Kinetics of 2,4-dichlorophenol dechlorination by Pd-Fe bimetallic nanoparticles in the presence of humic acid[*]

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Abstract: The remediation of groundwater which contains chlorinated organic compounds (COCs) by nanoscale bimetallic catalysts has received increasing interest in recent years. This report presents the dechlorination of 2,4-dichlorophenol (2,4-DCP) by Pd-Fe bimetallic nanoparticles in the presence of humic acid (HA) to investigate the feasibility of using Pd-Fe for the in situ remediation of contaminated groundwater. Our experimental results indicated that HA had an adverse effect on the dechlorination of 2,4-DCP by Pd-Fe nanoparticles. The rate constant k values of 2,4-DCP dechlorination were 0.017, 0.013, 0.009, 0.006 and 0.004 min^{-1} for HA concentrations of 0, 5, 10, 15 and 20 mg/L, respectively. The relationship between HA dosage and k values can be described as a linear model.

INTRODUCTION

Chlorinated organic compounds (COCs) have been so widely used that they can be found in nearly all major environments (Xu *et al*., 2005a; 2005b), such as in various waste oils and other organic liquids. Due to their reactive nature, they are highly toxic, mutagenic and possibly carcinogenic. Furthermore, they are biorefractory and tend to accumulate in animal tissues. Once released into the environment, they will accumulate in the surrounding areas and pose a great health threat to humans and ecosystems over a long period of time (Zhu *et al*., 2006; Oliver and Nicol, 1982; Schwarzenbach *et al*., 1979). This prompts an urgent need for effective means of dechlorination in order to reduce or eliminate chloroaromatics from both concentrated industrial effluents and diluted polluted groundwater.

Recently, chemical reduction of hazardous compounds such as COCs using zero-valent iron (Fe^0) has been intensively studied for either in situ or aboveground treatment of contaminated water. Some of the studies on metal iron technology showed that the use of zero-valent single metal to reduce chlorinated organics has very low observed rate constant k_{obs} for the dechlorination of trichloroethylene (TCE), which was in the order of 10^{-2} L/(g·h) (Schrick *et al*., 2002). Further attempts have been made to increase the dechlorination rate of COCs using hydrogen gas and noble bimetallic agents such as Ni/Fe, Pd/Fe and Cu/Fe (He and Zhao, 2005). Cheng and Wu (2001) reported that physical additions of Pd^0, Cu^0 or Ni^0 micro-sized powder could re-activate Fe^0 particles that have lost their surface activity. It is well known that the reduction of chlorinated organics by bimetallic particles occurs via hydrodechlorination, instead of inter-metalic electron transfer, in which Fe acts as the reducing agent whereas Ni, Pd, or Cu acts as a catalyst. The latter are considered as good hydrogenation catalysts and have a strong ability to disso-

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ciate H_2 (Cheng and Wu, 2001; Coq and Figueras, 2001; Schrick *et al*., 2002). The presence of a second metal not only increases the reactivity and reduces the accumulation of toxic byproducts, but also inhibits particle oxidation in air (Wu and Stephen, 2006; Zhang *et al*., 1998; Lien and Zhang, 2001).

Although both the microscale and the nanoscale bimetallic systems are quite effective in the dechlorination of contaminants, the reactivity of the zero-valent metals is highly controlled by the surface characteristics of metals and groundwater chemistry. In subsurface environments, natural humic matters are abundant and play important roles in both electron transfer and adsorption processes. The inhibition of the dechlorination of chlorinated hydrocarbons by zero-valent metals in the presence of natural humic matter was reported previously (Johnson *et al*., 1998; Tratnyek *et al*., 2001). They depicted that any non-reactive adsorbates that out-compete the contaminants for reactive surface sites would result in a decrease in the degradation rate. However, humic acid (HA) also can act as an electron mediator to enhance the reduction efficiency of chlorinated aliphatic compounds in aqueous solutions containing bulk reductants (Curtis and Reinhard, 1994). So far, it is not clear that whether HA enhances or inhibits the electron transfer process from bimetallic systems such as Pd-Fe to the target compounds during in situ treatment processes. Therefore, prior to its application to in situ remediation treatment, a good understanding of what role HA plays in the dechlorination of chlorinated hydrocarbons is vital.

