



Catalytic dechlorination of polychlorinated biphenyls in soil by palladium–iron bimetallic catalyst

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ABSTRACT

Pd/Fe bimetallic particles were synthesized by chemical deposition and used to dechlorinate 2,2',4,5,5'-pentachlorobiphenyl in soil. Batch experiments demonstrated that the Pd/Fe bimetallic particles could effectively dechlorinate 2,2',4,5,5'-pentachlorobiphenyl. Dechlorination was affected by several factors such as reaction time, Pd loading, the amount of Pd/Fe used, initial soil pH, and 2,2',4,5,5'-pentachlorobiphenyl concentration. The results showed that higher Pd loading, higher dosage of Pd/Fe, lower initial concentration of 2,2',4,5,5'-pentachlorobiphenyl and slightly acid condition were beneficial to the catalytic dechlorination of 2,2',4,5,5'-pentachlorobiphenyl. The degradation of 2,2',4,5,5'-pentachlorobiphenyl, catalyzed by Pd/Fe followed pseudo-first-order kinetics.

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1. Introduction

Polychlorinated biphenyls (PCBs) are a group of chemicals comprising 209 congeners ranging from mono- to decachlorobiphenyl that are very persistent to degradation and hazardous to the biosphere [1]. PCBs were produced in large volumes in the United States beginning in 1929. The excellent stability and thermoelectric properties of PCBs made them especially suitable as a heat-transfer media in electrical transformers and capacitor [2]. Because of widely publicized biological effects such as induction of skin lesion and tumors in animals, manufacture of PCBs ceased in 1977 under the Toxic Substances Control Act. Between 1965 and 1974, about 10 million kg of PCBs were produced in China. Ninety percent of PCBs ever produced are trichlorobiphenyl and 10% are pentachlorobiphenyl [3]. However, because of improper disposal and accidental leaks from transformers, heat exchangers, and hydraulic systems, a large fraction of all the PCBs ever produced are still present in the environment. It has been estimated that one-third of PCBs of the total quantity produced have been released into the environment as contaminants in soil and river, lake, and ocean sediments [4]. The PCBs are distributed throughout the biological food chain via bioac-

cumulation and may cause serious health problems in humans [5]. Therefore, remediation of PCB-contaminated soils, groundwater, and sediments has become a major problem in environmental management.

At present the most widely accepted method for removal of PCBs is by using specialty incinerators that are capable of reaching a temperature of 1200 °C [6]. Incineration, however, often produces more toxic compounds (polychlorinated dibenzofurans and polychlorinated dibenzodioxins) if the temperature is not carefully controlled. Several new remediation techniques for PCBs are currently under development including bioremediation, γ radiolysis, and dechlorination using zero-valent metals and other chemical reagents. Destruction of PCBs by zero-valent iron is one of the latest innovative technologies for environmental remediation. Different classes of compounds including halogenated organics, azoaromatics, nitroaromatics, and inorganics can be dechlorinated by zero-valent iron [7–14]. Laboratory research in the past few years has shown that zero-valent iron can also degrade PCBs, for example, dechlorination of PCBs by zero-valent iron has been demonstrated at temperatures of about 400 °C in the absence of water [2]. However, when temperature was 200 °C or below, little dechlorination of PCBs occurred. Research regarding reductive dechlorination with zero-valent iron led to the discovery that a bimetallic preparation of iron and palladium was a superior reductant for chlorinated organics. Pd/Fe bimetal, having catalytic ability,

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dramatically accelerated the reductive dechlorination [15–17]. The Pd/Fe bimetallic complexes have been found to degrade PCBs with all the chlorine replaced by hydrogen to yield biphenyl [18–20].

