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Catalytic dechlorination of *o*-chlorophenol by nanoscale Pd/Fe

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Abstract: Transformation of chlorophenols by nanoscale bimetallic particles represents one of the latest innovative technologies for environmental remediation. Nanoscale Pd/Fe bimetallic particles were synthesized in the laboratory for treatment of *o*-chlorophenol. Most of the nanoscale particles are in the size range of 20—100 nm. BET specific surface area of the nanoscale Pd/Fe particles is 12.4 m^2/g. In comparison, a commercially available Fe powder(< 100 mesh) has a specific surface area of just 0.49 m^2/g. Batch experiments demonstrated that the nanoscale Pd/Fe bimetallic particles can effectively dechlorinate *o*-chlorophenol. Dechlorination efficiency is affected by the mass fraction of Pd in the bimetal, nanoscale Pd/Fe mass concentration and mixing intensity.

Keywords: nanoscale particles; Pd/Fe; dechlorination; *o*-chlorophenol

Introduction

The use of zero valent iron for the treatment of chlorinated organic compounds (COCs) in water and groundwater has been the focus of much recent research. The studies were concerned with compounds such as carbon tetrachloride (Bradley, 1995), trichloroethene (Orth, 1996; Chen, 2001) and pesticides and related compounds(Sayles, 1997; Monson, 1998; Eykholt, 2001; Dombek, 2001). When iron is in contact with a less reductive metal, the metal couple can form galvanic cells. This has led to the discovery of Pd/Fe bimetallic complex in which palladium serves as a catalyst and iron as an electron donor. Pd/Fe bimetallic particles can effectively dechlorinate many COCs, such as chlorinated methanes, chlorinated ethenes, chlorophenols, pentachlorophenol and PCBs(Muftikian, 1995; Korte, 2000; Liu, 2001; Kim, 2000; Grittini, 1995; Doyle, 1998).

Compared to above-mentioned conventional large particles, nanoscale zero valent metal particles offer several advantages, including high specific surface area, high surface reactivity and flexibility in deployment. Zhang *et al*. reported using nanoscale bimetallic particles(Pd/Fe, Pt/Fe, Ni/Fe, Ag/Fe) for transformation of chlorinated ethenes, a mixture of chlorinated aromatic compounds, PCBs, and hexachlorobenzene(Zhang, 1998; Lien, 2001; Wang, 1997; Xu, 2000). The results showed that the chlorinated ethenes were all transformed to ethane or ethane and a small amount of ethene, no chlorinated intermediates or final products were generated. About 90 percent of the mixture of selected chlorinated aromatic compounds was dechlorinated within 24 h. PCB congeners of Aroclor 1254 were completely dechlorinated within 17 h. Hexachlorobenzene was transformed to a mixture of pentachlorobenzene, tetrachlorobenzenes, trichlorobenzenes and dichlorobenzenes within 400 h by subcolloidal Ag/Fe complex.

However, no study in the dechlorination of chlorophenols by nanoscale Pd/Fe bimetallic complex has been reported yet. Chlorophenols are widespread environmental contaminants, commonly used as the intermediates for synthesis of medicines, dyes and bactericides; they are carcinogenic and stable in water. In this paper, laboratory studies applying synthesized nanoscale Pd/Fe bimetallic particles for dechlorination of *o*-chlorophenol are presented. The nanoscale particles are characterized by transmission electron microscopy(TEM) and specific surface area analysis. The effects of experimental factors such as initial concentration of *o*-chlorophenol, mass fraction of palladium in the bimetal, mass concentration of the nanoscale Pd/Fe particles and mixing intensity on dechlorination efficiency of *o*-chlorophenol are examined.