In this study, we concentrate on the investigation of HA's role in the dechlorination of 2,4-dichlorophenol (2,4-DCP) by nanoscale Pd-Fe particles in the initial pH value, and its effect on the kinetics of the dechlorination of 2,4-DCP.

MATERIALS AND METHODS

Chemicals

Most of the chemicals, such as potassium hexachloropalladate (K_2PdCl_6, 99% (w/w), Aldrich, USA), iron sulfate hexahydrated (AR), 2,4-DCP, *o*-chlorophenol (*o*-CP), *p*-chlorophenol (*p*-CP), phenol (P) and other reagents were used as received without further purification. HA was obtained from Sigma-Aldrich (ash ~20%, Switzerland). The HA stock solution (500 mg/L) was prepared by dissolving 0.25 g of HA in 2 ml of a 0.1 mol/L NaOH aqueous solution, followed by sonication and dilution with deionized water to 500 ml, and its final pH was adjusted to 7. The product was then filtered through a 0.45 μm pore diameter Millipore membrane. Solutions were stored at 4 °C before use. 2,4-DCP was dissolved in deionized water and stored at 4 °C. Fe^0 and Pd-Fe nanoparticles were synthesized immediately before use.

Synthesis procedure

Pd-Fe bimetallic nanoparticles were produced by adding 0.54 mol/L $NaBH_4$ aqueous solution dropwise to a 1-L three-necked flask containing equal volume of 0.27 mol/L $FeSO_4 \cdot 6H_2O$ aqueous solution with mechanical stirring at 30 °C for 10 min. First of all, the ferrous iron was reduced to zero-valent iron according to the following reaction:

$$Fe(H_2O)_6^{2+} + 2BH_4^- \rightarrow Fe^0 + 2B(OH)_3 + 7H_2. \quad (1)$$
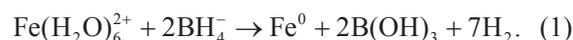
The Fe^0 nanoparticles were then rinsed 3 times with 400 ml deoxygenated deionized water under nitrogen atmosphere. Subsequently, the Pd-Fe bimetallic nanoparticles were synthesized by reacting the wet iron particles with desired amount of potassium hexachloropalladate aqueous solution under stirring and nitrogen atmosphere according to the following equation:

$$PdCl_6^{2-} + 2Fe^0 \rightarrow 2Fe^{2+} + Pd^0 + 6Cl^-. \quad (2)$$
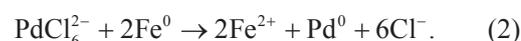
The bimetallic nanoparticles were then rinsed 3 times with 400 ml deoxygenated deionized water under nitrogen atmosphere to remove chloride ions.

Batch experimental procedures

The batch experiments for 2,4-DCP dechlorination were performed in the same three-necked flask into which Pd-Fe nanoparticles were added. Desired volume of HA, 2,4-DCP stock solution and a certain amount of deoxygenated deionized water were added into the flask containing freshly prepared Pd-Fe nanoparticles. The reaction solution was stirred under nitrogen flow. Aliquots of samples were periodically

collected with glass syringes and the reaction was stopped by passing each aliquot through 0.22 µm membrane filters.

Methods of analyses

Fresh metal nanoparticles (Pd bulk loading of 0.15 wt%) were visualized under a JEOL JEM 200CX transmission electron microscope (TEM) at 180 kV for morphological measurement. Prior to TEM analysis, the particles were dispersed by an ultra-sonicator.

