Enhanced dechlorination of 2,4-dichlorophenol by recoverable Ni/Fe–Fe₃O₄ nanocomposites

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Ni/Fe-Fe₃O₄ nanocomposites were synthesized for dechlorination of 2,4-dichlorophenol (2,4-DCP). The effects of the Ni content in Ni/Fe-Fe₃O₄ nanocomposites, solution pH, and common dissolved ions on the dechlorination efficiency were investigated, in addition to the reusability of the nanocomposites. The results showed that increasing content of Ni in Ni/Fe-Fe₃O₄ nanocomposites, from 1 to 5 wt.%, greatly increased the dechlorination efficiency; the Ni/Fe-Fe₃O₄ nanocomposites had much higher dechlorination efficiency than bare Ni/Fe nanoparticles. Ni content of 5 wt.% and initial pH below 6.0 was found to be the optimal conditions for the catalytic dechlorination of 2,4-DCP. Both 2,4-DCP and the intermediate product 2-chlorophenol (2-CP) were completely removed, and the concentration of the final product phenol was close to the theoretical phenol production from complete dechlorination of 20 mg/L of 2,4-DCP, after 3 hr reaction at initial pH value of 6.0, 3 g/L Ni/Fe-Fe₃O₄, 5 wt.% Ni content in the composite, and temperature of 22°C. 2,4-DCP dechlorination was enhanced by Cl⁻ and inhibited by NO₃⁻ and SO₄²⁻. The nanocomposites were easily separated from the solution by an applied magnetic field. When the catalyst was reused, the removal efficiency of 2,4-DCP was almost 100% for the first seven uses, and gradually decreased to 75% in cycles 8-10. Therefore, the Ni/Fe-Fe₃O₄ nanocomposites can be considered as a potentially effective tool for remediation of pollution by 2,4-DCP.

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Introduction

Chlorinated organic compounds have been so widely used that they can be found in nearly all major environmental compartments. For example, chlorinated phenols (CPs) are widely used in the production of wood preservers, biocides and pesticides, or in the synthesis of other chemicals (Yang et al., 2013; Zhang et al., 2009). Due to their reactive nature, CPs are highly toxic, mutagenic and possibly carcinogenic. Furthermore, CPs are biorefractory and tend to accumulate in animal tissues. Once released into the environment, they tend to accumulate in the surroundings and thereby pose risks to the safety of ecosystems and human health over a long period of time (Xiao et al., 2008; Yang et al., 2013). Most of the CPs are listed as priority pollutants by the USEPA (Cheng et al., 2007; Ma et al., 2014). Reductive dechlorination is an effective method to detoxify these contaminants and has been widely investigated (Chen et al., 2008; Doong et al., 2003; Yan et al., 2010; Xu and Gao, 2007; Zhu et al., 2010). Zero-valent iron (ZVI) has been proven to be effective for reductive dechlorination of some chlorinated pollutants.
However, the reactivity of ZVI alone is limited and its dechlorination efficiency is low toward most chlorinated organic compounds (Wei et al., 2006; Zhang et al., 2009). In recent years, double-metal-catalyzed dechlorination materials have been developed, which greatly improve the dechlorination efficiency, and have been used to remediate water and soil contaminated by chlorinated pollutants, such as chlorinated hydrocarbons, chlorophenols, chlorobenzenes, polychlorinated biphenyls and other polychlorinated aromatics (Jovanovic et al., 2015; Liu et al., 2014; Wei et al., 2014; Yang et al., 2014). In these bimetallic materials, Fe, as a metal with low standard redox potential, is an electron donor and hydrogen donor to reduce the chlorinated organic compounds (Doeng et al., 2003; Zhu et al., 2010), while the second metal (Ni, Pd, Cu, or Ag) with high standard redox potential, promotes the reactivity via hydrogenation and accelerating corrosion (DeVor et al., 2008; Nie et al., 2013; Wei et al., 2006; Zhang et al., 2009; Zhu et al., 2010), acting as a catalyst and accelerator. Among these materials, Pd/Fe has attracted a great deal of attention thanks to the low cost of Fe and excellent hydrogenation activity of Pd (Wei et al., 2006; Yan et al., 2010), but the cost of Pd greatly restricts the wide application of Pd/Fe catalysts. Ni, which is much cheaper than Pd, has been widely used as an alternative catalyst to dechlorinate chlorinated organic compounds recently (Ko et al., 2007; Schrick et al., 2002; Zhang et al., 2007). To date, these developed nanoparticle materials are normally restricted to once-off use owing to their tiny sizes, which cause difficulty in separation and reuse. This leads to high dechlorination cost and environmental pollution when disposing of these materials (Strigul et al., 2009). Well-known for its biocompatibility and environmental pollution when dealing with these materials (Strigul et al., 2009). Nanoscale Fe3O4 particles were generated according to the following equations (Chang et al., 2011):

