

Influential factors of 2-chlorobiphenyl reductive dechlorination by highly dispersed bimetallic nanoparticles

Junrong Jiang^{1,2}, Chong Fu² and Deming Zhao^{2a}

¹School of Biological & Chemical Engineering, Taizhou Vocational & Technical College, Taizhou 318000, China

²College of Chemical Engineering, Zhejiang University of Technology Hangzhou 310014, China

Abstract. Highly dispersed Pd-Fe⁰ bimetallic nanoparticles were prepared in the presence of 40 kHz ultrasonic irradiation in order to enhance disparity and reactivity, and simultaneously avoid agglomeration. Influential factors of 2-chlorobiphenyl (2-Cl BP) reductive dechlorination by highly dispersed Pd-Fe⁰ nanoparticles were investigated. Experimental results showed that highly dispersed Pd-Fe⁰ nanoparticles prepared in the presence of ultrasound could further improve the dechlorination efficiency of 2-Cl BP, meanwhile the biphenyl (BP) formation rates increased obviously and increased from 47.4% (in the absence of ultrasound) to 95.3% (in the presence of ultrasound) within 300 min. The catalytic reductive dechlorination efficiency of 2-Cl BP was dependent on Pd-Fe⁰ nanoparticles prepared methods, Pd-Fe⁰ nanoparticles dosage, Pd loading percentage over Fe⁰ and initial pH values

1 Introduction

Polychlorinated biphenyls (PCBs) are a sort of organic compounds of which there are 209 distinct chemical species known as congeners. PCBs as a class share a variety of properties (e.g., chemical and thermal stability) that made them popular for industrial applications in the latter part of the 20th century [1]. The high stability, low aqueous solubility, and high organic affinity of PCBs make them difficult to treat [2,3]. This raises an urgent need for efficient reductive dechlorination methods to eliminate chloroaromatics from both concentrated industrial effluents and diluted polluted groundwater.

Many remediation technologies, such as physical, chemical, and biological methods have been proposed, including dredging, landfilling, incineration, biodecomposition, *in situ* capping, and electrochemical degradation [2-4]. Among these technologies, the use of reactive metals such as nanoscale zero-valent iron (nZVI), as a mild and cost-effective reducing agent, has been documented to work efficiently for the reductive chlorinated organic compounds [5]. A rapid and complete catalytic reductive dechlorination method of chloroaromatics involving the use of bimetallic Pd-Fe⁰ nanoparticles that led to the formation of non-chlorinated hydrocarbons have also been reported [6]. As one of the noble metal, Pd can utilize the produced H₂ from Fe⁰ corrosion and accelerate the rates of dechlorination reaction [7]. However, the presence of Pd not only reduces the accumulation of toxic byproducts, but also inhibits particle oxidation in air. Pd-Fe⁰ bimetallic nanoparticles, when compared to the conventional large particles have some advantages with possessing highly dispersion, large specific surface area and high surface reactivity [6]. In order to obtain the highly dispersed, stabilized and high reactive Pd-Fe⁰ bimetallic

nanoparticles and decrease their agglomeration and accumulation in the effluent, ultrasound is applied to the preparation of Pd-Fe⁰ bimetallic nanoparticles. Sonochemistry arises from acoustic cavitation, the formation, growth, and implosive collapse of bubbles in a liquid. Acoustic cavitation can increase the surface area of the reactive solids by causing particles to rupture [8].

In the present work, highly dispersed Pd-Fe⁰ bimetallic nanoparticles were prepared in the presence of 40 kHz ultrasound and influential factors of 2-chlorobiphenyl (2-Cl BP) reductive dechlorination by highly dispersed Pd-Fe⁰ nanoparticles, such as Pd-Fe⁰ nanoparticles availability, Pd content over Fe⁰, initial 2-Cl BP concentration, reaction temperature and the initial pH values, were investigated.

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, FeSO₄·7H₂O (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 °C. Pd-Fe⁰ nanoparticles were synthesized immediately before use.

