# Kinetics of 2-chlorobiphenyl Reductive Dechlorination by Pd-fe$^0$ Nanoparticles

Junrong Jiang[1] Chong Fu[2] and Deming Zhao[2,a]
[1]School of Biological & Chemical Engineering, Taizhou Vocational & Technical College, Taizhou 318000, China
[2]College of Chemical Engineering, Zhejiang University of Technology Hangzhou 310014, China

**Abstract.** Kinetics of 2-chlorobiphenyl (2-Cl BP) catalytic reductive dechlorination by Pd-Fe$^0$ nanoparticles were investigated. Experimental results showed that ultrafine bimetallic Pd-Fe$^0$e nanoparticles were synthesized in the presence of 40 kHz ultrasound in order to enhance disparity and avoid agglomeration. The application of ultrasonic irradiation during the synthesis of Pd-Fe$^0$ nanoparticles further accelerated the dechlorinated removal ratio of 2-Cl BP. Up to 95.0% of 2-Cl BP was removed after 300 min reaction with the following experimental conditions: initial 2-Cl BP concentration 10 mg $L^{-1}$, Pd content 0.8 wt. %, bimetallic Pd-Fe$^0$ nanoparticles prepared in the presence of ultrasound available dosage 7 g $L^{-1}$, initial pH value in aqueous solution 3.0, and reaction temperature 25℃. The catalytic reductive dechlorination of 2-Cl BP followed pseudo-first-order kinetics and the apparent pseudo-first-order kinetics constant was 0.0143 $min^{-1}$.

## 1 Introduction

Historical and continued releases of polychlorinated biphenyls (PCBs) to the environment have resulted in polluted water, soil, and sediment [1]. These contaminated soils, sludges and groundwater need to be effectively remediated at ambient temperatures using either ex *situ* or in *situ* methods. Methods for PCBs dechlorination include chemical reduction, catalyzed hydrodechlorination, and electrolytic dechlorination. Most of these techniques use highly active reducing hydrogen from different sources to facilitate the dechlorination through the use of noble metal catalysts such as palladium (Pd) and rhodium (Rh), etc [2-4].

Pd-Fe$^0$ bimetallic nanoparticles have been improved to completely dechlorinate chloroaromatics and thoroughly purify a wide range of chlorinated organic compounds without leaving chlorinated side products [2-6]. As one of the noble metal, Pd can utilize the produced $H_2$ from zero-valent iron (ZVI) corrosion and improve the rates and efficiencies of dechlorination reaction [1,4]. In addition, the presence of Pd not only reduces the accumulation of toxic byproducts, but also inhibits particle oxidation in air [5]. Pd-Fe$^0$ bimetallic nanoparticles, when compared to the conventional large particles have some advantages with possessing large specific surface area and high surface reactivity [6]. In order to obtain the stabilized and high reactive Pd-Fe$^0$ bimetallic nanoparticles, ultrasound is applied to the preparation of Pd-Fe$^0$ nanoparticles because acoustic cavitation can enhance the surface area and surface properties of the reactive solids by causing particles to rupture [7].

In the present work, Pd-Fe$^0$ bimetallic nanoparticles were prepared in the presence of 20 kHz ultrasound and 2-chlorobiphenyl (2-Cl BP) dechlorination kinetic by Pd-Fe$^0$ bimetallic nanoparticles in aqueous solution was investigated. Meanwhile, other influential factors contributing to 2-Cl BP reductive dechlorination, such as Pd-Fe$^0$ nanoparticles availability, Pd content over Fe$^0$, initial 2-Cl BP concentration, reaction temperature and the initial pH values, were also studied

## 2 Experimental

### 2.1 Chemicals

2-chlorobiphenyl (AP grade), biphenyl (CP grade) and potassium hexachloropalladate (AP grade) were purchased from the J&K Chemical Reagent Co., Ltd., China, $FeSO_4 \cdot 7H_2O$ (AR grade), sodium borohydride (AR grade) purchased from Tianjin Chemical Reagent Research Institute. 2-Cl BP is dissolved in a methanol/deoxygenated deionized water solution (50:50, *V*/*V*) and stored at 4 ℃. Pd-Fe$^0$ nanoparticles were synthesized immediately before use.

