Effect of pH on DDT degradation in aqueous solution using bimetallic Ni/Fe nanoparticles

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ABSTRACT

In this study, bimetallic Ni/Fe nanoparticles were prepared and the ability of this material to degrade DDT in aqueous solution was investigated at room temperature. Besides comparing the degradation rates of DDT using monometallic zero-valent iron and bimetallic Ni/Fe, batch investigations with bimetallic Ni/Fe nanoparticles were conducted to explore the influence of pH value on the degradation rate of DDT in aqueous solution. Results indicate that weakly acidic ($4 \leq \text{pH} < 7$) or alkaline reaction ($7 < \text{pH} \leq 10$) conditions afford faster degradation rates, whereas higher or lower pH inhibits the DDT degradation. In addition, the DDT degradation exhibits an interesting pathway and mechanism at higher pH value ($\text{pH} > 10$) in reaction solution. In strong alkaline solution, the DDT degradation becomes slow but is not quenched. The electron transfer for DDT degradation is enhanced by creating numerous galvanic cells under the Ni catalysis, and promotes the dehydrochlorination reaction. The hydrodechlorination reaction in alkaline condition is also unbroken. This phenomenon is quite different from those reported in other studies previously.

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1. Introduction

DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane) has been used extensively since the 1940s as a pesticide for agricultural purpose and public health to check malaria and other mosquito borne diseases (yellow fever, encephalitis). But its persistence, bioaccumulation, toxicity and long-range atmospheric transport bring many risks to human health and environment. Although it has been regulated under the Stockholm Convention [1], and banned by many countries in the 1970s, DDT and its metabolites are still found at numerous sites in the world [2–4].

Over the past two decades, a number of methods for the DDT degradation have been developed, including biological treatments [5], photochemical reactions [6] and metal-catalyzed reactions [7]. In recent years, a promising technology is the use of zero-valent metals, such as Fe and Zn. This technology has many advantages in the treatment of water and soil DDT contaminates, including free of environmental pollution and high efficiency by direct injection of zero-valent metal nanoparticles into contaminant source zones. However, the use of zero-valent metals to reduce chlorinated organics has some drawbacks. For example, even if nanoscale zero-valent iron particles are used, the metal mass normalized observed rate constant for dechlorination of chlorinated organics is still very low

[8]. More important is that a hydroxide or oxide layer forms on the metal particle surface during the reaction, significantly decreases the effective use of the metal particles. Further efforts to improve the performance of the zero-valent metal technology were the use of bimetallic nanoparticles such as Pd/Fe, Pd/Mg. The introduction of catalytic metal Pd could increase surface area, enhance the formation of atomic hydrogen or hydride on the surface and inhibit the corrosion products from accumulating on the surface reactive sites of zero-valent metal [9]. However, high expense of Pd noble metal limits its wide application for pollutant treatment.

There are number of studies demonstrating successful dechlorination of chlorinated compounds like trichloroethylene (TCE) [8], pentachlorophenol (PCP) [10] and carbon tetrachloride (CCl_4) [11] by Ni/Fe nanoparticles. The proposed mechanism is that the catalytic nickel enhances the formation of atomic hydrogen or hydride on the surface and alters the electronic properties of the iron. Then C–Cl bond of adsorbed chlorinated compound onto the surface of the Ni/Fe nanoparticles is broken, and the chlorine atom is replaced by hydrogen [8,12]. The reaction process can be represented as follows:

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The above equations indicate that pH value is a crucial parameter that affects the degradation rate of chlorinated compounds. At higher pH, less atomic hydrogen or hydride on the catalyst surface attacks chlorinated molecules to replace the chlorine atom and to form dechlorinated molecule and chlorine ion. Meanwhile, the ferrous and hydroxyl ions form ferrous hydroxide and precipitate. The surface passivating layer of the ferrous hydroxide and precipitate could hinder the transport of the chlorinated molecules and block the reactive sites on Ni/Fe and hence depress the overall reaction rate [13].