2.2 Experimental procedures

In a 500 mL three-necked flask, Pd-Fe⁰ bimetallic nanoparticles were prepared in the presence of 40 kHz and 150 W ultrasound under nitrogen gas. Nanoscale zero-valent iron (nZVI) particles were synthesized by

^a Corresponding author: dmzhao@zjut.edu.cn

drop wise addition of stoichiometric amounts of NaBH_4 aqueous solution into a flask containing $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ aqueous solution simultaneously with mechanical stirring at $25\text{ }^\circ\text{C}$. nZVI particles were then rinsed several times with deoxygenated deionized water. nZVI particles were then rinsed several times with deoxygenated deionized water. Subsequently, Pd-Fe⁰ 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-Fe⁰ 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-Fe⁰ particles into 500 mL of total reaction volume. The reaction solution was stirred under nitrogen flow to simulate anaerobic environment at $25\text{ }^\circ\text{C}$. Aliquots of samples were periodically collected with glass syringes and the reaction was quenched by passing through $0.22\text{ }\mu\text{m}$ polyether sulphone (PES) membrane filters.

2.3 Methods of analysis

All fresh prepared synthesized bimetallic Pd-Fe⁰ nanoparticles (with Pd content 0.3 wt. %) were immersed in absolute ethyl alcohol and dispersed by an ultrasonicator. Brunauer–Emmett–Teller (BET) specific surface area of all synthesized bimetallic Pd-Fe⁰ 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 $25\text{ }^\circ\text{C}$ for 24 h and then hydrogen flow at $260\text{ }^\circ\text{C}$ for further 4 h. Scanning electron microscope (SEM) images were obtained through a microscope (HITACHI S-4800 HITACHI Instruments Corp., JP). X-ray diffraction (XRD) analysis was performed by using X'Pert Pro advanced X-ray diffractometer ($\lambda = 1.5418\text{ \AA}$). Organic compounds such as 2-chlorobiphenyl and BP were analyzed by Thermofish Trace 1310 Gas Chromatography. ECD and FID detector, Thermofish TR-5 Column ($30\text{ m} \times 0.32\text{ mm}$, $1.0\text{ }\mu\text{m}$), inlet temperature $300\text{ }^\circ\text{C}$, detector temperature $250\text{ }^\circ\text{C}$, no split injection, injection volume $1\text{ }\mu\text{L}$, carrier gas nitrogen (purity $\geq 99.99\%$), column flow 1.5 mL/min (constant current), program temperature: column temperature $100\text{ }^\circ\text{C}$, holding 0.5 min , $25\text{ }^\circ\text{C/min}$ was raised to $300\text{ }^\circ\text{C}$, maintained 2 min .

3 Results and Discussions

3.1 Characterization of Pd-Fe⁰ Nanoparticles

The BET specific surface area of Pd-Fe⁰ nanoparticles prepared in the presence and absence of 40 kHz ultrasound were $41.68\text{ m}^2\text{ g}^{-1}$ and $22.39\text{ m}^2\text{ g}^{-1}$, respectively. The SEM images of the fresh synthesized Pd-Fe⁰ nanoparticles in the presence of 40 kHz ultrasound, and the aged (after 300 min) Pd-Fe⁰

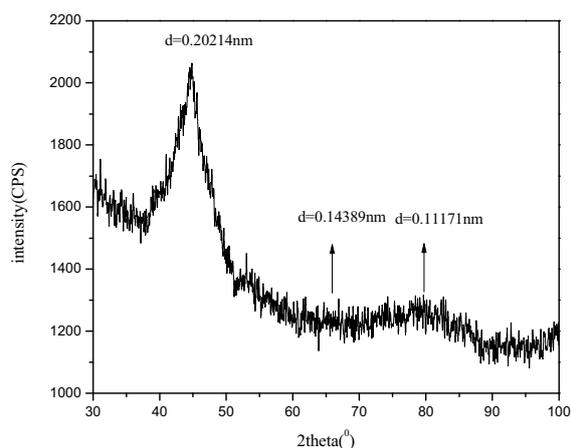
nanoparticles prepared in presence of 40 kHz ultrasound are shown in Fig. 1 (a, b). Fig. 1 (a) shows many Pd-Fe⁰ nanoparticles aggregate to form flocks and dendrites. After 300 min of reaction, the white platelet-shaped crystals appeared on the surface of Pd-Fe⁰ nanoparticles and fraction of Pd-Fe⁰ nanoparticle's diameter getting larger (Fig. 1(b)), suggests the formation of iron oxides resulting from iron corrosion. These minerals were likely composed of FeOOH, or Fe_3O_4 [9]. This is generally agreement with our observation in XRD patterns. Fig. 1(e, f) shows the XRD patterns of the fresh and the 300 min reacted Pd-Fe⁰ nanoparticles prepared 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-Fe⁰ 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 agrees with the previous work [10].