### 2.2 Experimental procedures

In a 500 mL three-necked flask, Pd-Fe$^0$ bimetallic nanoparticles were prepared in the presence of 40 kHz and 150 W ultrasound under nitrogen gas. Firstly, nanoscale zero-valent iron (nZVI) particles were synthesized by drop wise addition of stoichiometric amounts of $NaBH_4$ aqueous solution into a flask containing $FeSO_4 \cdot 7H_2O$ aqueous solution

[a] Corresponding author: dmzhao@zjut.edu.cn

simultaneously with mechanical stirring at 25℃. nZVI particles were then rinsed several times with deoxygenated deionized water. nZVI particles were then rinsed several times with deoxygenated deionized water. Subsequently, Pd-$Fe^0$ nanoparticles were prepared by reacting with the wet nZVI particles in an aqueous solution of potassium hexachloropalladate under mechanical stirring. Batch experiments of 2-Cl BP catalytic reductive dechlorination were performed in the same flask into which nanoscale bimetallic Pd-$Fe^0$ particles were added. 2-Cl BP stock solutions and a certain amount of deoxygenated deionized water and methanol solution (50:50,*V/V*) were added into the flask containing fresh prepared nanoscale Pd-$Fe^0$ particles into 500 mL of total reaction volume. The reaction solution was stirred under nitrogen flow to simulate anaerobic environment at 25 ℃. Aliquots of samples were periodically collected with glass syringes and the reaction was quenched by passing through 0.22 $\mu$m polyether sulphone (PES) membrane filters.

### 2.3 Methods of analysis

All fresh prepared synthesized bimetallic Pd-$Fe^0$ nanoparticles (with Pd content 0.3 wt. %) were immersed in absolute ethyl alcohol and dispersed by an ultrasonator. Transmission electron microscope (TEM) images were obtained through a microscope (JEOL JEM 200CX JEOL Electronics Co., JP). X-ray diffraction (XRD) analysis was performed by using X'Pert Pro advanced X-ray diffractometer ($\lambda$ = 1.5418 A°). Brunauer–Emmett–Teller (BET) specific surface area of all synthesized bimetallic Pd-$Fe^0$ nanoparticles were measured using nitrogen adsorption method with a surface analyzer (ASAR2020M+, Micromeritics Instrument Corp., US). Before the analysis, the particles were dried in vacuum at 25 ℃ for 24 h and then hydrogen flow at 260 ℃ for further 4 h. Organic compounds such as 2-chlorobiphenyl and BP were analyzed by Thermofish Trace 1310 Gas Chromatography. ECD and FID detector, Thermofish TR-5 Column (30 m×0.32 mm, 1.0 μm), inlet temperature 300℃, detector temperature 250 ℃, no split injection, injection volume 1 μL, carrier gas nitrogen (purity ≥99.99%), column flow 1.5 mL/min (constant current), program temperature: column temperature 100 ℃, holding 0.5min, 25 ℃/min was raised to 300 ℃, maintained 2 min.