Chen's study verified the kinetic model for the dechlorination reaction by using bimetallic Ni/Fe is a pseudo first-order treatment of the parent compound [13]:

$$-\frac{dC}{dt} = k_{SA}\alpha_S\rho_m C \quad (5)$$

where C represents the concentration of chlorinated compound, k_{SA} is the specific reaction rate constant ($L/h\ m^2$), α_S is the specific surface area of Ni/Fe (m^2/g), and ρ_m is the mass concentration of Ni/Fe (g/L). Variations in the k_{SA} value were attributed to impurities within the metal matrix, which can affect the distribution of active sites [12]. The value of k_{SA} reported by Schrick et al. for TCE dechlorination using Ni/Fe nanoparticles (1:3.4 Ni/Fe ratio) is $9.8 \times 10^{-2} L/h\ m^2$, which is much higher compared to $2.0 \times 10^{-3} L/h\ m^2$ for nanoiron [8]. Tee et al. [14] found that a maximum rate of dechlorination is achieved with a Ni content of 25 wt%, similar to the Ni/Fe ratio designed by Schrick et al. [8] to obtain the faster TCE dechlorination rate. The decrease in reaction rates as the Ni content increase beyond this level is attributed to high levels of Ni with respect to Fe at the particle edges, which hinder the ability of Fe to transfer electrons to the reaction sites.

The objective of this work is to study the degradation of DDT using bimetallic Ni/Fe nanoparticles, which has not been reported to our knowledge. 1:3.5 was chosen for Ni/Fe ratio. The effect of pH on the degradation of DDT using Ni/Fe nanoparticles is investigated. Furthermore, the mechanism of DDT degradation is also proposed.

2. Experimental

2.1. Materials

p,p'-DDT was purchased from Aldrich. Calibration standards of DDTs, including p,p'-DDE, p,p'-DDD and p,p'-DDT that obtained from AccuStandard, Inc., were prepared by dissolving the mix in n-hexane, then stored in polytetrafluoroethylene-lined screw cap vials at 4 °C. n-Hexane (HPLC) was offered by J&K Chemical Ltd. The other chemicals used: ferrous sulfate ($FeSO_4 \cdot 7H_2O$, Beijing Chemical Reagent Factory, China), nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, Beijing Shuanghuan Chemical Reagent Factory, China), potassium borohydride (KBH_4 , Tianjin Jinke Fine Chemical Research Institute, China). Sodium sulfate (Na_2SO_4 , Beijing Chemical Reagent Factory, China) was oven-dried at 150 °C for 2 h to act as a desiccant. All solutions were prepared in ultrapure water ($R = 18\ m\Omega$).

2.2. Synthesis of Ni/Fe nanoparticles

Ni/Fe nanoparticles were synthesized by modifying the method described by Schrick et al. [8]. 0.03 g $FeSO_4 \cdot 7H_2O$ and 0.009 g $Ni(NO_3)_2 \cdot 6H_2O$ (Ni/Fe molar ratio is 1:3.5) were dissolved in 75 mL of ultrapure water with shaking by hands. Then the salts were reduced to black particles by adding dropwise a certain amount of KBH_4 solution ($BH_4^-/M^{2+} = 3$, M represents as Fe or Ni). The KBH_4 amount was excessive to ensure all of salts reduced. The zero-valent iron nanoparticles were synthesized by the same method.

No special precautions were taken to eliminate oxygen from the reaction vessel. After shaking for 20 min, the mixture was centrifuged, washed with ultrapure water for several times, and rinsed by ethanol. At last, the particles were collected and stored in ethanol for subsequent experiments.

2.3. Characterization of Ni/Fe nanoparticles

Transmission Electron Microscope (TEM) images were obtained using a Hitachi H-7500 microscope. A typical TEM sample was prepared by depositing several droplets of the nanoparticles/ethanol mixture onto a carbon-coated Cu-grid.

2.4. DDT degradation studies

DDT stock solution (100 $\mu g/mL$) was prepared in analytical-grade acetone, and diluted with a water–acetone solution, which had been deoxygenated by purging N_2 for 1 h. The final water–acetone ratio was adjusted to 9:1 (v/v) using water or acetone, referential to Gautam's study [15]. 150 mL of DDT solution with desired concentration was then added into a 150-mL glass reactor. Reaction was initiated by the addition of zero-valent metals (0.05 mg/mL). All experiments were conducted in nitrogen atmosphere, with constant stirring.

At predetermined time intervals, 10 mL suspension was sacrificed and extracted with 4 mL n-hexane to recover DDT. After passing through a glass column containing about 1 g anhydrous sodium sulfate (Na_2SO_4) and diluted for four times, about 1 mL aliquots from the diluted hexane extracts were removed in 2 mL glass vials. The vials were immediately sealed with Teflon-lined septa caps and later analyzed for DDT and its degradation products using GC–MS.

To investigate pH effect, the degradation experiments were carried out at an initial pH ranging from 2 to 12 adjusted with NaOH or HCl.

