Degradation of 4-chlorophenol reductive dechlorination by Pd/Fe@SiO_2 composite nanoparticles

Yang Xinyu, Wu Jie, Xie Shuai, Zhao Deming*

College of Chemical Engineering Zhejiang University of Technology Hangzhou, People's Republic of China

*Corresponding author: dmzhao@zjut.edu.cn

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Abstract: Kinetics of 4-chlorophenol (4-CP) dechlorination by Pd/Fe@SiO_2 composite nanoparticles synthesized under ultrasound irradiation was explored. The diameters and specific surface areas of most Pd/Fe@SiO_2 composite nanoparticles that prepared by liquid phase reduction method under 40 kHz and 150 W ultrasonic irradiation were obviously modified. The optimized experimental conditions were obtained and up to 92.08% of 4-CP was removed in 300 min with Pd/Fe dosage 4.00 g/L, mass fraction of Pd in Pd/Fe@SiO_2 composite nanoparticles 0.40% (wt/%), 2.5mL TEOS per gram of Pd/Fe, reaction temperature 30℃, initial pH value 3.0,and initial 4-CP concentration 30mg/L. The degradation of 4-CP followed pseudo-first-order kinetics reaction and the apparent pseudo-first-order kinetics constants k was 2.98×10^{-2} min^{-1}.

1. Introduction

Chlorophenols (CPs) is one of the twelve persistent organic pollutants, which required the inventory and the action plan by the Stockholm Convention. Because of the special organic structure and the presence of chlorine atom, chlorophenols are especially recalcitrant towards chemical reactions aimed at their destruction. Moreover, it has harmful effects on human beings and the environment. Powerful and high cost-effective technologies were required to remediate them and clean the sites up [1-4]. An effective and rapid reductive dechlorination technology of CPs including the use of Pd/Fe compostite nanoparticles that brought out the formation of non-chlorinated hydrocarbons has been reported. Although Pd/Fe nanoparticles can effectively treat chlorine-containing organic compounds, it also has some defects that the magnetic nanoparticles are easy to agglomerate with the reaction proceeding, which reduces the activity of catalyst reaction. Meanwhile, the surface of nanoparticles will gradually form hydroxide, which will make it passivated, hinder the reaction and even produce more toxic byproducts. Bimetallic Pd/Fe@SiO2 composite nanoparticles prepared by introducing ultrasound irradiation [3] and SiO2 particles [5,6], which can improve the nanoparticles stability, disparity and recycling effects, and the above defects were all solved. In this paper, the dechlorination of 4-chlorophenol (4-CP) in Pd/Fe@SiO2 composite nanoparticles prepared by ultrasonic enhanced liquid-phase reduction method was explored. The effects of mass fraction of Pd, Pd/Fe dosage, TEOS dosage, reaction temperature and initial pH value on the system were explored. The degradation mechanism and kinetics of 4-CP were established.

2. Experiments

2.1 Chemicals

4-CP and phenol (standard), J&K Chemical Reagent Co. Ltd., China; $NaBH_4$ (98%, AR), Aladdin Chemicals Co. Ltd., China; K_2PdCl_6 (Pd 26.2%), Sigma Aldridge Trading Co. Ltd., China; methanol (≥99.8%), Aladdin Reagent Co. Ltd., China; N_2 (high purity N_2), Hangzhou Jingong Special Gas Compa，China; $FeSO_4\cdot7H_2O$ (99.0-101.0% AR), Sinopharm Chemical Reagent Co.

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Ltd., China.

2.2 Experimental Procedures

Under N_2 protection and ultrasound (40 kHz, 150 W) irradiation, a certain amount of $FeSO_4 \cdot 7H_2O$ was added and dissolved in a certain volume of deionized water without oxygen, then the same volume of $NaBH_4$ solution with the molar ratio of $FeSO_4 \cdot 7H_2O$ solution to $NaBH_4$ solution at 1:2 was dropped in 15 min, and the reaction time was 60 min at 15℃ in water bath. Therewith, Pd/Fe composite nanoparticles were synthesized by adding a certain amount of K_2PdCl_6 solution and reacted for 1h.Then, Pd/Fe@SiO_2 composite nanoparticles were synthesized by reacting with the wet Pd/Fe composite nanoparticles in an aqueous solution of TEOS through mechanical stirring. Pd/Fe@SiO_2 composite nanoparticles were firstly flushed with a certain volume of ultrapure water and then washed with anhydrous acetone and stored in anhydrous acetone. 4-CP solution of a certain concentration was added to the 500 mL flask containing a certain amount of Pd/Fe@SiO_2 composite nanoparticles, and the whole degradation process was carried out at 25 ℃ under N_2 protection. The taking samples were carried out at regular intervals.The sample was filtered by 0.45 μm polyethersulfone (PES) microporous membrane, and the filtrate was left for analysis.