\[
\text{Fe}^3+ + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3
\]

\[
\text{Fe(OH)}_3 \rightarrow \text{FeO(OH)} + \text{H}_2\text{O}
\]

\[
\text{Fe}^2+ + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2
\]

\[
2\text{FeO(OH)} + \text{Fe(OH)}_2 \rightarrow \text{Fe}_2\text{O}_4 + 2\text{H}_2\text{O}
\]

After that, the fresh nFe3O4 was washed three times and mixed with a solution containing another 7.4676 g of FeSO4·7H2O, and then a stoichiometric amount of NaBH4 solution was further added dropwise under mechanically stirring to form nano zero-valent iron (nZVI)-nFe3O4 nanocomposites (Eq. (5)). Subsequently, NiCl2·6H2O aqueous solution was added to the wet nZVI-nFe3O4 with intensive stirring for 2–3 hr. Afterwards, Ni was deposited on the nZVI surface (Eq. (6)), giving contents of 1–8 wt.% Ni. Following this, excess SO42−, Cl−, and Na+ ions on the Ni/Fe3O4 nanocomposites were removed by washing with deoxygenated water six times. Then the nanocomposites were washed with acetone three times. Finally, Ni/Fe3O4 nanocomposites were dried under a flow of N2 gas and stored under N2 atmosphere. Following the literature (Xu et al., 2013a), the metal and oxide content were calculated as 0.32 g Fe3O4 and 1.5 g ZVI nanocomposites in this study.

\[
\text{nFe}_3\text{O}_4 - \text{Fe}^{2+} + 2\text{BH}_4^- + 6\text{H}_2\text{O} \rightarrow \text{nFe}_3\text{O}_4-\text{Fe}^0 + 2\text{B(OH)}_3^- + 7\text{H}_2
\]

\[
\text{Fe}^0 + \text{Ni}^{2+} \rightarrow \text{Fe}^{2+} + \text{Ni}^0
\]

### 1. Materials and methods

#### 1.1. Materials

Phenols (2,4-DCP, 2-CP, 4-CP, P) of analytical reagent grade and methanol of HPLC grade were purchased from the Aladdin Reagent Co. Ltd., China, and other reagents (FeSO4·7H2O, FeCl3·6H2O, NaBH4, NH4H2O, NaCl, FeSO4·7H2O) of analytical reagent grade were purchased from the Hong Sheng Technology Co. Ltd., China. Deionized water was deoxygenated by bubbling N2 gas for 1 hr.

#### 1.2. Preparation of Ni/Fe3O4 nanocomposites

The Ni/Fe3O4 nanocomposites’ preparation was conducted under nitrogen atmosphere following previous works (Xu et al., 2013a; Zhang et al., 2009). First, 0.7437 g of FeCl3·6H2O and 0.3825 g of FeSO4·7H2O were added with a molar ratio of 2:1 into a three-neck flask prefilled with 100 mL of deoxygenated water under N2 purging, and ultrasonically treated for 10 min to achieve an uniform dispersion of Fe3+ and Fe2+. Then a stoichiometric amount of NH3·H2O solution was slowly added to precipitate nanoscale Fe3O4. Nanoscale Fe3O4 particles were generated according to the following equations (Chang et al., 2011):

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\]

Batch tests for dechlorination of 2,4-DCP were carried out in 100 mL serum vials prefilled with 50 mL of 2,4-DCP solution (20 mg/L) and 0.15 g of nanocomposites. In the investigation of Ni loading (wt.%) on the dechlorination, Ni/Fe3O4 of 0 or 1, 5 and 8 wt.% Ni loading was added to 2,4-DCP solution at initial pH 7.0. In the investigation of initial pH effect on the dechlorination, 5 wt.% Ni/Fe3O4 was added to 2,4-DCP solution at initial pH ranging from 3.0 to 10.0. The vials were sealed and 5 wt.% Ni/Fe3O4 nanocomposites were synthesized (Xu et al., 2013a; Zhang et al., 2009).