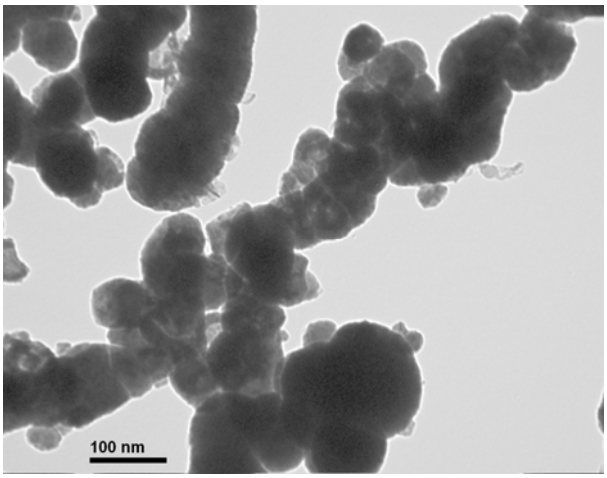
## 3 Results and Discussions

### 3.1 Pd-$Fe^0$ nanoparticles Characterization

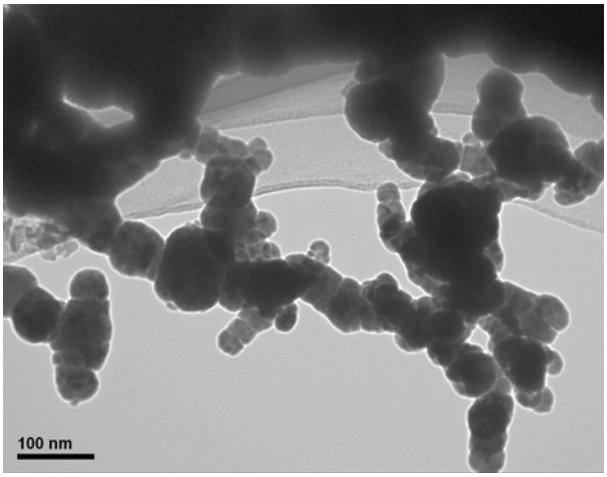
Fig. 1 (a, b) shows TEM images of the freshly synthesized bimetallic Pd-$Fe^0$ nanoparticles in the presence and absence of ultrasound. The freshly prepared Pd-$Fe^0$ nanoparticles in the absence of ultrasound, were spherical in shape with particle size ranging from 20 to 100 nm, and appeared to aggregate together (Fig. 1(a)). However, Pd/Fe nanoparticles synthesized in the presence of ultrasound were also spherical, but the particle size ranges from 10 to 100 nm, mainly foused on 30 to 75 nm, and appeared to be smaller particles diameter and better dispersion (Fig. 1(b)). The sizes and specific surface area of most particles synthesized in the presence of ultrasound were obviously modified. The ultrafine and highly dispersion nanoparticles were obtained.

Fig. 2(a, b) shows the XRD patterns of the fresh and the 300 min reacted bimetallic Pd-$Fe^0$ nanoparticles synthesized in the presence of ultrasound. The XRD pattern for the fresh sample presents a strong peak 44.66° which corresponds to the body-centered cubic N–$Fe^0$ at the (110) plane. The peak in the XRD pattern of the reacted sample shows evidence of iron oxides, possibly $Fe_3O_4$ or $Fe_2O_3$, or their mixture. This is consistent with the previous work [8].

In addition, BET specific surface area of the synthesized Pd-$Fe^0$ nanoparticles in the presence and absence of 40 kHz ultrasonic irradiation were 41.68 $m^2$ $g^{-1}$ and 22.39 $m^2$ $g^{-1}$, respectively.Therefore, bimetallic Pd-$Fe^0$ nanoparticles were synthesized by using ultrasound strengthened liquid phase reductive method in the following experiments.

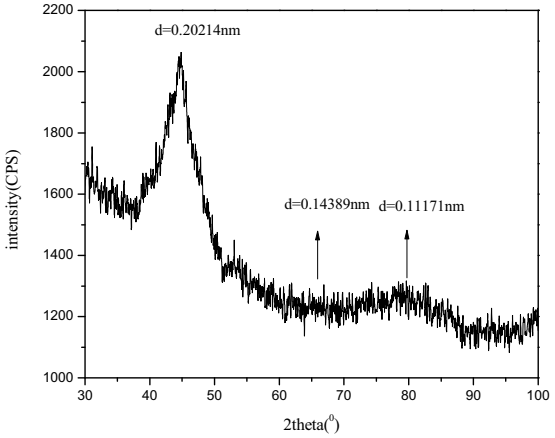



(a)