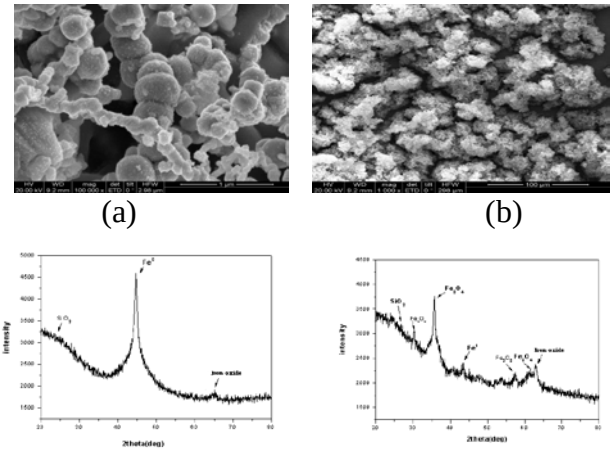
2.3 Methods of Analysis

ASAR2020M+ surface analyzer (Micromeritics Instrument Corp., US) was used in the measurement of BET specific surface area of Pd/Fe-MWCNTs-Fe_3O_4 nanoparticles. HITACHI S-4800 microscope (HITACHI Instruments Corp., JP) was used in the characterization of SEM images. X'Pert Pro advanced X-ray diffractometer (λ=1.5418 A˚) was used in XRD analysis. Organic compounds such as 4-CP and phenol were analyzed by SHIMADZU H PLC. Agilent C18 Column, 150 mm×4.6 mm, mobile phase: flow rate: 1.0 mL/min, MeOH/H_2O (70/30, v/v), sample size: 20 μL, detector: UV at 280 nm.

3. Results and discussions

3.1 Pd/Fe@SiO_2 Composite Nanoparticles Characterization

BET specific surface area of the prepared Pd/Fe@SiO_2 composite nanoparticles(Pd mass fraction 0.5%, wt%) in the presence and absence of ultrasound irradiation were 233.1 m^2/g and 193.7 m^2/g, respectively.



(a) (b)

(c) (d)

Figure1 (a) SEM image of new Pd/Fe@SiO_2 composite nanoparticles synthesized under ultrasonic irradiation, (b) SEM image of Pd/Fe@SiO_2 nanoparticles synthesized under ultrasonic irradiation after reaction; (c) XRD patterns of new Pd/Fe@SiO_2 nanoparticles synthesized under ultrasonic irradiation and (d) XRD patterns of Pd/Fe@SiO_2 nanoparticles synthesized under ultrasonic irradiation after reaction.

Fig. 1 (a) shows SEM image of the new synthesized Pd/Fe@SiO_2 composite nanoparticles synthesized under ultrasonic irradiation. Newly synthesized Pd/Fe@SiO_2 composite nanoparticles under ultrasonic irradiation, were spherical in shape with particle size ranging from 20 to 80 nm, and showed to be smaller particles diameter and better disparity. Fig. 2 (b) shows SEM image of Pd/Fe@SiO_2 composite nanoparticles prepared under ultrasonic irradiation after reaction. It is found that the surface of the nanoparticles becomes rough after the dechlorination, the spherical structure is basically destroyed, and part of the particles agglomerate obviously, which is due to the fact that the magnetic and van der Waals force cause the inevitable reunion as the reaction goes on. Some of the particles and the surface of SiO_2 adhere to a layer of floc, which may be due to the formation of iron oxide, hydroxide and the passivation layer formed by Fe_3O_4 on the surface of the particles, but a relatively complete dendrimer can still be seen.