2.5. GC–MS analysis

GC–MS analysis was conducted on an Agilent 6890 gas chromatograph equipped with an Agilent 5973 mass selective detector. An HP-5 capillary column (0.25 μm , 0.25 mm $\times$ 30 m) was used. Ultrahigh purity helium (flow rate of 1.0 mL/min) was used as the carrier gas. The injection volume was 1 μL . The column temperature was ramped as follows: initial temperature of 70 °C was kept for 2 min following the injection, increased by 20 °C/min to 200 °C and by 10 °C/min to 280 °C, and maintained at the final temperature for 1.5 min. The net run time for the analysis was 18 min. The identification and quantification of DDT and its metabolites were done using selective ion monitoring.

3. Results and discussion

3.1. Characterization of materials

Fig. 1 shows TEM of the monometallic zero-valent iron and bimetallic Ni/Fe nanoparticles. The synthesized particles are both approximately spherical, and form chains of beads, especially for monometallic zero-valent iron. This type of aggregation is attributed to magnetic interaction between the primary metal particles [16]. The Ni/Fe particles are in the range of 80–140 nm in diameter, smaller than the particles of zero-valent iron (145–230 nm). We propose that the addition of Ni could limit the nanocrystalline growth of Fe and decrease the particle size of Ni/Fe.

Fig. 1. TEM of Fe (left) and Ni/Fe (right) nanoparticles.

3.2. Effect of materials on DDT degradation

Although the excellent degradation rates of DDT using zero-valent iron nanoparticles were reported before [17,18], the rate of DDT degradation using bimetallic Ni/Fe nanoparticles is evidently faster than that using zero-valent iron (Fig. 2), indicating that the presence of Ni promotes the degradation reaction of DDT as the action on other chlorinated compounds such as TCE and PCP. Fig. 2 shows that almost 90% of DDT degrades within 4 h.

3.3. Effect of initial pH on DDT degradation

The concentration profiles for DDT degradation using Ni/Fe nanoparticles at different pH values are shown in Fig. 3. Over 85% degradation of DDT can be obtained in 8 h, except the experiment at elevated pH 12.

To describe the initial kinetics of DDT degradation, the first-order rate constants (k_{obs}) derived from Eq. (5) is used (Table 1):

$$\rho_a = \alpha_s \rho_m \quad (6)$$

$$k_{\text{obs}} = k_{\text{SA}} \rho_a \quad (7)$$

$$-\frac{dC}{dt} = k_{\text{obs}} C_0 \quad (8)$$

or

$$k_{\text{obs}} t = \ln \left(\frac{C_0}{C} \right) \quad (9)$$

Fig. 2. Degradation of DDT in aqueous solution using Fe only and bimetallic Ni/Fe nanoparticles ($C_0 = 1.09 \mu\text{g/mL}$, Fe or Ni/Fe: 0.05 mg/mL , pH 7).

Fig. 3. Effect of pH value on the degradation of DDT in aqueous solution using Ni/Fe nanoparticles ($C_0 = 1.09 \mu\text{g/mL}$, Ni/Fe: 0.05 mg/mL).

Where ρ_a is the surface area concentration of Ni/Fe (m^2/L), and C_0 is the initial concentration of DDT.

$k_{\text{obs}}(2)$ and $k_{\text{obs}}(4)$ are used to represent the first-order rate constants within 2 h and 4 h, respectively. Fig. 3 and Table 1 show that at initial pH values below 7, the k_{obs} value decreases with pH at the reaction time of either 2 h or 4 h. The slow degradation rate is attributed to the fast disappearance of zero-valent iron due to iron corrosion. With extending the reaction time from 2 h to 4 h, the k_{obs} at pH 10 becomes higher than at pH 4. It is known that the ferrous and hydroxyl ions generally form ferrous hydroxide and precipitate at higher pH. The precipitation of ferrous hydroxide on the surface of zero-valent iron could hinder the transport of the chlorinated molecules and decrease the reaction rate [13]. However, in our experiment, faster degradation rate of DDT at pH 10 than at pH 4 is obtained at reaction time of 4 h. The reason for this could be the increase of dehydrochlorination reaction rate at higher pH value ($\text{pH} \geq 10$, as shown in Fig. 4).

Fig. 4 shows the degradation of DDT and its metabolites as a function of time at different pH values. The presence of the metabolites

Table 1

Apparent rate constant, k_{obs} for DDT degradation using Ni/Fe at different initial pH value.

k_{obs}	pH				
	2	4	7	10	12
$k_{\text{obs}}(2) (\text{h}^{-1})$	0.8938	0.9697	0.4739	0.8819	0.1088
$k_{\text{obs}}(4) (\text{h}^{-1})$	0.535	0.6073	0.5183	0.6517	0.1971

Fig. 4. Degradation of DDT and its metabolites in aqueous solution using Ni/Fe nanoparticles (0.05 mg/mL) at different pH values: (a) pH 2; (b) pH 4; (c) pH 7; (d) pH 10; (e) pH 12.