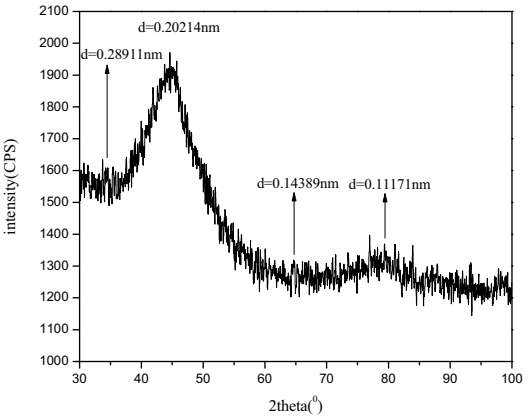



(b)

**Figure. 1.** (a) TEM image of fresh Pd/Fe nanoparticles prepared in the absence of ultrasound, (b) TEM image of fresh Pd/Fe nanoparticles prepared in the presence of 40 kHz ultrasound




(a)




(b)

**Figure. 2.** (a) XRD patterns of fresh Pd/Fe nanoparticles prepared in the presence of 40 kHz ultrasound and (b) XRD patterns of reacted Pd/Fe nanoparticles prepared in the presence of 40 kHz ultrasound.

### 3.2 Kinetic modeling of 2-Cl BP catalytic reductive dechlorination by bimetallic Pd-Fe$^0$ nanoparticles.

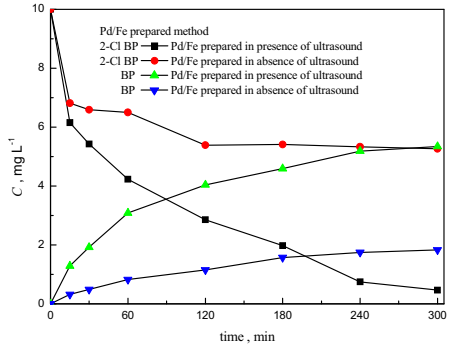



**Figure. 3.** Reductive dechlorinations of 2-Cl BP by Pd-Fe$^0$ nanoparticles prepared in different methods .

Figure 3 shows the hypothetical reductive dechlorated pathways of 2-chlorobiphenyl (2-Cl BP) by Pd-Fe$^0$ nanoparticles prepared in different methods. Biphenyl (BP) is the sole final organic product. In addition, ased on the previous studies, the catalytic reductive dechlorination of chloroaromatics by bimetallic Pd-Fe$^0$ nanoparticles involves three main steps [2,4,9-13]: (1) chloroaromatics in solution diffuse to Pd-Fe$^0$ nanoparticles surface and adsorb in the surface of catalyst; (2) the adsorbed chloroaromatics takes reduction reaction under the effect of Pd-Fe$^0$ nanoparticles; (3) the products of reaction desorbs from Pd-Fe$^0$ nanoparticles and diffuses to the bulk solution. It is well established that the pseudo-first-order kinetics could be applied in the reductive dechlorination of chloroaromatics if Pd-Fe$^0$ nanoparticles availability is excessive in the reaction. Therefore, the pseudo-first order reaction kinetics was adopted to model the 2-Cl BP dechlorination reaction by Pd-Fe$^0$ nanoparticles. Therefore, it is assumed that 2-Cl BP was hydrodechlorinated according to the following sequence of steps.

$$2-\text{Cl BP} \xrightarrow{k_1} \text{BP} + \text{Cl}^- \quad (1)$$

The corresponding reaction rate equations for the disappearance of 2-Cl BP and the accumulation of BP in the batch system are shown as follows:

$$\frac{dC_{2-\text{Cl BP}}}{dt} = -kC_{2-\text{Cl BP}} \quad (2)$$

$$\frac{dC_{BP}}{dt} = kC_{2-\text{Cl BP}} \quad (3)$$

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

$$\alpha_{2-\text{Cl BP}} = e^{-kt} \quad (4)$$

$$\alpha_{BP} = 1 - \alpha_{2-\text{Cl BP}} \quad (5)$$

Where $\alpha$ represents the molar fraction of the subscript organic compound to the initial concentration of 2-chlorobiphenyl. Since a fraction of 2-Cl BP and BP were absorbed on the larger surface of Pd-Fe$^0$ nanoparticles, the actual concentration of the 2-Cl BP and BP in aqueous phase has to be amended. As the production of BP was step wise, equilibrium time for organic compounds absorbed onto Pd-Fe$^0$ nanoparticles was little, and the total molar fraction of 2-Cl BP and BP did not change, the ratio of BP in the aqueous phase can be seen as invariable, as a result, Eq. (5) can be revised as follows:

$$\alpha_{Bp}' = \alpha_{BP}(1-a) \quad (6)$$

Where $\alpha'$ represents the molar fraction of the organic compounds which were adsorbed onto bimetallic Pd-Fe$^0$ nanoparticles to the initial concentration of 2-chlorobiphenyl. Then $k$ values were derived from fitting the experimental data into Eq. (6) according to the non-linear least-square regression. The influential factors, such as the preparation method of bimetallic Pd-Fe$^0$ nanoparticles, Pd content over Fe$^0$, bimetallic Pd-Fe$^0$ nanoparticles dosage, reaction temperature, initial pH values and initial 2-Cl BP concentration on the 2-Cl BP dechlorination efficiency were investigated in the

following sequences. Kinetic constant $k$ values in different experimental conditions were listed in Table 1.

The experimental results showed that $k$ values obviously increased from 0.0018 to 0.0143 $min^{-1}$ under bimetallic Pd/Fe nanoparticles prepared in the absence and presence of ultrasound, respectively. They increased from 0.0119 $min^{-1}$ to 0.0203 $min^{-1}$ as the Pd content over $Fe^0$ was increased from 0.70 wt. % to 0.90 wt. %, and they increased from 0.0098 $min^{-1}$ to 0.0309 $min^{-1}$ as the bimetallic Pd-$Fe^0$ nanoparticles available dosage was increased from 5 g $L^{-1}$ to 9 g $L^{-1}$. In short, $k$ values increased with the increasing Pd content over $Fe^0$, Pd/Fe nanoparticles available dosage and reaction temperature, with the decrease of initial pH values.

## 4 Conclusion

The experimental results indicate that the prepared Pd-$Fe^0$ nanoparticles method in the presence of ultrasound was a better technique to enhance the surface special properties. 2-Cl BP dechlorination efficiency was dependent on a number of influential factors including bimetallic Pd-$Fe^0$ nanoparticles dosage, Pd content over $Fe^0$, reaction temperature, mechanical stirring speed and initial pH values. The degradation of 2-Cl BP followed pseudo-first-order kinetics reaction and $k$ values increased with the increasing Pd/Fe nanoparticles dosage, stirring speed and reaction temperature, with the decrease of initial pH values.

## Acknowledgements

The authors are grateful for the financial support provided by Zhejiang Provincial Natural Science Foundation of China (LY15B070005) and by the Science and Technology Department of Zhejiang Province（No. 2015C33233）.

Table 1 $k$ values in different experimental conditions

| Reaction conditions | | $a$ | $k$/ $min^{-1}$ | $R$ |
|---|---|---|---|---|
| 1. Pd-$Fe^0$ nanoparticles prepared method | in the absence of ultrasound | 0.3563 | 0.0018 | 0.91 |
| | in the presence of ultrasound | 0.3566 | 0.0143 | 0.99 |
| 2. Pd content over $Fe^0$ | 0.70 wt. % | 0.4326 | 0.0119 | 0.99 |
| | 0.75 wt. % | 0.3977 | 0.0125 | 0.99 |
| | 0.80 wt. % | 0.3566 | 0.0143 | 0.99 |
| | 0.85 wt. % | 0.3339 | 0.0164 | 0.99 |
| | 0.90 wt. % | 0.3322 | 0.0203 | 0.99 |
| 3. Pd-$Fe^0$ nanoparticles dosage g $L^{-1}$ | 5.00 | 0.6944 | 0.0098 | 0.97 |
| | 6.00 | 0.4258 | 0.0069 | 0.97 |
| | 7.00 | 0.3566 | 0.0143 | 0.99 |
| | 8.00 | 0.3542 | 0.0168 | 0.99 |
| | 9.00 | 0.3755 | 0.0309 | 0.96 |
| 4. Reaction temperature | 15 ℃ | 0.8811 | 0.0035 | 0.97 |
| | 25 ℃ | 0.3566 | 0.0143 | 0.99 |
| | 35 ℃ | 0.8133 | 0.0092 | 0.99 |
| 5. Initial pH values | 3 | 0.3566 | 0.0143 | 0.99 |
| | 5 | 0.5622 | 0.0087 | 0.99 |
| | 7 | 0.8090 | 0.0038 | 0.99 |

