hydrazine hydrate (50%, Tianjin Chemical Reagent Company) was added into the solution until the color of the solution became light purple. The purple solution was heated to the boiling point of EG (197 °C), then refluxing for 3 h under intense magnetic stirring. Finally the black precipitate was separated, and washed with distilled water and anhydrous ethanol. The obtained sample was the tubular porous Ni. As for the Ni nanochains, UV radiation was applied for 1 h in the crystal growth process. For Ni with net shape, the refluxing time was 12 h.

The morphologies of the iron and nickel nanomaterials were observed with scanning electron microscopy (SEM, FEI Quanta 200F), and the structure and composition of the samples were determined by X-ray diffraction (XRD, Rigaku Dmax 2200) analysis.

**Experimental methods**

Taking reagent bottles (18 mL) with rubber plugs as reactors, 15 mL PCP solutions (Beijing Changping ShiYing Chemical Factory, CP) were added into each reaction bottle, 15 mg ZVI NPs and 5 mg Ni nanomaterials were put into the solution, then the reagent bottles were sealed with rubber plugs and were put into the table constant-temperature incubator shaker (TZ-2EH, Beijing Ward Company). The initial concentration of the PCP (\(C_0\)) was 50 mg·L−1, the temperature was 30 °C and the rotation speed was 150 r/min. Sampling at different times, the concentrations of residual PCP and released Cl− were analyzed. Based on the initial concentration of PCP, the removal of PCP and relative concentration of released Cl− were calculated, then the removal rate of PCP and the dechlorination efficiency were obtained. PCP solutions without ZVI NPs or Ni nanomaterials were used as a control.

**Analysis methods**

PCP was measured with a high performance liquid chromatograph (HPLC, Agilent 1200, Shanghai Agilent Company), equipped with a C18 reversed phase chromatographic
column and 1,200 photodiode array detector, and manual sampling. The mobile phase was methanol and ultrapure water with volume ratio \( V(\text{CH}_3\text{OH})/V(\text{H}_2\text{O}) = 85/15 \), the volume flow rate was 0.8 mL·min\(^{-1}\), and the detection wavelength was 320 nm. The intermediates of PCP were analyzed qualitatively by mass spectrometer (PE API 3000 MS), and then were quantitatively analyzed by HPLC. The corresponding detection wavelengths of 2-chlorophenol (2-CP), 3-chlorophenol (3-CP) and 4-chlorophenol (4-CP) were 275 nm, 279 nm and 280 nm, respectively.

Cl\(^{-}\) was measured with ion chromatography (DX-100, German DIONEX Company). The eluent consisted of 3.5 mmol·L\(^{-1}\) Na\(_2\)CO\(_3\) and 1.0 mmol·L\(^{-1}\) NaHCO\(_3\), the volume flow rate was 1.2 mL·min\(^{-1}\), and manual sampling; the sampling volume was 250 \( \mu \)L, the analysis time was 6 min. Deionized water was taken as blank.

All of the samples were filtered with 0.45 \( \mu \)m microporous membranes.

**RESULTS AND DISCUSSION**

The structure and morphology of the nanomaterials

Through XRD analysis, the peaks of the XRD spectra of synthesized ZVI NPs corresponded to the diffraction peak of the Fe (110) face and (211) face (JPDS#06-0696), and the diffraction peak of iron oxide was not detected in the XRD spectra, which indicated the prepared ZVI NPs were not oxidized obviously. The SEM image (Figure 1(a)) showed that the ZVI NPs were spherical, and the diameters of the particles were <100 nm and were relatively uniform. The agglomeration of

**Figure 1** | SEM images of nanomaterials: (a) Fe nanoparticles; (b) Ni nanochains; (c) tubular porous Ni nanomaterial; (d) Ni nanomaterials with net shape.
some particles may be caused by the surface effect of ultrafine particles and the magnetic action of ZVI NPs.

All the diffraction peaks of the prepared Ni nanomaterials corresponded to the face-centered cubic structure of pure Ni (JCPDS 04-0850). The apparent morphology of the three kinds of Ni nanomaterials was displayed as Ni nanochains (Figure 1(b)), tubular porous Ni (Figure 1(c)) and Ni with net shape (Figure 1(d)), respectively.

The removal of PCP and Cl\textsuperscript{-} release

The removal rate of PCP and the relative concentrations of Cl\textsuperscript{-} (C\textsubscript{0}: the initial concentration of PCP) after different reaction times were determined. The results showed that the tubular porous Ni nanomaterials inhibited the removal of PCP while those with net shape and nanochains expressed a certain promotion. For example, after reacting for 20 h (Figure 2), the removal rate of PCP in the ZVI NP system was 76.7\%, and that in the tubular porous Ni system was 33.1\%, and that in the Ni nanochain and net-shape Ni systems were 80.2\% and 78.8\%, respectively. However, the relative concentrations of released Cl\textsuperscript{-} in each system showed completely different trends. The relative concentration of Cl\textsuperscript{-} was up to 108.2\% in the tubular porous Ni system, and that in the nanochain Ni system and net-shape Ni system was 40.4\% and 68.2\%, respectively, while in the ZVI NP system, the relative concentration of Cl\textsuperscript{-} was only 25.7\%. It can be concluded that the introduction of Ni nanomaterials would improve the dechlorination of PCP; however, the tubular porous Ni nanomaterials inhibited the removal of PCP. Among the three kinds of Ni nanomaterials, the tubular porous Ni showed the most evident promotion in dechlorination, followed by the net-shape Ni and the Ni nanochains.