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#### 1.3. Dechlorination experiments

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1.4. Analytical methods

A field emission scanning electron microscope (FESEM, S-4800, Hitachi, Tokyo, Japan) equipped with an energy dispersive X-ray spectroscopy (EDS) system was used to characterize the morphology and elemental mapping of the Ni/Fe-Fe₃O₄ nanocomposites. X-ray diffraction (XRD) analysis was performed using a Rigaku D/Max Ultima III high resolution X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu Kα irradiation. Phenols (2,4-DCP, 2-CP, 4-CP, P) were analyzed by Shimadzu HPLC 2010-AT (Zhang et al., 2009). Conditions were: Shimadzu ODS-SP Column, 150 mm × 4.6 mm, mobile phase MeOH/H₂O (60/40, V/V), flow rate 1.0 mL/min, detector UV at 280 nm, and sample size 5 μL. Ni²⁺ and total iron were analyzed by an atomic absorption spectrometer (Agilent 240AA Duo, USA).

2. Results and discussion

2.1. Improvement of 2,4-DCP dechlorination by Fe₃O₄

In order to understand the role Fe₃O₄ played in the dechlorination of 2,4-DCP, the removal efficiencies of 2,4-DCP by nZVI, nFe₃O₄, nFe₃O₄-Fe, Ni/Fe nanoparticles and Ni/Fe-Fe₃O₄ nanocomposites were compared, as shown in Fig. 1. The removal of 2,4-DCP in 1 hr by nZVI, nFe₃O₄ alone or by nFe₃O₄-Fe, was below 10%. The removal efficiency was increased to 77.7% when Ni/Fe was used and 91.5% when Ni/Fe-Fe₃O₄ was used (Fig. 1). Addition of Ni catalyst greatly increased the dechlorination rate, and addition of Fe₃O₄ further increased the dechlorination efficiency. The enhancement by nFe₃O₄ could be mainly attributed to the fact that nFe₃O₄ would restrain the formation of passivated layer on nZVI surface with magnetic force and act as a medium to promote the electron transfer between nZVI and 2,4-DCP (Xu et al., 2013a).

2.2. Influence of Ni loadings on the dechlorination efficiency

2,4-DCP is normally dechlorinated by three routes: (1) reduction to 2-CP and finally to phenol; (2) reduction to 4-CP and finally to phenol; and (3) direct reduction to phenol (Wei et al., 2006). In this study, 4-CP was undetectable at all times, suggesting that reaction route (2) might be nonexistent in this study. The above result was consistent with the study of Zhang et al. (2009), who reported that high concentrations of 2-CP were generated while almost no 4-CP was detectible during the dechlorination of 2,4-DCP with Ni/Fe nanoparticles.

It is considered that Fe⁰ can promote the hydrogenolysis reaction, through which the chlorine atom in chlorophenols can be replaced by a hydrogen atom. Ni is a well-known catalyst for hydrogenolysis (Xu et al., 2012b). Therefore, the Ni loading percentage on Ni/Fe-Fe₃O₄ nanocomposites may be one of the important influencing factors on the reductive dechlorination efficiency. The concentration-time curves of 2,4-DCP, phenol and 2-CP varied with the Ni loading, as presented in Fig. 2.