Specific surface area of the Pd-Fe bimetallic particles was measured using nitrogen adsorption method with ST-03 surface analyzer. Prior to measurement, the metal particles were dried in vacuum at 25 °C for 24 h and then dried at 260 °C for 4 h under a flow of hydrogen.

Organic compounds such as 2,4-DCP, p-CP, o-CP and phenol were measured by SHIMADZU High Performance Liquid Chromatography. Agilent TC-C18 Column, 150 L×4.6. Mobile phase: MeOH/H_2O (60/40, v/v); flow rate: 1.0 ml/min; detector: UV at 280 nm; sample size: 20 µl.

RESULTS AND DISCUSSION

Inhibition by humic acid (HA)

The chemical compositions of the catalytic dechlorination of 2,4-DCP over Pd-Fe bimetallic nanoparticles with and without 20 mg/L HA are shown in Fig.1. 2,4-DCP was first adsorbed by the nanoparticles then reduced to o-CP or p-CP, and later converted to phenol, the sole final organic product of the dechlorination. No other chlorinated intermediates or final organic products were detected.

The concentration of 2,4-DCP decreased quickly and its removal percentage reached 50.0% in 30 min, 98.1% in 180 min, and 99.6% in 300 min for Pd-Fe nanoparticles in the absence of HA. In contrast, only about 14.0%, 52.4% and 69.6% of removal percentages were obtained in the presence of 20 mg/L HA for the same time periods described before, respectively. And the concentration of p-CP remained low during the whole reaction with and without the addition of 20 mg/L HA. As for o-CP, its concentration peaked after 60 min in the absence of HA. The addition of 20 mg/L HA made the removal percentage of 2,4-DCP slow
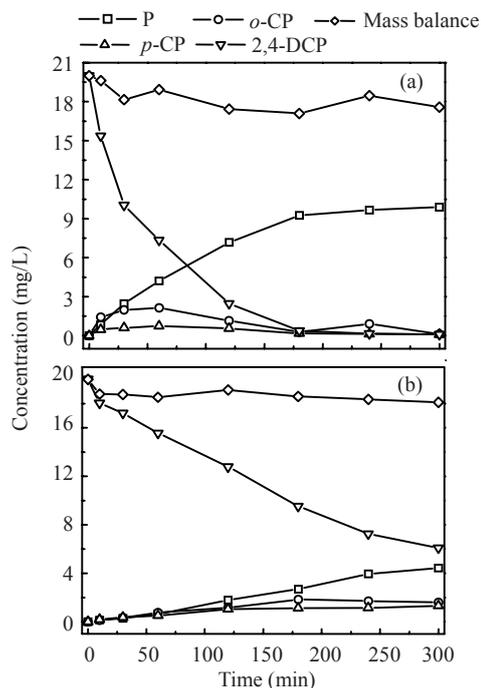

Fig.1 Dechlorination of 2,4-DCP and distribution of products by Pd-Fe nanoparticles (a) in the absence and (b) in the presence of 20 mg/L humic acid
T=30 °C; pH_{in}=5.7; $C_{2,4\text{-}DCP}$=20 mg/L; $C_{Pd\text{-}Fe}$=6 g/L; stirring at 400 r/min; the palladium content 0.15 wt%

down, and o-CP peaked after 120 min. Meanwhile, the addition of 20 mg/L HA decelerated the production rate of phenol, which could be expressed as the ratio between the total amount of phenol produced and the theoretical yield of phenol after the total dechlorination of 2,4-DCP, from 85.8% in the absence of HA to 38.2% in 300 min. Fig.2 gives the chromatograms of organic compounds in different reaction time. It is evident that as a result of the reduction of 2,4-DCP, more and more phenol was formed, while o-CP and p-CP increased in the pro-phase reaction, then their concentrations decreased slowly. Phenol and inorganic chlorine were detected as final products.