Previous studies focused on PCB transformation by zero-valent iron and Pd/Fe bimetal in aqueous system, and no work describing the use of zero-valent iron and Pd/Fe to remediate PCBs contaminated soil at room temperature was found in the peer-viewed literature. Therefore, this study focused on 2,2',4,5,5'-pentachlorobiphenyl transformation by Pd/Fe in a soil system. We report here an efficient method of synthesizing Pd/Fe bimetallic particles and the use of these metal particles for transformation of PCBs. The purpose of this work was to conduct a feasibility study for remediation of PCB-contaminated soil by using Pd/Fe. The experimental parameters for the process, such as reaction time, Pd loading, dosage of Pd/Fe, and initial soil pH, and applicable concentration of 2,2',4,5,5'-pentachlorobiphenyl were determined. Thus, the experimental results obtained from the batch system may be expected optimistically to provide additional possibility of application for full-scale site remediation operation or joint bioremediation to the remediation of contaminated soil.

2. Materials and methods

2.1. Chemical reagents

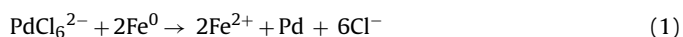
2,2',4,5,5'-Pentachlorobiphenyl ($C_{12}H_5Cl_5$, 99.4 ± 4%, hereafter abbreviated to BZ#101) and 2,2',4-trichlorobiphenyl ($C_{12}H_7Cl_3$, 100 ± 4%, hereafter abbreviated to BZ#17) were purchased from AccuStandard Inc., New Haven, CT, USA and used without further purification. Iron metal powder (Fe^0 , 93%) was purchased from Shanghai Metal Machining Factory, China. Potassium hexachloropalladate (K_2PdCl_6 , 99%) was purchased from Aldrich Chemical Company, Milwaukee, WI, USA. HPLC grade hexane and HPLC grade acetone were purchased from Tianjin Concord Technical Company, China.

2.2. Experimental soil

Surface soil sample (top 20 cm) was collected from the Ecological Station of the Shenyang Institute of Applied Ecology, Chinese Academy of Sciences. Analysis of the brown soil provided the following data: TOC, 1.78%; TN, 0.11%; TP, 0.035%; TK, 0.604% and pH 6.9 and no detectable PCBs. Prior to testing, soils were air-dried, passed through a 2-mm sieve, and stored at 4 °C.

2.3. Pd/Fe preparation and characterization

Pd/Fe bimetallic catalysts were prepared using a method that was a slightly modified version of the method used by Grittini et al. [20]. Iron particles in a fine (<10 μm) powder were pretreated by washing with 0.1 mol/L H_2SO_4 , and then rinsed with successively with acetone and distilled water to remove most of the surface oxide layers and undesired organic compounds prior to palladisation. An aqueous solution of potassium hexachloropalladate was prepared and used to deposit enough elemental palladium on the iron powder to give 0.05% (w/w) Pd coverage. The palladium was deposited on the iron surface by the redox reaction (1), in which an orange solution of K_2PdCl_6 was stirred with the iron powder until a pale yellow solution was formed in a few minutes. The Pd/Fe bimetallic system was then rinsed with distilled water and used for reaction without drying.



The surface area (BET adsorption area) of iron and palladised iron was measured using the nitrogen adsorption method with a

ST-03 adsorption apparatus (Beijing Beifenruili Analytic Instrument (Group) Co. Ltd.). Prior to the measurements, Pd/Fe was obtained with the same way as described above and dried at 100 °C for 6 h under a flow of N_2 . Morphology of the particles was observed using a JSM-T300 (JEOL, Japan) scanning electron microscope (SEM) at 20 kV a magnification of 20,000.

2.4. Batch experiment procedure

The target compound was spiked with the soil that contains no BZ#101 to simulate the contaminated soil. Ten milliliters of BZ#101 hexane solution (10 mg/L) was added to 2 g uncontaminated soil sample to produce to a final BZ#101 level of 50 mg/kg. After the spiked samples were left in a fume hood for 24 h to allow the hexane to evaporate, leaving the target compound distributed homogeneously in the soil.

Experiments were conducted in a glass vial containing 2 g of soil. Both the Fe^0 and Pd/Fe were added into spiked soil samples with 2-mL deionized water and then shaken at 150 rpm at a constant temperature of 25 °C. The experimental variables were reaction time, Pd loading, dosage of Pd/Fe, initial soil pH and BZ#101 concentration. All of the samples were conducted in triplicate, and blank samples were carried out using deionized water without Fe^0 and Pd/Fe addition.