The concentration of 2,4-DCP decreased 9.5%, 23.6% and 81.6% within the first 15 min at Ni loading of 1, 5 and 8 wt.% respectively, while little 2-CP and phenol were detected. This result suggested that in the initial 15 min, 2,4-DCP was adsorbed onto the Ni/Fe-Fe₃O₄ nanocomposites, but dechlorinated little. Moreover, the higher the Ni loading, the larger the amount of 2,4-DCP was adsorbed. A similar result was reported by Wei et al. (2006), who mentioned that the higher the palladium loading, the larger the amount of 2,4-dichlorophenol adsorbed over nanoscale Pd/Fe. The increased adsorption ability of the catalyst with Pd or Ni loading might be attributed to the increased specific surface area. It has been reported that the specific surface area of Ni/Fe particles was increased with increasing Ni loading (Schrick et al., 2002; Zhu et al., 2011), and the adsorption capacity of nanoparticles was increased with increasing specific surface area (Xu et al., 2013b). It has been proven that the reductive dehalogenation reaction involving halogenated organic compounds and ZVI is a surface-mediated reaction, so that the larger the amount of halogenated organic compounds adsorbed in a given period, the higher the removal ratio of halogenated organic compounds achieved (Zhu et al., 2008).

The concentration of the intermediate product 2-chlorophenol sharply increased within the first 4.5, 1 and 1 hr respectively at Ni loadings of 1, 5 and 8 wt.% gradually decreased afterwards and was almost all removed after 21 hr (Fig. 2). At the same time, the phenol concentration sharply increased within the first 4.5 hr and then leveled off after 21 hr (Fig. 2). The final concentration of phenol was 11.50, 11.52 and 11.11 mg/L within 28 hr of reaction at Ni loading of 1, 5 and 8 wt.% (Fig. 2), close to the theoretical phenol production of 11.53 mg/L from complete dechlorination of 20 mg/L of 2,4-DCP.

The concentration of phenol was by far higher than that of 2-chlorophenol. The above results suggested that there was a considerable quantity of 2,4-DCP directly reduced to phenol. This phenomenon is in agreement with other reports (Wei et al., 2006; Xu et al., 2013b).

Only 9.5% of 2,4-DCP was removed by Fe-Fe₃O₄ nanoparticles in 28 hr (Fig. 2), during which neither 2-CP nor phenol was detectable (Fig. 2), suggesting that the decreased concentration of 2,4-DCP was only due to adsorption. This result further proved that nickel plays a principal role in accelerating the catalytic dechlorination reaction. As the Ni loading was increased from 1 to 5 wt.%, the catalytic dechlorination rate of 2,4-DCP and the formation rate of phenol significantly
increased (Fig. 2). The 2,4-DCP removal rate at 4.5 hr climbed from 55.4% to 95.4%, and the phenol production rate increased from 29.3% to 90.5% correspondingly. Further increase in the Ni loading from 5 to 8 wt.% only caused slight improvement in the catalytic dechlorination of 2,4-DCP. Although much more 2,4-DCP was adsorbed within the first 15 min for Ni loading of 8 wt.% than for 5 wt.% Ni loading, it showed a much lower phenol formation rate. This could be attributed to the accumulation of excessive hydrogen gas, which hinders the contact between the target organic pollutants and metal nanoparticles, and as a result decreases the available surface area for 2,4-DCP dechlorination. This phenomenon is consistent with the previously reported studies (Wang et al., 2008; Zhang et al., 2009). Therefore, in order to promote the cost-effective use of nickel and efficient 2,4-DCP dechlorination, Ni loading of 5 wt.% was employed in the following study.

Mass balance was studied by calculating all the aqueous phenols as equivalent amounts of 2,4-DCP (mg/L). Mass loss was approximately 10% in the test group of Fe–Fe₃O₄ within 28 hr reaction (Fig. 2), and this mass loss was considered to be the result of adsorption by the nanocomposites. Similarly, in the test group of Ni/Fe–Fe₃O₄, the 2,4-DCP equivalent masses in the aqueous phase were all lower than the initial concentration of 20 mg/L in the first 4.5 hr (Fig. 2), suggesting that a portion of phenols was adsorbed onto the nanocomposites (Xu et al., 2013a; Zhang et al., 2009). This was also evidenced by the fact that the 2,4-DCP concentration dropped rapidly in the first 15 min, while the concentration of phenol generated was much less than the maximum attainable amount, especially in the test group of 8% Ni/Fe–Fe₃O₄. After 21 hr reaction, the mass balances in the aqueous phase became close to 20 mg/L, indicating that the reductive dehalogenation reaction was the major reaction. 2,4-DCP was first adsorbed onto the Ni/Fe–Fe₃O₄ surface, and then was quickly reduced to 2-CP and phenol. A portion of the product phenols was adsorbed by the nanoparticles during the dechlorination process, but they could be easily desorbed from the surface of the nanocomposites (Yang et al., 2013). The deficit in the mass balance was lower than 4.0% after 28 hr reaction. The minor mass loss may be attributed to the loss of compounds via irreversible adsorption and/or the undetectable further hydrogenation of phenol.