Compared to the initial concentration (20 mg/L), approximately 10% mass loss was observed (Fig.1). This might suggest that a fraction of organic compounds was absorbed or covered by surface passivating layers due to the precipitation of metal hydroxides on the surface of iron and Pd-Fe particles for their large surface areas (Burris *et al*., 1995; Allen-King *et al*., 1997; Doong and Lai, 2005). This is also evidenced by the fact that the 2,4-DCP concen-
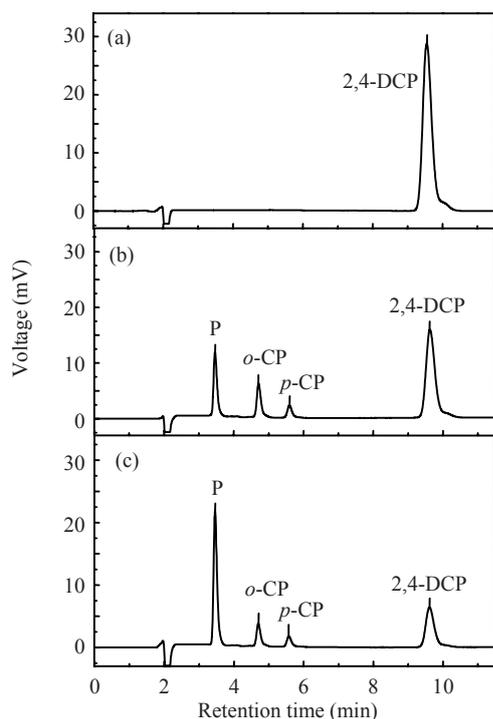
Fig.2 The chromatograms of organic compounds in different reaction time. (a) 0 min; (b) 120 min; (c) 300 min
T=30 °C; pH$_{in}$=5.7; $C_{2,4-DCP}$=20 mg/L; C_{HA}=20 mg/L; C_{Pd-Fe}= 6 g/L; stirring at 400 r/min; the palladium content 0.15 wt%

tration dropped rapidly in the first 120 min, but the phenol generated was much less than the maximum attainable. The non-detected fraction of intermediates may be attributed to the fact that the high surface area to volume ratios of Pd-Fe nanoparticles appear to serve as non-reactive sorption sites for intermediates (Burris *et al.*, 1995).

Effect of HA on 2,4-DCP dechlorination

The concentration effect of HA on the dechlorination of 2,4-DCP by Pd-Fe catalysts was further examined. Fig.3 illustrates the dechlorination of 2,4-DCP by Pd-Fe at various concentrations of HA ranging from 0 to 20 mg/L. The HA concentration increased from 0, 5, 10, 15 to 20 mg/L led to the decrease in 2,4-DCP removal percentages from 99.6%, 99.0%, 98.4%, 88.0% to 69.6% in 300 min, respectively, and this same trend was quite evident at much lower concentrations, with the production rates of phenol dropping from 85.8%, 78.4%, 76.8%, 58.5% to 38.2%, respectively, which were far less than those of the dechlorination. The decrease of both 2,4-DCP

removal percentages and phenol production rates with the increase of HA concentrations suggests that the existence of HA has significant adverse impact on the efficiency of the 2,4-DCP dechlorination.
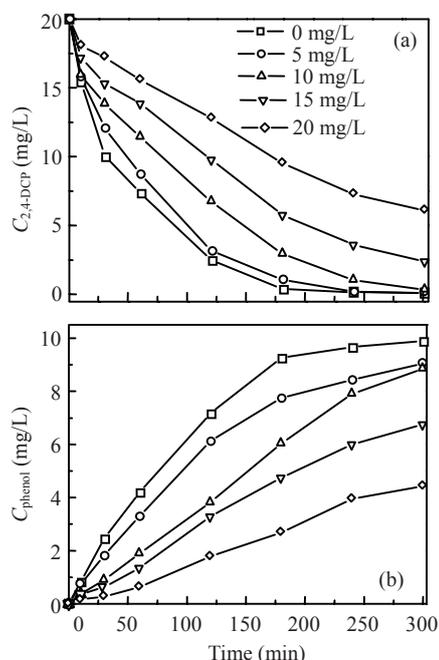