2.5. Sample extraction and cleanup

The soil was freeze-dried in order to avoiding volatilization after reaction. Two grams of freeze-dried soil sample, together with 10 mL mixed solvent (5 mL *n*-hexane and 5 mL acetone) was added to the extraction vessel and extracted in an ultrasonic bath for 1 h. The mixture was centrifuged and the supernatant was collected. The soil sample was re-extracted twice as described before. The two extracts were combined dried with anhydrous sodium sulfate and then concentrated to around 1 mL by rotary evaporation. The concentrated supernatants were passed through a silica gel column with a layer of 0.5 g Na_2SO_4 at the top. The silica gel column was eluted with 10 mL hexane and the eluate was concentrated down to 1 mL by rotary evaporation. The solution was finally concentrated to below 100 μL under a gentle stream of pure nitrogen, and then was transferred to a glass micro-vial for gas chromatograph (GC) injection and made up to 100 μL.

2.6. BZ#101 analysis

A Hewlett-Packard 6890 GC system equipped with a ^{63}Ni electron capture detector (μECD , Agilent Technology Co., USA) was used to perform the gas chromatographic analysis using the splitless mode. The solution was chromatographed on a 30 m × 0.32 mm i.d. HP-5 capillary column with a film thickness of 0.25 μm at a pressure of 50 kPa. High purity (99.99%) nitrogen was used as carrier gas at 1.4 mL/min. The temperature program was 50 °C for 2 min, from 50 °C to 280 °C at 15 °C/min, from 280 °C to 290 °C at 10 °C/min, then 290 °C for 2 min. The injector and the detector were set at 270 °C and 300 °C, respectively. The chromatographs were recorded and analyzed using HP Chem-station software. BZ#101 was qualitatively identified by comparing retention times with standard samples and then quantified using a calibration curve.

3. Results and discussion

3.1. Characterization of Pd/Fe

The surface morphology of both the Fe and Pd/Fe bimetallic catalysts is shown in Fig. 1. The surface of Fe is smooth, but the surface of