2.3. Influence of initial pH on the dechlorination efficiency

pH is considered to be an important impact factor on the reductive dechlorination rate using ZVI (Zhou et al., 2010). The 1-hr 2,4-DCP removal efficiency by Ni/Fe–Fe₃O₄ nanocomposites
was respectively 95.9%, 91.3%, 67.2%, and 33.5% at initial pH of 3.0, 6.0, 7.0 and 10.0, as shown in Fig. 3. The intermediate products of 2-CP and phenol were also detected (Fig. 3). The dechlorination rate of 2,4-DCP was the highest at initial pH 3.0, slightly lower at pH of 6.0, and drastically declined at initial pH of 7.0 or above. Alkaline conditions were unfavorable because carbonate and hydroxide would precipitate on the Ni/Fe–Fe3O4 surface, and eventually significantly inhibited further iron decomposition and electron transfer (Fang and Al-Abed, 2008; Jovanovic et al., 2005).

Acidic conditions (such as pH of 3.0 and 6.0) were more favorable for 2,4-DCP dechlorination. Appropriate acidity enabled sites to be exposed to 2,4-DCP, which accelerated the nZVI corrosion and promoted 2,4-DCP dechlorination (Choi and Al-Abed, 2010; Liu and Lowry, 2006; Zhang et al., 2009). Moreover, Fe2+ could be released under acidic conditions and thereafter may enhance the nZVI reactivity (Huang and Zhang, 2004; Xu et al., 2012a). In acidic conditions (pH of 3.0 and 6.0), both 2,4-DCP and the intermediate product 2-chlorophenol were completely removed, and the final production of phenol approached the theoretical phenol production from complete dechlorination of 20 mg/L of 2,4-DCP after a 3 hr reaction. The solution with pH of 3.0 demonstrated more intensive corrosion of iron and Ni, with the concentration of total iron and Ni2+ after 3 hr reaction being 0.18 and 0.01 mg/L, respectively, both higher than the corresponding value of 0.089 and 0.005 mg/L in the solution of initial pH 6.0. The more quickly iron and nickel were corroded, the more easily the dechlorination activity of the nanocomposites was lost (Xu et al., 2012b). According to the discharge standard of pollutants for municipal wastewater treatment plants (GB 18918-2002) and the integrated wastewater discharge standard of China (GB 8978-1996), the emission limit concentration of nickel is 0.05 and 1.0 mg/L respectively. Therefore, although loss of Ni was observed during the reaction, the effluent could meet the national discharge standards under carefully controlled conditions.

The pH value increased to 7.9, 8.2, and 8.2 respectively at initial pH of 3.0, 6.0 and 7.0 after 3 hr reaction (Fig. 3). The increase of pH could be attributed to consumption of H+ or generation of OH− in iron corrosion reactions (Xu et al., 2012b). The pH value slightly decreased to 9.3 at initial pH of 10.0 after reaction for 3 hr. The decrease might be attributed to the fast consumption of OH− via the formation of iron hydroxide precipitate (Liu et al., 2006; Xu et al., 2012b). The pH tended to be stable after 3 hr, being 8.0, 8.3, 8.3, and 9.3 respectively after 21 hr reaction at initial pH of 3.0, 6.0, 7.0 and 10.0. It is well-known that iron hydroxide may deposit on material
surfaces and form passivating films, which could hinder the transport of the chlorinated molecules and decrease the reaction rate, or even completely stop the reaction (Xu et al., 2012b). At high solution pH, this passivating film is formed easily (Xu et al., 2012b).

Solution pH not only affects the dechlorination of 2,4-CP and the dissolution of Fe and Ni, but also influences the formation of iron hydroxide precipitate and passivation. So it is crucial to control solution pH within a reasonable range in order to balance the dechlorination, the lifetime of Ni/Fe-Fe3O4 nanoparticles, and passivation.