Fig.3 Effect of humic acid on 2,4-DCP dechlorination by nanoscale Pd-Fe. (a) 2,4-DCP removal; (b) Phenol production
T=30 °C; pH$_{in}$ =5.7; $C_{2,4-DCP}$=20 mg/L; C_{Pd-Fe}=6 g/L; stirring at 400 r/min; the palladium content 0.15 wt%

Several hypotheses were proposed to explain the phenomenon. The accumulation of adsorbed HA on the nanoscale Pd-Fe surface may depress the 2,4-DCP reduction rate (Muftikian *et al.*, 1996; Johnson *et al.*, 1998; Doong and Lai, 2005). The complexation between HA and the generated Fe(II) may inhibit 2,4-DCP reduction by Fe(II) or occupy the active surface sites and inhibit iron corrosion. On the other hand, excavation of active surface sites by dissolution of passive iron oxides may accelerate the 2,4-DCP reduction. The redox-active moieties in HA or in Pd-Fe-HA complexes may act as reductants to reduce 2,4-DCP to phenol or serve as electron-transfer mediators between Pd-Fe and 2,4-DCP (Xie and Shang, 2005).

Considering the 2,4-DCP reduction (Fig.3), it may be concluded that HA effects are limited by insufficient reaction time when added simultaneously with 2,4-DCP. However, in the long run, the amount

of HA adsorbed on the Pd-Fe surface may increase, while the 2,4-DCP is continuously reduced, and this may eventually affect the 2,4-DCP reduction.

On the other hand, after a certain decrease in the initial 2,4-DCP concentration, the reaction becomes retarded and the onset of the "slowing down" seems to depend on the initial HA loading. It is hypothesized that the similarity in initial rates caused by the existence of specific active surface sites designated for 2,4-DCP reduction, not for HA adsorption; with the reactions proceeding to exhaust those specific sites, the common active sites (available for both 2,4-DCP reduction and HA adsorption) become limited (Johnson *et al.*, 1998; Tratnyek *et al.*, 2001; Doong and Lai, 2006). The adsorption of HA on the Pd-Fe surface eventually led to large changes in the later reaction.

Characterization of Pd-Fe nanoparticles

Fresh Pd-Fe nanoparticles appeared to be black and flocculent. Since the size of these nanoparticles is smaller than the wavelength of visible light, they act as a perfect black body for absorbing light. Fig.4 shows the TEM images of freshly synthesized Pd-Fe nanoparticles in ethanol and aged Pd-Fe nanoparticles after 5 h reaction. The particles are of spherical shape with the sizes ranging from 20 to 100 nm in diameter. And that scale is in accordance with the report by Zhang *et al.*(1998) who reported most of the Pd-Fe nanoparticles were in the range of 1~100 nm. The total specific surface area of the Pd/Fe (0.15%) measured by BET is about 15 m^2/g, while a commercially available fine iron powder (Jinshan Metallurgical Factory, >98.0%, <100 mesh) has a specific surface area of just 0.5 m^2/g. Spherical particles tend to aggregate to form dendrites due to geomagnetic forces
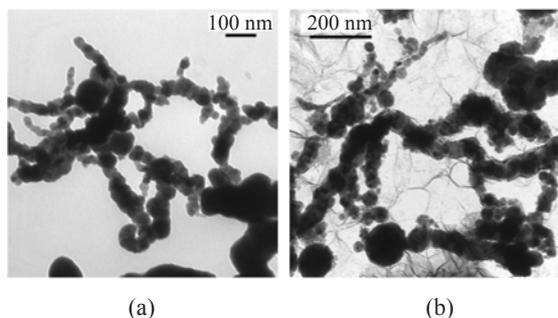

Fig.4 TEM images of (a) freshly synthesized nanoscale Pd-Fe particles in ethanol and (b) nanoscale Pd-Fe particles after 5 h reaction

between nanoscale particles and small particles, and their surface tension interactions (Wang *et al.*, 1999). A thicker mucous layer was clearly adhered onto the surface of Pd-Fe after 5 h reaction, reflecting the possibility of lowering the dechlorination efficiency. More organic components such as HA and 2,4-DCP inhibited the active sites of nanoscale Pd-Fe particles, likely leading to a lower dechlorination efficiency.