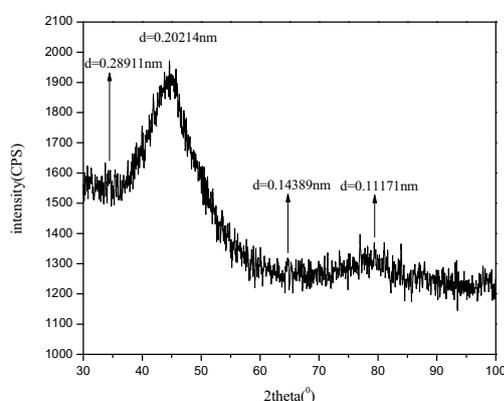
(a)



(b)



(c)



(d)

Figure 1. (a) SEM image of fresh synthesized Pd-Fe⁰ nanoparticles in the presence of 40 kHz ultrasound, (b) SEM image of reacted Pd-Fe⁰ nanoparticles synthesized in the presence of 40 kHz ultrasound (300 min), (c) XRD patterns of fresh synthesized Pd-Fe⁰ nanoparticles in the presence of 40 kHz ultrasound and (d) XRD patterns of reacted Pd-Fe⁰ nanoparticles synthesized in the presence of 40 kHz ultrasound.

3.2 Comparisons on 2-Cl BP catalytic reductive dechlorinated efficiency by Pd-Fe⁰ nanoparticles synthesized in different methods

Effects of different Pd-Fe⁰ nanoparticles prepared methods on 2-Cl BP catalytic reductive dechlorination were investigated at initial 2-Cl BP concentration of 10 mg L⁻¹, Pd-Fe⁰ nanoparticles dosage of 3 g L⁻¹, Pd content of 0.8 wt. %, initial pH value of 3.0, reaction temperature of 25 °C and mechanical stirring speed of 600 rpm. Fig. 2 shows reductive dechlorinations of 2-Cl BP by Pd-Fe⁰ nanoparticles prepared in different methods.

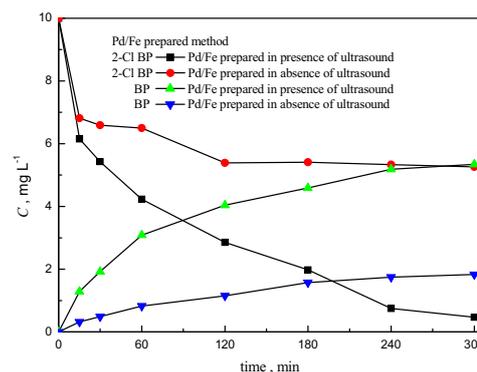


Figure 2. Effects of Pd-Fe⁰ nanoparticles prepared methods on 2-Cl BP dechlorination

2-Cl BP was first adsorbed by Pd-Fe⁰ nanoparticles, then reduced to BP. No other chlorinated intermediates or final organic products were found. The concentration of 2-Cl BP decreased rapidly and the removal rate reached 80.2% in 180 min, then further improved to nearly 95.3% in 300 min for Pd-Fe⁰ nanoparticles prepared in the presence of 40 kHz ultrasonic irradiation. However, only about 45.8% and 47.4% of the removal rate were obtained for Pd-Fe⁰ nanoparticles prepared in the absence of ultrasonic irradiation at the same stages, respectively. Obviously, the catalytic reductive chlorination process quickly proceeded with bimetallic Pd-Fe⁰ nanoparticles synthesized in the presence of ultrasonic irradiation than with bimetallic Pd-Fe⁰ nanoparticles prepared in the absence of ultrasonic irradiation. So, highly dispersed bimetallic Pd-Fe⁰ nanoparticles were synthesized in the presence of 40 kHz ultrasonic irradiation during the following experiments.