Fig. 1(c, d) show the XRD patterns of the new and the 300 min reacted Pd/Fe@SiO_2 composite nanoparticles synthesized under ultrasound irradiation. The XRD pattern for the new sample presents a strong diffraction peaks of Fe^0 ($2\theta=44.66^\circ$) and some diffraction peaks of Fe_2O_3 and Fe_3O_4 ($2\theta=29.9^\circ$, 35.5°, 57.1°, 62.7°) can be detected before and after the reaction. The increase of diffraction peak intensity of Fe_2O_3 and Fe_3O_4 is due to the formation of magnetic oxides, which can explain the reductive dechlorination of CPs. At the same time, the characteristic peak of SiO_2 ($2\theta=27.3^\circ$) can also be observed, the intensity of diffraction peak is not strong, which may be due to the small dosage of tetraethyl silicate (TEOS), and the surface is covered by Pd/Fe, so the absorbed X-ray is reduced and the intensity is weakened. The characteristic peak of Pd was not founded in the XRD spectra, mainly because the mass fraction of Pd was too low. This agrees the previous work [2,3,7,8].

3.2 B. Reductive dechlorination of 4-CP by catalysts prepared with different methods

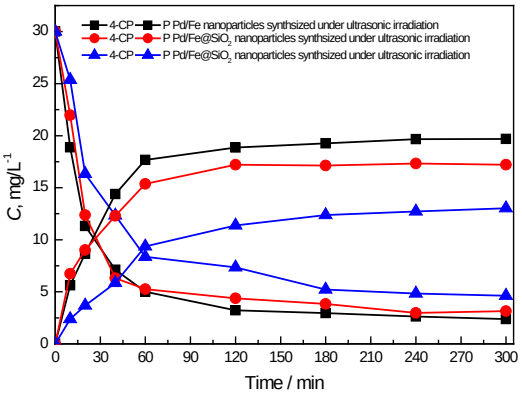


Figure.2 Reductive dechlorination of 4-CP by catalysts prepared with different methods

Fig. 2 shows the 4-chlorophenol, and phenol (P) concentrations changed with reaction time , which are effects of Pd/Fe@SiO_2 composite nanoparticles synthesized with different methods on the removal rate of 4-chlorophenol,. It can be seen that the Pd/Fe@SiO_2 composite nanoparticles prepared by ultrasonic enhanced liquid-phase reduction method has the best removal effect on 4-chlorophenol, and the removal rate of 4-chlorophenol can reach 92.08% after the reaction of 300 min. The 4-chlorophenol, removal rate in 300 min is only 84.57%, which was treated with Pd/Fe synthesized by common liquid phase reduction, and the concentration of final product such as phenol (P) is obviously higher, that is to say, it exists in the form of intermediate products and was not completely degraded into the final product phenol(P). Consequently, Pd/Fe@SiO_2 nanocomposites were synthesized through ultrasonic enhanced liquid-phase reduction method in the following experiments.

3.3 Mechanism of 4-Chlorophenol Degradation by Pd/Fe@SiO_2 Composite Nanoparticles

The degradation pathway of 4-chlorophenol by Pd/Fe@SiO_2 composite nanoparticles is shown

in the figure3. The [H] produced by the hydrogenolysis reaction of Pd/Fe@SiO_2 composite nanoparticles with water in acidic environment is adsorbed by the loaded Pd, and a high concentration reaction phase is formed on the surface, which is beneficial for the catalytic reductive dechlorination of 4-chlorophenol. Because O_2 is a gas molecule and its volume is large, it is not easy to pass through the SiO_2 coating layer to contact the nZVI, which slows down the oxidation of Fe^0. The volume of electrons, [H] and Fe^{2+} are much smaller than that of O_2, which can pass through the SiO_2 coating and react with the target pollutants on the surface of the catalyst. The precipitation of iron (hydrogen) oxide produced in the reaction will cover the outer surface of SiO_2 coating layer, but not directly cover the surface of nZVI, thus delaying the passivation of nZVI and improving the activity of catalyst.