Just as what have been validated in the previous FTIR (Fourier transform infrared reflection) images before and after the reaction, the observations of the shifts at stretching bands of OH, C=C, and COO$^-$ or phenolic OH, although some of which may not be conclusive, are consistent with many studies of HA adsorption on surface minerals, especially on the surfaces of iron oxides (Murphy *et al.*, 1990; Xie and Shang, 2005). Similar peak shifts at the sites of OH, C=C, and COO$^-$ were also observed in the spectra of the formed Fe(III)-HA complex. This limited FTIR evidence suggests that the aromatic COOH and hydroxyl or phenolic OH are the main functional groups that complex with and adsorb onto the iron oxide surfaces (Xie and Shang, 2005).

Dechlorination kinetics of 2,4-DCP with freshly synthesized Pd-Fe nanoparticles

Previous studies have shown that the degradation rate of chlorinated solvents by Pd-Fe nanoparticles follows a pseudo-first-order reaction, if the dosage of Pd-Fe nanoparticles is excessive in the reaction (Wei *et al.*, 2006). Chlorines of 2,4-DCP might be removed from the benzene ring following a stepwise pathway (2,4-DCP→CP→P) as below:

$$2,4\text{-DCP} \xrightarrow{k_1} CP + Cl \xrightarrow{k_2} P + 2Cl, \quad (3)$$

where CP represents the total amount of both *o*-CP and *p*-CP in the reaction. The corresponding reaction rate equations for the transformation of 2,4-DCP, the transient formation of CP intermediate, and the accumulation of phenol in the batch system are as follows:

$$-dC_{2,4\text{-DCP}}/dt = k_1 C_{2,4\text{-DCP}}, \quad (4)$$
$$dC_{CP}/dt = k_1 C_{2,4\text{-DCP}} - k_2 C_{CP}, \quad (5)$$
$$d[P]/dt = k_2 C_{CP}. \quad (6)$$

The solution of above simultaneous rate equations therefore leads to the following molar fractions:

$$\alpha_{2,4\text{-DCP}} = e^{-k_1 t}, \tag{7}$$

$$\alpha_{CP} = \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}), \tag{8}$$

$$\alpha_P = 1 - \alpha_{2,4\text{-DCP}} - \alpha_{CP}, \tag{9}$$

where α represents the molar fraction of the daughter compounds to the initial concentration of parent compound (i.e., 2,4-DCP). Since a fraction of organic compounds will be absorbed by the Pd-Fe nanoparticles due to their large surface area, the concentration of organic compound in aqueous-phase has to be adjusted. Hence, Eq.(9) can be revised as below:

$$\alpha' = \alpha \times (1-a), \tag{10}$$

where a expresses the molar fraction of the organic compounds which were adsorbed onto Pd-Fe nanoparticles to the initial concentration of parent compound (i.e., 2,4-DCP). Then k values were derived from fitting the experimental data into Eq.(10) according to the non-linear least-square regression.

k values in different HA dosages were listed in Table 1. It shows that k_1 values for 2,4-DCP dechlorination dropped from 0.017, 0.013, 0.009, 0.006 to 0.004 min^{-1} with the increasing of HA concentrations from 0, 5, 10, 15 to 20 mg/L, which further testified the inhibitive impact of HA on 2,4-DCP dechlorination by Pd-Fe nanoparticles. Fig.5 demonstrates the relationship between HA dosages and k. And they can be described as the following linear model:

$$k_1 = -0.0007 C_{HA} + 0.016, \tag{11}$$
$$k_2 = -0.0013 C_{HA} + 0.033. \tag{12}$$