1 Experimental

1.1 Method for synthesis

Nanoscale iron particles were synthesized by adding 0.54 mol/L $NaBH_4$ (96%, Shanghai Chemical Company) aqueous solution dropwisely to a 1000 ml three-necked flask containing equal volume of 0.27 mol/L $FeSO_4 \cdot 7H_2O$ (99.0%—101.0%, Juhua Chemical Company) aqueous solution with electrical stirring at ambient temperature. Fe^{2+} was reduced to Fe^0 according to the following reaction:

$$Fe(H_2O)_6^{2+} + 2BH_4^- \rightarrow Fe^0 \downarrow + 2B(OH)_3 + 7H_2 \uparrow . \quad (1)$$

Synthesized iron particles were washed three times with deionized water. Bimetallic particles were then prepared by reaction of the wet iron particles with aqueous solution of potassium hexachloropalladate (K_2PdCl_6, 99%, Aldrich) under stirring according to the following equation:

$$PdCl_6^{2-} + 2Fe^0 \rightarrow 2Fe^{2+} + Pd^0 \downarrow + 6Cl^- . \quad (2)$$

The bimetallic particles were washed with deionized water to remove chloride ions.

1.2 Characterization of synthesized nanoscale Pd/Fe particles

Morphology of the synthesized nanoscale particles was observed with a JEOL JEM 200CX transmission electron microscope(TEM) at 160 kV to determine the size. 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℃ for 24 h and then at 260℃ for 4 h under a flow of hydrogen.

1.3 Batch experiments

Batch experiments for dechlorination of *o*-chlorophenol (99%, Shanghai Reagent Factory) were performed in the same three-necked flask at 30℃. *o*-chlorophenol aqueous solution was added into the flask containing nanoscale Pd/Fe particles. The reaction was conducted under nitrogen flow.

1.4 Methods of analysis

At selected time intervals, a 6 ml liquid aliquot was withdrawn by a glass syringe and then passed through a 0.45 μm membrane filter. *o*-chlorophenol and phenol were measured by HPLC (Shimadzu LC-10ATvp). The concentration of chloride ions was determined with Metrohm 792 basic ion chromatograph equipped with a Metrosep A Supp 4 column(250 mm × 4.0 mm), a Metrosep A Supp 4/5-guard column, and a conductivity detector. Sodium

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carbonate(2.0 mmol/L) and sodium bicarbonate(1.0 mmol/L) was used as an eluent.

2 Results and discussion

2.1 Characterization of nanoscale Pd/Fe

Fig. 1 shows the transmission electron microscopy image of the synthesized nanoscale Fe and Pd/Fe particles. Most of the particles are in the size range of 20—100 nm. BET specific surface area of nanoscale Pd/Fe particles is 12.4 m^2/g, while a commercially available fine iron powder (Jinshan Metallurgical Factory, > 98.0%, < 100 mesh) has a specific surface area of just 0.49 m^2/g.

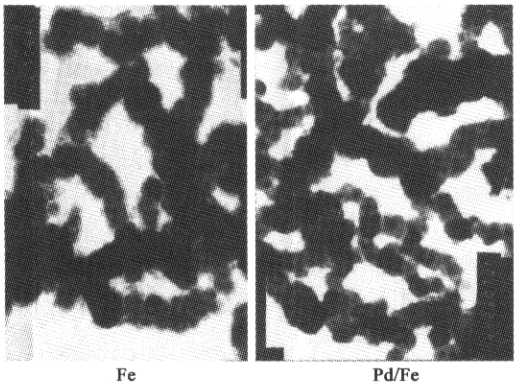


Fig.1 TEM images of nanoscale Fe and Pd/Fe

2.2 Effects of experimental factors on dechlorination efficiency

2.2.1 Effects of initial concentration of *o*-chlorophenol

Four initial concentrations of *o*-chlorophenol in reaction mixture(20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L) were tried in this study. Stoichiometric excess of nanoscale particles was applied as all the other research(Zhang, 1998; Lien, 2001; Wang, 1997; Xu, 2000). Fig. 2 shows the increase of dechlorination efficiency during reaction period under various initial concentrations. It is obvious that about 90 percent of chlorine was removed within 5 h for initial concentrations from 20—80 mg/L.