3.3 Effects of Pd content over Fe⁰ on 2-Cl BP reductive dechlorination

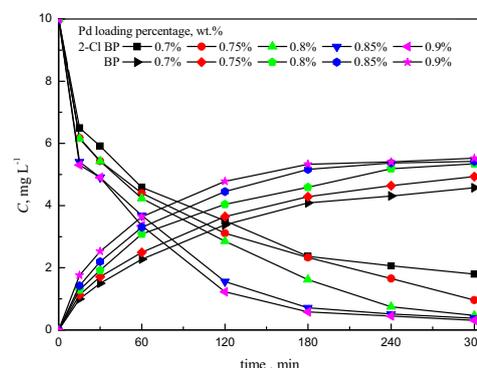


Figure 3. Effects of Pd loading content over Fe⁰ in Pd-Fe⁰ nanoparticles on 2-Cl BP dechlorination

Fe⁰ can enhance the hydrogenolysis reaction in which a chlorine atom in the organochlorides is replaced by a hydrogen atom. Palladium is an excellent catalyst for the hydrogenolysis reaction. Co-existence of Pd and Fe⁰ in the nanoparticles has been confirmed to be very

effective to quicken the catalytic reductive dechlorination reaction. Then, the Pd content over Fe^0 on Pd- Fe^0 nanoparticles may be one of the important influential factors on the reductive dechlorinated ratio. As Fig. 3 shows the efficiencies of reductive dechlorination and BP formations were obviously promoted as Pd content over Fe^0 increased from 0.70 to 0.90 wt. %. The removal ratio of 2-Cl BP reached from 82 to 97% within 300 min. The increase in the Pd loading content over Fe^0 from 0.75 to 0.85 wt. % only caused slight improvement to the 2-Cl BP removal percentage. The most likely cause for this is that the maximum Pd coverage is less than one layer, and in this way, the loss of available catalytic reactive sites due to the overlapping between Pd atoms can be excluded. Nonetheless, the amount of hydrogen gas absorbed by Pd atoms promoted with the increasing Pd loaded content over Fe^0 [11], and so make possible to accelerate the ratios of dechlorination and BP formations. The slight improvement of the removal ratio at Pd content over $\text{Fe}^0 > 0.80$ wt. % is that the accumulation of excessive hydrogen gas hinders the contact between 2-Cl BP and Pd- Fe^0 nanoparticles, and reduces the surface area available for 2-Cl BP dechlorination. This phenomenon is in agreement with previously reported studies [6,10]. Pd loading content over Fe^0 in bimetallic Pd- Fe^0 nanoparticles was selected at about 0.80 wt. % for optimized and efficient reductive dechlorination and yet minimal palladium content over Fe^0 .

3.4 Effects of Pd- Fe^0 nanoparticles dose on 2-Cl BP reductive dechlorination

Because the reductive dechlorination by Pd- Fe^0 nanoparticles happens on the surface of bimetallic Pd- Fe^0 nanoparticles, therefore bimetallic catalyst nanoparticles to 2-Cl BP ratio (g bimetallic Pd- Fe^0 nanoparticles /mg 2-Cl BP) is also an important influential factor. The quantity of available surface area is among the most significant experimental variables affecting 2-Cl BP reductive dechlorination efficiency. With increasing the dose of Pd- Fe^0 nanoparticles in the solution, it is insignificant to the final removal ratio in excess of Pd- Fe^0 nanoparticles dose. However, it will accelerate the initial reacted velocity and provide more active sites of Pd- Fe^0 nanoparticles for collision with 2-Cl BP during the reductive reaction. Effects of different Pd- Fe^0 nanoparticles dose on 2-Cl BP dechlorination were investigated as shown in Fig. 4. With the addition of the Pd- Fe^0 nanoparticles dose from 5 to 9 g L^{-1} , obviously differences were detected, the removal ratio of 2-Cl BP increased from 63 to 91% after 180 min of the reaction. Increasing the Pd/Fe nanoparticles dose means the larger catalysts surface area. The higher the catalysts surface area concentration is, the faster the reaction velocity. The removal ratio of 2-Cl BP is similar for a dose of Pd- Fe^0 nanoparticles of 7 or 8 g L^{-1} after 300 min of the reaction. Hence, the appropriate dose of Pd- Fe^0 nanoparticles in the level of 7 g L^{-1} is chosen for 2-Cl BP reductive dechlorination.