The simulated results of 2,4-DCP degradation by the 0.15 wt% Pd-Fe are shown as curves in Fig.6, with the corresponding rate constants as listed in Table 1. It shows that the experimental results fit very well with the simulation. It also confirmed that the degradation reaction of chlorinated solvents by Pd-Fe nanoparticles indeed follows a pseudo-first-order kinetics.

Table 1 k values in different HA dosage

HA dosage (mg/L)	$1-a$	k_1	k_2
0	0.90	0.017	0.034
5	0.86	0.013	0.027
10	0.86	0.009	0.018
15	0.92	0.006	0.013
20	0.89	0.004	0.008
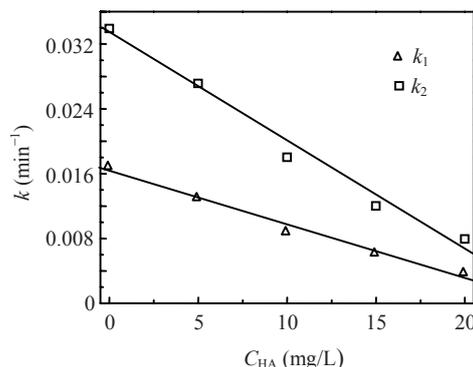
Fig.5 Relationship between HA dosages and k
T=30 °C; pH$_{in}$=5.7; $C_{2,4\text{-DCP}}$=20 mg/L; $C_{Pd\text{-}Fe}$=6 g/L; stirring at 400 r/min; the palladium content 0.15 wt%
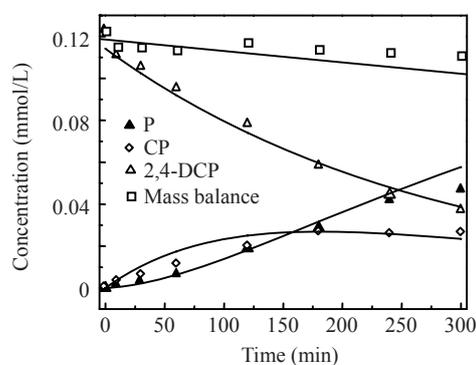
Fig.6 Dechlorination of 2,4-DCP in presence of 20 mg/L HA by nanoscale Pd-Fe
T=30 °C; pH$_{in}$=5.7; $C_{2,4\text{-DCP}}$=20 mg/L; C_{HA}=20 mg/L; $C_{Pd\text{-}Fe}$=6 g/L; stirring at 400 r/min; the palladium content 0.15 wt%

CONCLUSION

Our experimental results suggest that HA has an inhibitory effect on the 2,4-DCP dechlorination, and this inhibitory effect becomes more evident in lower HA concentrations. During the dechlorination of chlorinated hydrocarbons, HA appeared to act as an adsorbate for competing reactive sites on the surface of Pd-Fe nanoparticles, which led to the decrease of the dechlorination efficiency. Kinetics of 2,4-DCP dechlorination by Pd-Fe bimetallic nanoparticles in the presence of HA shows that the catalytic dechlorination rate of 2,4-DCP by Pd-Fe nanoparticles follows a pseudo-first-order reaction. And the higher the HA dosages are, the smaller the reaction rates. In natural environments, a variety of natural organic matters such as HA are commonly found in ground-

water, while they play important roles in various adsorption processes. The concentrations of HA in groundwater usually vary in different areas. It is of great importance to clarify the inhibitory effects of HA on 2,4-DCP dechlorination reaction and seek for appropriate conditions in the dechlorination of chlorinated hydrocarbons in order to reduce those inhibitory effects.

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