2.2.2 Effects of the mass fraction of Pd in the bimetal

The variation of dechlorination efficiency during the reaction period under various Pd mass fractions in the bimetal is presented in Fig.3. The dechlorination efficiency increases with the increase of the mass fraction of Pd when the fraction is lower than 0.0666%, but the dechlorination efficiencies change not too much when the fraction is higher than 0.0666%, reaching to 90% after 5 h of reaction. The dechlorination efficiency increases in the first hour then decreases gradually at low mass fraction of Pd. It was proposed that in the case of insufficient Pd, the total dechlorination efficiency is very small, and some chloride ion generated by the dechlorination process can be chelated by ferrous ions and covered by surface passivation layers, i. e., the precipitated of metal hydroxides and metal carbonates on the surface of Fe and Pd/Fe. In fact, organic matter also can be covered or adsorbed, so dechlorination efficiency is commonly less than 100% while *o*-chlorophenol can be removed after 5 h of reaction (which can be seen by HPLC figures in the following). It needs to be elucidated by more works.

2.2.3 Effects of nanoscale Pd/Fe mass concentration

Fig.4 shows the increase of dechlorination efficiency with reaction time at the selected nanoscale Pd/Fe mass concentrations (nanoscale Pd/Fe to solution ratio). At the nanoscale Pd/Fe mass concentration of 3 g/L, only 64.35% of chlorine can be removed after 5 h of reaction. But at the

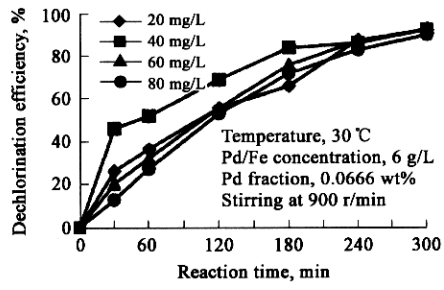


Fig. 2 Dechlorination efficiency at various initial concentrations of *o*-chlorophenol

nanoscale Pd/Fe mass concentration of 15 g/L, it takes just 2 h to remove more than 90% of chlorine. It is believed that the dechlorination reaction occurs on the nanoscale Pd/Fe surface. Palladium acts as a catalyst adsorbing hydrogen and iron as an electron donor. As the nanoscale Pd/Fe mass concentration increases, the reactive Fe site concentration and adsorptive Pd site concentration increase simultaneously, so reaction rate increases. The metal to solution ratio in our experiment is much lower than the research applying microscale Pd/Fe(Liu, 2001).

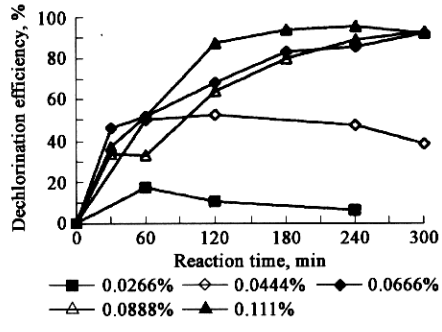


Fig.3 Effect of Pd mass fraction on dechlorination efficiency (T: 30℃, Pd/Fe concentration: 6 g/L, stirring speed: 900 r/min, C_0 = 40 mg/L)

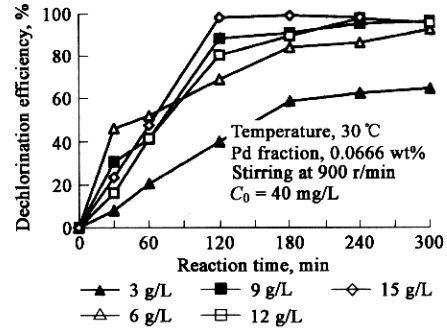


Fig.4 Dechlorination efficiency at various nano Pd/Fe mass concentrations

2.2.4 Effects of mixing intensity

Fig. 5 shows the increase of dechlorination efficiency with reaction time at the selected stirring speeds. At every stirring speed, the dechlorination efficiency increases to more than 85% within 4 h, but at stirring speed of 300 r/min and 500 r/min, the dechlorination efficiency decreases after four hours probably because some complex is produced and covered by the precipitated of metal hydroxides and metal carbonates on the surface of Fe and Pd/Fe, however, the surface passivation layers can be brushed off at larger mixing speed, so larger mixing intensity is favourable to the dechlorination reaction.