2.4. Influence of common anions on the dechlorination efficiency

Anions can influence the pollutant removal performance by nZVI (Choi and Al-Abed, 2010). Batch experiments were carried out in order to investigate the impact of some dissolved anions on 2,4-DCP dechlorination by Ni/Fe-Fe3O4 as shown in Fig. 4. All the anions were added in the form of sodium salts, since Na⁺ had much lower standard reduction (−2.71 V) than Fe²⁺ (−0.44 V), therefore Na⁺ would not influence the dechlorination of organic compounds with nZVI.

The 1.5 hr removal efficiency of 2,4-DCP was 81.3% in the negative control. The removal efficiency was increased to 83%, 91.5% and 99% in the groups dosed with Cl⁻ of 10, 20 and 30 mmol/L, slightly decreased to 78%, 76.5% and 75.5% in the groups dosed with SO₄²⁻ of 10, 20, 30 mmol/L, and significantly decreased to 59%, 53.5%, and 35% in the groups dosed with NO₃⁻ of 1, 3, 5 mmol/L, respectively. The 2,4-DCP dechlorination was enhanced by Cl⁻, which tended to accelerate the iron corrosion by diffusing aggressively into passivating oxides and forming strong complexes with iron centers (Kim et al., 2013a). Also, in this study the peak of Ni⁰ was not observed, which indicated that Ni and Fe formed an amorphous alloy. A gelatinous layer was observed on the surface of the nanocomposites before use are spherical particles of 10–100 nm in diameter, which aggregate to form dendrites (Fig. 8b). The above change in the morphology might be attributed to the deposition of iron hydroxide and carbonate on the material surface, which could hinder the transport of the chlorinated molecules and thereby decrease the dechlorination efficiency (Tian et al., 2009).

Fig. 7a shows the XRD patterns of Ni/Fe-Fe3O4 nanocomposites. The particle size distribution of Ni/Fe-Fe3O4 determined by laser reflectometry ranged from 955.4 to 3091 nm, as shown in Fig. 8c. The size was much larger than that in the FESEM.

2.5. Recovery and reuse of the Ni/Fe-Fe₃O₄ nanocomposites

The Ni/Fe nanoparticles could not be efficiently separated from water in a magnetic field, while those nanoparticles combined with nFe₃O₄ were efficiently separated from water after 20 sec (Fig. 5a). In addition, Fe₂O₃, NiFe₂O₄, and NiFe nanoparticles could not be separated from water after 20 sec without a magnetic field (Fig. 5b). That is to say, the efficient separation of Ni/Fe-Fe₃O₄ in a magnetic field was due to the effect of magnetic force, not the effect of gravity or something else.

Ten consecutive cycles of 2,4-DCP dechlorination tests were carried out in order to confirm the stability of the recovered Ni/Fe-Fe₃O₄ nanocomposites. Each cycle consisted of a dechlorination experiment with 20 mg/L of 2,4-DCP for 24 hr. As shown in Fig. 6, the removal efficiency of 2,4-DCP was almost 100% over the first seven cycles and then gradually decreased to 86.5%, 78.7%, and 74.5% in cycle 8–10, respectively. Even after being reused for ten cycles, 74.5% of 2,4-DCP could still be removed.

2.6. Characterization of the Ni/Fe-Fe₃O₄ nanocomposites

Fig. 4 – Influence of common anions on 2,4-DCP removal by 3 g/L of Ni/Fe-Fe₃O₄ after 1.5 hr (initial pH = 6.0, 20 mg/L of 2,4-DCP, 5 wt.% of nickel loading). 2,4-DCP: 2,4-dichlorophenol.
image. This is because the nanocomposite tends to aggregate in the solution, especially at high concentrations. A similar study was reported by Xu et al. (2013a). The specific surface area calculated by the Brunauer–Emmett-Teller (BET) equation was 35.1, 26.5 and 13.8 m$^2$/g for the nFe$_3$O$_4$, 5 wt.% Ni/Fe and 5 wt.% Ni/Fe–Fe$_3$O$_4$ nanocomposites, respectively. The decrease of specific surface area from 26.5 to 13.8 m$^2$/g after the introduction of nFe$_3$O$_4$ was due to overlap between nZVI and nFe$_3$O$_4$ (Xu et al., 2013b).