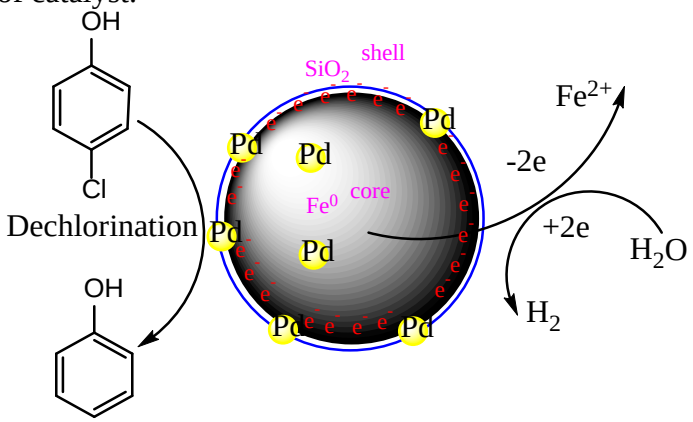


Figure.3 Degradation mechanism of 4-chlorophenol by Pd/Fe@SiO_2 composite nanaoparticles

3.4 Kinetic Modeling of 4-CP Dechlorination by Pd/Fe@SiO_2 Nanoparticles

As can be seen from Fig. 2, Fig.3 and the previous studies[2,3,7,8], the dechlorination of 4-chlorophenol(4-CP) by Pd/Fe@SiO_2 nanocomposites includes the following steps:(1) the diffusion of 4-chlorophenol to Pd/Fe@SiO_2 nanocomposites surface; (2) 4-chlorophenol was adsorbed on Pd/Fe@SiO_2 nanocomposites surface, (3) the adsorbed 4-chlorophenol reacted with Pd/Fe@SiO_2 nanocomposites for reductive dichlorination, (4) dechlorination products of 4-chlorophenol were desorbed from Pd/Fe@SiO_2 nanocomposites surface, (5) the dechlorination products of 4-chlorophenol diffused to the host solution. Although the Pd/Fe@SiO_2 nanocomposites have a certain adsorption effect on 4-chlorophenol, the amount of adsorption is less than the amount of degradation, and the adsorption occurs mainly in the first 10 minutes before the reaction begins. The amount of intermediate and final product formed during this period is not right, so the reductive dechlorination process plays a leading role in the whole dechlorination process. The control step in the reductive dechlorination process is the surface chemical reaction.Phenol (P) is the sole final organic product, so it is assumed that 4-chlorophenol was dechlorinated according to the following sequence of steps:

$$4\text{-CP} \xrightarrow{k} \text{P} + \text{Cl}^- \tag{1}$$

the corresponding reaction rate equations are shown as follows:

$$\frac{dC_{4-CP}}{dt} = -kC_{4\text{-CP}} \tag{2}$$

$$\frac{dC_P}{dt} = kC_{4-\text{CP}} \tag{3}$$

The above simultaneous rate equations are integrated, leading to the following molar fractions:

$$\alpha_{4-\text{CP}} = e^{-kt} \tag{4}$$

$$\alpha_{\text{P}} = 1 - \alpha_{4-\text{CP}} \tag{5}$$

Where α_p is the molar ratio of phenol in the reaction solution to its initial theoretical concentration in the reaction system. Pd/Fe@SiO_2 nanocomposites can adsorb part of4-chlorophenol(4-CP) because of it's large specific surface area, so the concentration of 4-chlorophenol(4-CP) in the reaction system needs to be modified. During the whole process of dechlorination, the adsorption of chlorinated biphenyls on Pd/Fe@SiO_2 nanocomposites surface reached equilibrium in an instant, so the total concentration of chlorinated biphenyls in the reaction system was considered to be constant. The formula can be summarized as follows:

$$\alpha_p' = \alpha_p(1-a) \tag{6}$$

Where a represents is the ratio of the final product biphenyl adsorbed on Pd/Fe@SiO_2 nanocomposites surface to the total amount of the organic chemical compounds. Then the reaction rate constants k_1 and k_2 were calculated through fitting the experimental datas into Eq. (8). The experimental affecting factors, such as the synthesized method of Pd/Fe@SiO_2 nanocomposites, Pd percentage, Pd/Fe nanoparticles dosage, initial pH value, the amount of TEOS and reaction temperature on the 4-chlorophenol dechlorination rate were explored in the following sequences. *k* under varying experimental conditions was obtained in Table 1.