2.3 Mechanism of catalytic dechlorination

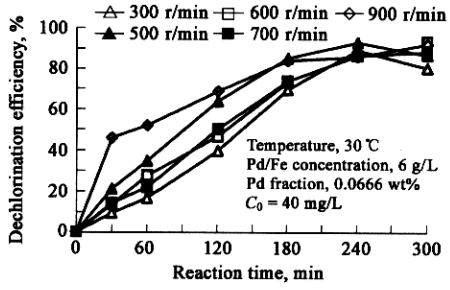


Fig.5 Dechlorination efficiency at various stirring speeds

Fig. 6 illustrates the HPLC chromatograms of *o*-chlorophenol dechlorination by nanoscale Pd/Fe at different time, after 5 h dechlorination, all *o*-chlorophenol is transformed to phenol. From Fig. 6 it can be seen that no chlorinated intermediates or final products were generated except phenol. But the dechlorination efficiency is commonly less than 100% at the end of reaction because a small amount of Cl^- and organic matters is covered by surface passivation layers.

It is hypothesized that the dechlorination of *o*-chlorophenol occurs when it is adsorbed on the Pd/Fe surface. The Pd on the Fe surface acts as a collector of hydrogen gas, which is produced by the reaction of Fe with water:

$$Fe + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- . \quad (3)$$

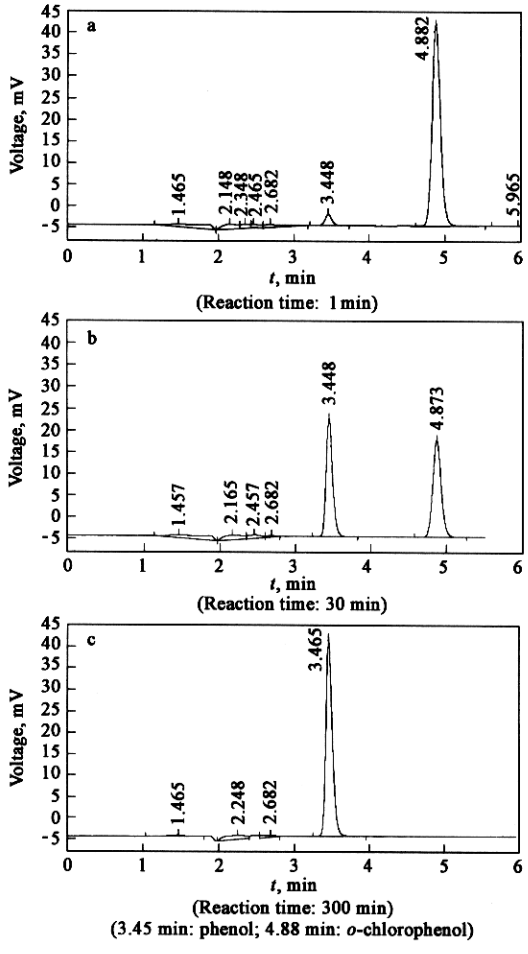
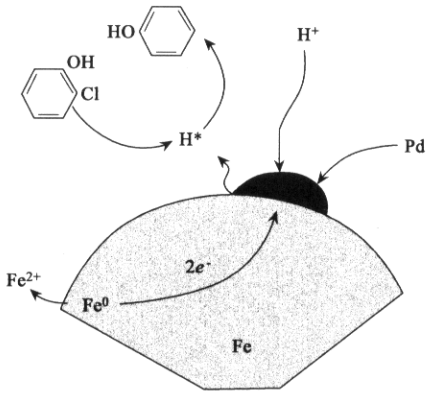


Fig.6 HPLC chromatograms of *o*-chlorophenol dechlorination by nanoscale Pd/Fe at different time

The *o*-chlorophenol that is adsorbed on Pd or Pd/Fe is reductively dechlorinated. The reaction products, phenol and chloride ion are released into solution, the dechlorination reaction can be proposed as follows:



3 Conclusions

The nanoscale Pd/Fe bimetallic particles have been shown to be very effective for the dechlorination of *o*-chlorophenol. Dechlorination efficiency is affected by the mass fraction of Pd in the bimetal, nanoscale Pd/Fe mass concentration and mixing intensity. It is believed that the approach outlined here offer opportunities for both fundamental research and technological application of nanoscale particle technology.

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