*Note*: Exp.1.$T$=25 ℃, $pH_{in}$= 3.0, $C_{2\text{-Cl BP}}$=10 mg $L^{-1}$, $C_{Pd/Fe}$=7 g $L^{-1}$, mechanical stirring speed at 600 rpm, Pd content was 0.8 wt. %; Exp.2.$T$=25 ℃, $pH_{in}$= 3.0, $C_{2\text{-Cl BP}}$=10 mg $L^{-1}$, $C_{Pd/Fe}$ =7 g $L^{-1}$, mechanical stirring speed at 600 rpm; Exp.3.$T$=25 ℃, $pH_{in}$= 3.0, $C_{2\text{-Cl BP}}$=10 mg $L^{-1}$, mechanical stirring speed at 600 rpm, Pd content was 0.8 wt. %; Exp.4. $pH_{in}$= 3.0, $C_{2\text{-Cl BP}}$=10 mg $L^{-1}$, $C_{Pd/Fe}$ =7 g $L^{-1}$, mechanical stirring speed at 600 rpm, Pd content was 0.8 wt. %; Exp.5.$T$=25 ℃, $C_{2\text{-Cl BP}}$=10 mg $L^{-1}$, $C_{Pd/Fe}$ =7 g $L^{-1}$, mechanical stirring speed at 600 rpm, Pd content was 0.8 wt. %. Bimetallic Pd-$Fe^0$ nanoparticles were synthesized by using ultrasound strengthened liquid phase reductive method in Exp.2 to 5.

## References

1. T. Luigi, D Luca, Propulsion physics (EDP Sciences, Les Ulis, 2009
2. G.V. Lowry, K.M Johnson, Environ. Sci. Technol. **38**,5208-5216 (2004)
3. Z. Zhang, Q.H. Shen, N. Cissoko, J.J.Wo, X.H. Xu, J. Hazard. Mater. **182**,252-258 (2010)
4. T. Zhou, Y.Z. Li, T.T. Lim, Separation and Purification Technology.**76**, 206-214 (2010)
5. J.J. Wei, X.H. Xu, Y. Liu, D.H. Wang, Water Research.**40**,348-354 (2006)
6. H.L. Lien, W.X. Zhang, Colloid Surface. A. **233**,103-112 (2001)
7. W.H. Zhang, X. Quan, J.X. Wang, Z.Y. Zhang, S. Chen, Chemosphere. **65**,58-64 (2006)
8. K.S. Suslick, M. Fang, T.Hyeon, Journal of American Chemical Society.118,11960-11961 (1996)
9. D.M. Zhao, M. Li, D.X. Zhang, S.A. Baig, X.H. Xu, Ultrason Sono. **20**,64–871 (2013)
10. G.N. Jovanovic, P.Z. Plazl, P. Sakrittichai, K. Al-Khaldi, Ind. Eng. Chem. Res. **44**,5099-5106 (2005)
11. G.Yuan, M.A.Keane, Catal. Commun. **4**,195-201 (2003)

12. F. Cheng, Q. Fernando, N. Korte, Environ. Sci. Technol. **31**,1074-1078 (1997)
13. J.L. Chen, S.R. Al-Abed, J.A. Ryan, Z.B. Li, J. Hazard. Mater. B.**83**,243-254 (2001)
14. Z. Zhang, N. Cissoko, J.J. Wo, X.H. Xu, J. Hazard. Mater..**165**,78-86 (2009)