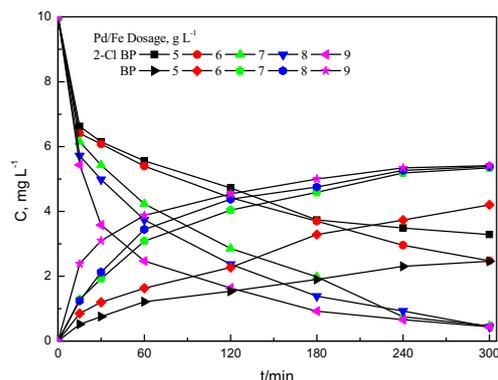


Figure 4. Effects of Pd- Fe^0 nanoparticles dose on 2-Cl BP dechlorination

3.5 Effects of the initial pH value on 2-Cl BP reductive dechlorination

Initial pH value in aqueous solution is an important influential parameter in catalytic reductive dechlorination of organic chlorinated compounds using Fe^0 . Low pH prefers more Fe^0 surface available for hydrogenolysis reaction with the chlorinated molecules or at least increase the corrosion velocity, leading to generate of chloride ions. Fig. 5 shows the effect of different initial pH values on the 2-Cl BP reductive dechlorination by bimetallic Pd- Fe^0 nanoparticles. Prior to initializing reaction, all reactant solutions were adjusted to different pH values by dilution with H_2SO_4 and NaOH , and during the reaction pH values were not adjusted. When the initial pH values changed from 3, 5, 7 to 9, the removal ratios of 2-Cl BP dropped from nearly 95.3, 70.6 to 54.8%, respectively in 300 min. The increase of initial pH values of the reactant solutions from 7 to 9, leads to the reactant solution change from acidic to alkaline condition, consequently the removal ratios of 2-Cl BP dropped obviously. It shows that the presence of H^+ largely promotes the 2-Cl BP reductive dechlorination rate. The feasible reasons may be that (1) the surface of Pd- Fe^0 nanoparticles would be oxidized inevitably during the synthesis and storage, which had been confirmed by the earlier published literatures [12]. However, at lower pH values, the oxides on the catalyst particles surface were dissolved, and the active sites of the catalyst particle surface were exposed and it was beneficial to the reductive reaction; (2) at lower pH values, Fe^0 corrosion could be accelerated, producing enough hydrogen (or hydrogen atoms), which were beneficial to hydrogenation reaction [13]; (3) Iron corrosion in solution of pH higher than 7 tends to form a passive film of iron oxides and hydroxide on Fe^0 surface, which inhibits further reductive reaction. In the previous study [10,14], detection of the solution pH during the entire period of the hydrogenation reaction, and ferrous ions/total iron ions produced in the reaction could further support our assumptions.

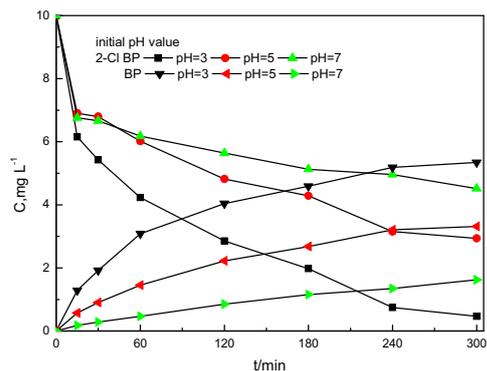


Figure 5. Effects of solution initial pH on 2-Cl BP dechlorination

4 Conclusion

The experimental results indicate that the prepared bimetallic Pd-Fe⁰ nanoparticles in the presence of ultrasound was a better technique to enhance dispersion and the surface special properties. 2-Cl BP reductive dechlorination efficiency was dependent on a series of influential factors including highly dispersed bimetallic Pd-Fe⁰ nanoparticles prepared method, Pd-Fe⁰ nanoparticles dose, Pd loading content over Fe⁰ and initial pH values. Up to 95.0% of 2-Cl BP was removed after 300 min reaction with these experimental conditions: initial 2-Cl BP concentration 10 mg L⁻¹, Pd loading content over Fe⁰ 0.8 wt. %, Pd-Fe⁰ nanoparticles prepared in the presence of 40 kHz ultrasonic irradiation available dose 7 g L⁻¹, initial pH value 3.0, and reaction temperature 25 °C. The removal ratio of 2-Cl BP degradation increased with the increasing Pd-Fe⁰ nanoparticles dosage, and with the decrease of pH values.

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