The three kinds of Ni nanomaterials with different morphologies expressed great differences in the process of removing PCP, which proved that the Ni morphology would influence the progress of the reaction. The reaction process in the tubular porous Ni system was investigated (Figure 3), and the results indicated that Ni nanomaterials alone also showed a certain removal efficiency of PCP, which was mainly due to the adsorption effect of tubular porous Ni on PCP. Cl\textsuperscript{-} was not detected in the Ni system, which further illustrated that the removal of PCP resulted from the adsorption with Ni. The removal rate of PCP was lower after adding Ni nanomaterials into the ZVI NP system; it persisted at about 50\% and showed no significant growth as the reaction time extended. That phenomenon had a great relationship with the tubular porous morphology of the Ni: iron nanoparticles and PCP molecules could both enter the pores of the Ni, and if they entered the same pore, they would react quickly, which led to the dechlorination of PCP after they contacted each other. If iron nanoparticles and PCP molecules entered different pores, the PCP molecules would stay in the pores of the Ni, and they could not be chemically degraded. Because some iron nanoparticles were ‘stuck’ in the pores of the Ni, they could not react with PCP molecules. Such comprehensive effects led to the
removal process of PCP in the Fe/Ni system reaching a balance quickly, but the removal rate was lower after adding nano-Ni into the nano-Fe system. Cheng & Reinhard (2007) have studied the effect of zeolites on 2,2-dichloropropane (2,2-DCP), and they found that the adsorption of hydrophobic zeolite pores on 2,2-DCP obviously inhibited the dechlorination process of 2,2-DCP, and they considered that the inhibition was the result of lacking the solvation effects of water.

In this paper, although the removal rate of PCP in the mixed system was lower than that in the nano-Fe system and remained basically unchanged, the concentration of Cl⁻ significantly increased over time (Figure 4), suggesting that the dechlorination process occupied an important proportion in the nano-Fe/Ni mixed system, and the proportion of dechlorination increased with reaction time. A hypothesis can be proposed as follows: after the solution and metal powders mixed evenly, some PCP molecules and iron nanoparticles entered into the same pores of the Ni and then the nano-Fe started to dechlorinate the PCP in order or remove some chlorine atoms at the same time. The reaction between nano-Fe and PCP molecules was faster and the dechlorination process was more thorough in the same pores of the Ni than in the solution. However, the process needs microscopic analysis for further study.

**Intermediates analysis**

In order to further investigate the effect of Ni nanomaterials on the dechlorination process, the intermediates in the PCP degradation process were also analyzed. MS spectra showed that chlorophenols with different numbers of chlorine atoms existed in the PCP degradation process, among which the accumulation of dichlorophenols was the highest, followed by monochlorophenols. In the ZVI NP system and nano-Fe/Ni mixed system (taking Ni nanochains as an example) the solutions after reaction were analyzed with HPLC, and three kinds of monochlorophenols were detected (Figures 5 and 6). Phenol was also detected in the nano-Fe/Ni system. The concentration of several monochlorophenols in the mixed system was higher than that in the ZVI NP system. This indicated that the dechlorination process was dominant in the mixed system, which is consistent with the release of Cl⁻ mentioned above.

![Figure 4](https://iwaponline.com/ws/article-pdf/16/3/810/412503/ws016030810.pdf) | The effect of tubular porous Ni nanomaterials on Cl⁻ release.

![Figure 5](https://iwaponline.com/ws/article-pdf/16/3/810/412503/ws016030810.pdf) | The concentrations of several chlorophenols in the ZVI NP system.

![Figure 6](https://iwaponline.com/ws/article-pdf/16/3/810/412503/ws016030810.pdf) | The concentrations of several chlorophenols in the nano-Fe/Ni system.
The concentration fluctuation of these monochlorophenols in the ZVI NP system and nano-Fe/Ni system showed that these monochlorophenols were not the final products and would be degraded continually. However, in the nano-Fe/Ni system, the ‘wave peak’ of chlorophenol concentration was delayed, which resulted from the effect of Ni on the PCP degradation process. Although phenol showed a tendency of slow growth in the nano-Fe/Ni system, it was not the final product, which had been proved in our related study (Cheng et al. 2010). The concentration of three kinds of chlorophenols showed the pattern 2-CP > 4-CP > 3-CP in both systems, which indicated more accumulation of 2-CP in the systems.

Transformation of nanomaterials

The particles after the reaction were examined with XRD. As shown in Figure 7, Ni nanoparticles were still pure Ni after the reaction, which indicated that Ni performed as a catalyst, while Fe nanoparticles transformed into magnetite (Fe₃O₄) and/or maghemite (Fe₂O₃) in the Fe/Ni system. Magnetite and maghemite are isostructural, and were effectively indistinguishable by XRD data, so either oxide might have been present. In the ZVI NP system, lepidocrocite (γ-FeOOH) was also detected. The XRD results indicated that Fe nanoparticles were oxidized in the reaction and Fe (II) formation was an intermediate step in the transformation process. When Ni nanomaterials were present, no lepidocrocite was detected, which indicated that oxidation of Fe nanoparticles was less rigorous in the Fe/Ni system.

CONCLUSIONS

The apparent morphology of Ni affected the PCP removal rate in the nano-Fe/Ni system: the tubular porous Ni nanomaterials inhibited the removal of PCP, and those with net shape and nanochains expressed a certain promotion. The dechlorination of PCP was promoted by the Ni nanomaterials, among which the tubular porous Ni nanomaterials expressed the most promotion, then those with net shape and nanochains. The accumulation of some intermediates, such as 2-chlorophenol (2-CP), 3-CP and 4-CP showed the pattern 2-CP > 4-CP > 3-CP. When Ni nanomaterials were present, the accumulation of chlorophenol was increased and the ‘wave peak’ of chlorophenol concentration was delayed. It is concluded that the introduction of Ni nanomaterials would improve dechlorination of PCP, but the removal of PCP might be inhibited or improved as the morphology of the Ni is changed.

REFERENCES


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