2.7. Mechanism of 2,4-DCP dechlorination by Ni/Fe–Fe$_3$O$_4$

Based on the above results, the dechlorination mechanism of 2,4-DCP by Ni/Fe–Fe$_3$O$_4$ nanocomposites could be deduced as follows:

$$\text{Fe}^0 + R-\text{Cl} \rightarrow \text{Fe}^0 - R-\text{Cl}$$ (8)

$$\text{Fe}^0 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \text{(in acidic solution)}$$ (9)

$$\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}^+ + 2\text{OH}^- \text{(in neutral/alkaline solution)}$$ (10)

$$\text{H}_2 \xrightarrow{\text{Ni}} 2\text{H}^+$$ (11)

$$\text{H}^+ + e^- \xrightarrow{\text{Ni}} \text{H}_2$$ (12)

$$\text{Fe}^0 - R-\text{Cl} + \text{H}^+ + e^- \xrightarrow{\text{Fe}_3\text{O}_4} \text{Fe}^2+ - R-\text{H} + \text{Cl}^- \text{ or Fe}^0 + R-\text{H} + \text{Cl}^-$$ (13)

The iron was corroded and produced H$_2$ as the actual reductant for dechlorinating 2,4-DCP. Iron corrosion was greatly promoted and the activated hydrogen atom (H$^*$) was generated around the Ni catalyst (Xu et al., 2012b). Moreover, nFe$_3$O$_4$, with low electrical resistance ($10^{-3}$ $\Omega$·cm), acted as a medium to accelerate the electron transfer between nZVI and chlorophenol (Ryu et al., 2011; Schlicker et al., 2000). The iron oxide deactivation layer on the nZVI surface would be restrained due to the magnetic force between deactivated iron oxides and preexisting nFe$_3$O$_4$ (Xu et al., 2013a); and in this study, the pathway for 2,4-DCP dechlorination by Ni/Fe–Fe$_3$O$_4$ could be deduced as follows: 2,4-DCP was first adsorbed onto

2,4-DCP: 2,4-dichlorophenol.
the surface of Ni/Fe–Fe₃O₄ nanocomposites, then quickly reduced to 2-CP, and finally to phenol, or 2,4-DCP was directly dechlorinated to phenol.

3. Conclusions

Ni/Fe–Fe₃O₄ nanocomposites were effective in dechlorination of 2,4-DCP. Catalysis by Ni significantly increased the dechlorination rate, and nFe₃O₄ further enhanced the effectiveness of the Ni/Fe bimetallic nanoparticles. The nanoparticles were efficiently separated in a magnetic field, and the recovered nanoparticles were able to be reused more than ten times. The Ni bulk loading was optimized at 5 wt.%, and an initial pH below 6.0 was considered beneficial for the catalytic dechlorination. 2,4-DCP was mostly directly reduced to phenol, and a minor amount was reduced to 2-CP before finally being reduced to phenol. Both 2,4-DCP and the intermediate product 2-chlorophenol were completely removed by 3 g/L of Ni/Fe–Fe₃O₄ nanocomposites (5 wt.% of Ni loading) after 3 hr of reaction at an initial pH of 6.0, and the final product phenol approached the theoretical phenol production from complete dechlorination of 20 mg/L of 2,4-DCP. The 2,4-DCP dechlorination could be enhanced by Cl⁻, while it was inhibited by NO₃⁻ and sulfate.

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Fig. 7 – (a) XRD pattern of Ni/Fe–Fe₃O₄ nanocomposites (5 wt.% of nickel loading) and (b) EDS spectra of Ni/Fe–Fe₃O₄ nanocomposites (5 wt.% of nickel loading). XRD: X-ray diffraction; EDS: energy dispersive X-ray spectroscopy.

Fig. 8 – FESEM images of Ni/Fe–Fe₃O₄ nanocomposites before (a) and after (b) dechlorination, (c) particle size distribution of Ni/Fe–Fe₃O₄ (Ni/Fe–Fe₃O₄ with 5 wt.% of Ni loading). FESEM: field emission scanning electron microscope.


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