TABLE 1 *k* values in different experimental conditions

Reaction conditions		*a*	*k*/ min^{-1}	*R*
1. Synthesized method	no ultrasonic irradiation	0.0418	0.0020	0.9621
	ultrasonic irradiation	0.1009	0.0298	0.9919
2. Pd% (wt. %)	0.25	0.0937	0.0066	0.9766
	0.30	0.1232	0.0257	0.9759
	0.35	0.1217	0.0262	0.9525
	0.40	0.1009	0.0298	0.9919
	0.45	0.1001	0.0307	0.9848
3. Pd /Fe (g/L)	2.0	0.1593	0.0103	0.9765
	3.0	0.1232	0.0257	0.9919
	4.0	0.1009	0.0298	0.9759
	5.0	0.1184	0.0309	0.9881
	6.0	0.1246	0.0299	0.9436
4. Reaction temperature (℃)	20	0.0817	0.0049	0.9803
	30	0.1008	0.0298	0.9919
	40	0.0936	0.0268	0.9698
	50	0.2347	0.0211	0.9861
5. Initial pH values	3	0.1009	0.0298	0.9919
	5	0.1476	0.0234	0.9871
	7	0.0604	0.0061	0.9965
	9	0.5763	0.0105	0.9684
6.TEOS dosage(mL/g(Pd/Fe))	1.25	0.1058	0.0264	0.9640
	2.50	0.1009	0.0298	0.9919
	3.75	0.1549	0.0135	0.9863
	5.00	0.1733	0.0048	0.9861
7.4-CP initial concentration(mg/L)	20.0	0.9231	0.0269	0.9586
	30.0	0.1009	0.0298	0.9919
	40.0	0.1684	0.0151	0.9821
	50.0	0.1034	0.0127	0.9899

Note: Exp.1. $C_{4\text{-CP}}$=30 mg/L, *T*=30℃, pH_{in}=3.0, $C_{Pd/Fe}$ =4 g/L, rotation speed 500 rpm, Pd mass fraction was 0.40 wt.%, C_{TEOS}=2.5 mL/(g Pd/Fe); Exp.2. $C_{4\text{-CP}}$=30 mg/L,*T*=30℃, pH_{in}=3.0, $C_{Pd/Fe}$=4 g/L, rotation speed 500 rpm, C_{TEOS}=2.5 mL/(g Pd/Fe); Exp.3. *T*=30℃, pH_{in}= 3.0, $C_{4\text{-CP}}$=30 mg/L, rotation speed 500 rpm, Pd mass fraction was 0.40 wt. %, C_{TEOS}=2.5 mL/(g Pd/Fe); Exp.4. pH_{in}= 3.0, $C_{4\text{-CP}}$=30 mg/L, $C_{Pd/Fe}$ =4g/L, rotation speed 500 rpm, Pd mass fraction was 0.40 wt. %, C_{TEOS}=2.5 mL/(g Pd/Fe); Exp.5. *T*=30℃, $C_{4\text{-CP}}$=30 mg/L, $C_{Pd/Fe}$ =4 g/L, rotation speed 500 rpm, Pd mass fraction was 0.40 wt.%, C_{TEOS}=2.5 mL/(g Pd/Fe);Exp.6. *T*=30℃, pH_{in}= 3.0, $C_{4\text{-CP}}$=30 mg/L, $C_{Pd/Fe}$ =4 g/L, rotation speed 500 rpm, Pd mass fraction was 0.40 wt.%; Exp.7. C_{TEOS}=2.5 mL/(g Pd/Fe), *T*=30℃, pH_{in}=3.0, $C_{Pd/Fe}$ =4 g/L, rotation speed 500 rpm, Pd mass fraction was 0.40 wt.%.

From Table 1, it can be observed that the influential factors such as Pd mass fraction, TEOS dosage, Pd/Fe dosage,, reaction temperature, initial pH value and catalysts prepared method, have obvious effects on the apparent rate constants. The apparent rate constants *k* increases with the increasing of Pd mass fraction, and Pd/Fe dosage, and with the decreasing of TEOS dosage, reaction temperature, pH values and initial 4-chlorophenol concentration.

4. Conclusions

The experimental results show that Pd/Fe@SiO_2 nanoparticles synthesized under ultrasonic irradiation was a better method to improve the surface characteristics. The affecting factors including Pd mass fraction, Pd/Fe dosage, TEOS dosage, reaction temperature, initial pH value, significantly affect the the degradation of 4-chlorophenol. The degradation of 4-chlorophenol followed pseudo-first-order kinetics, and the apparent rate constants *k* increased with the increasing Pd mass fraction, and Pd/Fe dosage, and with the decreasing of TEOS dosage, temperature, pH values and initial 4-chlorophenol concentration.

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