DDD and DDE at the reaction time of 0 h is because of the impurity of DDT stock material. The results indicate that the main metabolite of DDT using Ni/Fe nanoparticles is DDD. But the dehydrochlorination reaction rate after 2 h at higher pH (pH 12) increases, which is unexpected. The proposed reason and main reaction mechanism will be discussed in the following section.

The trends of DDT and its metabolites with the proceeding of the reaction shown in Fig. 4 also indicates that the DDD concentration is maximized at reaction time between 1 h and 4 h, and then slowly decreases during the later reaction stages. At initial pH value ranging from 4 to 10, DDD concentration maximizes at the reaction time of 2 h, and 4 h at pH 12. This suggests that too high pH seems to

be detrimental for the DDD degradation, but not quench the degradation, as in the case of the DDT degradation. It might be deduced that the degradation mechanism of DDD at different pH values is similar with that of DDT. The shortest time when DDD reaches the maximum amount is 1 h at pH 2, but the increased extent of DDD concentration is the minimum, indicating the slow degradation of DDT to DDD.

3.4. Degradation mechanism of trichloromethyl group of DDT

As we know, DDT can be transformed into DDD and DDE by hydrodechlorination and dehydrochlorination pathways, respec-

Fig. 5. Tentative degradation mechanism of trichloromethyl group of DDT.

tively. Laboratory researches showed that the hydrodechlorination pathway happens under neutral or acidic condition using zero-valent metals and bimetallic systems, higher pH could quench the hydrodechlorination reaction of DDT [15,17]. Sayles et al. [17] reported that no transformations of DDT were observed in reactors with addition of 25 mM NaOH and zero-valent iron. It is known that the dehydrochlorination reaction is almost impossible in alkaline aqueous solution without alcohols or heating [19,20]. However, in our work, the dehydrochlorination reaction apparently occurred at higher pH values, we estimate this could be due to the promoting function of Ni.

The proposed degradation mechanism is shown in Fig. 5. In alkaline condition, the ferrous hydroxide forms and deposits on the surface of zero-valent iron, and numerous analogously galvanic cells can be created between ferrous hydroxide and zero-valent iron under the catalysis of Ni [21]. This may enhance the electron transfer from zero-valent iron to DDT. In the dehydrochlorination pathway, after abstracting single electron, a chloride anion and an alkyl radical DDT are obtained since the reductive cleavage of aliphatic halides does not afford anion radicals as discrete intermediates [22]. Subsequently, the alkyl radical DDT loses the hydrogen

at the benzylic position to form DDE. Meanwhile, a hydrogen chloride produces and is scavenged by NaOH to form NaCl, which also promotes the dehydrochlorination rate. In the hydrodechlorination pathway, similarly to the process in acidic solution, H_2O abstracts electrons and is reduced to adsorbed hydrogen on the catalytic Ni surface. DDT is adsorbed onto the surface of the Ni/Fe nanoparticles where the C–Cl bond is broken, and the chlorine atom is replaced by hydrogen. It can be seen that the significant difference is that the electrons come from galvanic cells between ferrous hydroxide and iron in alkaline condition, whereas the electrons in acidic and neutral solution are obtained by iron corrosion.

4. Conclusions

Bimetallic Ni/Fe nanoparticles were synthesized and used in the DDT degradation studies. The DDT degradation rate using bimetallic Ni/Fe nanoparticles is evidently faster than that using monometallic zero-valent iron, over 90% of DDT is transformed within 4 h in neutral condition. First-order rate constants (k_{obs}) based on the pseudo first-order reaction model is determined to explore the effects of pH value on the degradation rate in bimetallic Ni/Fe system. The results

show that the degradation rate is highly pH dependent. Because the disappearance of zero-valent iron by iron corrosion could be accelerated in acidic condition and the ferrous hydroxide and precipitate are produced at higher pH, weaker acid ($4 \leq \text{pH} < 7$) and alkaline ($7 < \text{pH} \leq 10$) reaction conditions are more favorable to fast degradation of DDT in aqueous solution. In addition, the pH value also influences the degradation mechanism. Higher pH does not quench the DDT degradation, but promotes the dehydrochlorination reaction, which is mainly due to the formation of galvanic cells under the catalysis of Ni to enhance the electron transfer. The hydrodechlorination reaction in alkaline condition is also unbroken with the electrons transfer of galvanic cells between ferrous hydroxide and iron.

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