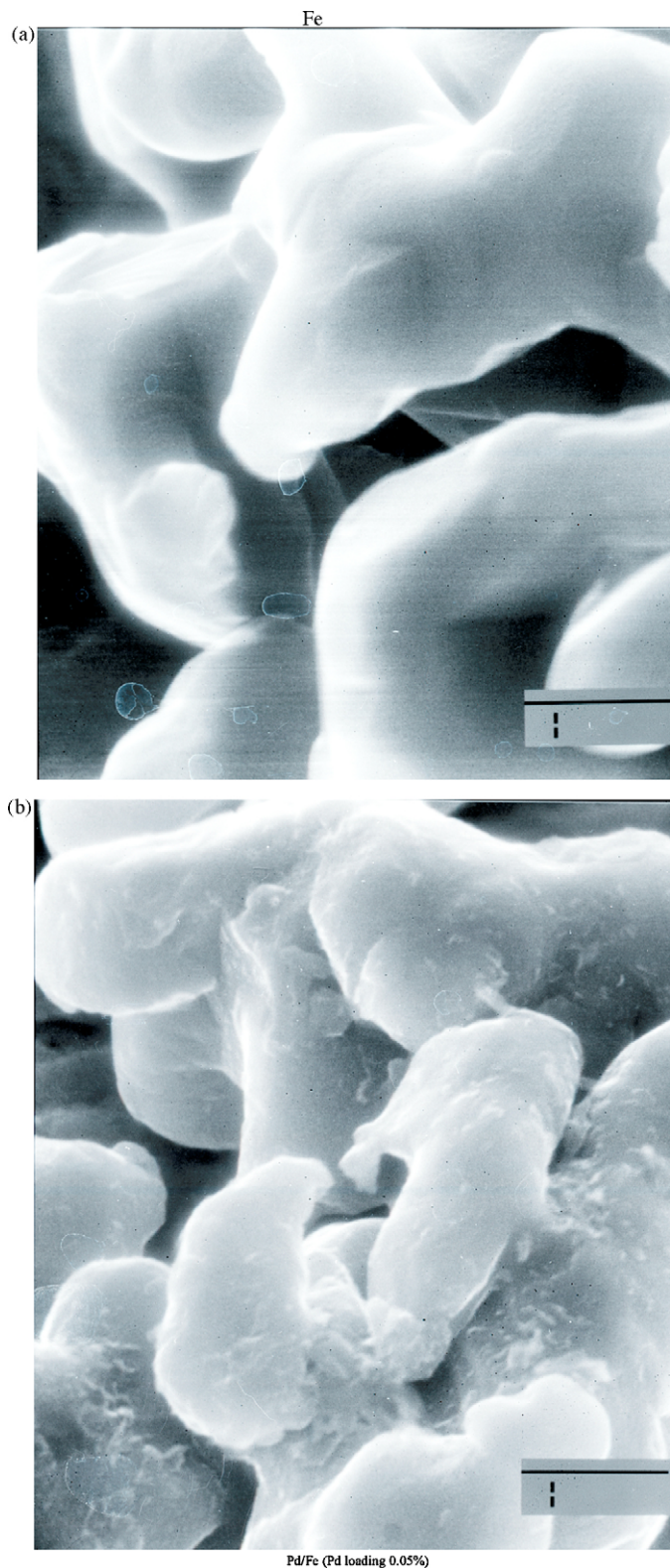


Fig. 1. SEM images of un-palladised (a) and palladised (b) iron particles.

Pd/Fe is rough due to palladium deposition on the iron surface. The specific surface areas of the Fe and Pd/Fe measured by the BET-N₂ method were 0.67 m²/g and 0.92 m²/g, respectively. The increased surface indicated that Pd is dispersed on the surface rather than forming clumps on the iron powder surface. It is consistent with

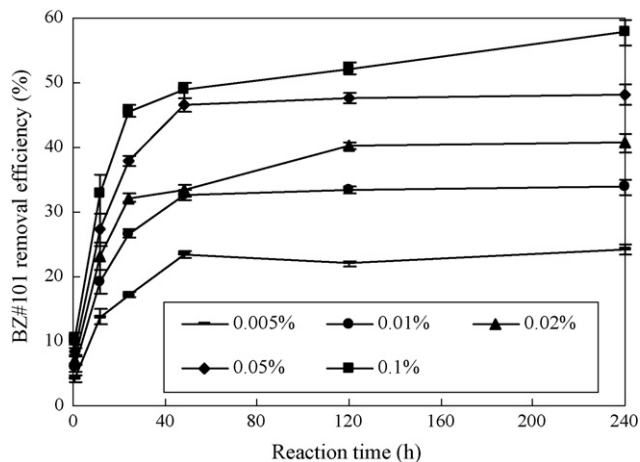


Fig. 2. Effect of Pd loading on the removal efficiency of BZ#101: C₀ = 50 mg/kg, Pd/Fe powder = 0.5 g/g soil, T = 25 °C, pH 6.9.

the information revealed in the SEM image of the catalyst. Most of the Pd/Fe particles are in the size range of 1–2 μm.

3.2. Effect of some experimental parameters on dechlorination of BZ#101

3.2.1. Effect of Pd loading on dechlorination of BZ#101

Pd/Fe bimetallic particles with different palladium loadings were prepared and their Pd loadings (wt%) were 0.005%, 0.01%, 0.02%, 0.05% and 0.1%. However, the actual Pd loading could vary slightly because a small amount of fine iron particles and Pd/Fe particles were lost during acid washing and the post-deposition water washing. Thus, the actual Pd loading were 0.0041%, 0.0078%, 0.016%, 0.039% and 0.087%, respectively. (The bulk loading of palladium in the bimetallic system was quantified by Hitachi 180-50 atomic absorption spectrometer (AAS).) The variation of removal efficiency for the same reaction period under different Pd loadings in the bimetallic particles is presented in Fig. 2. With the increase of Pd loading, the removal efficiency of BZ#101 increased correspondingly. The final removal efficiencies of BZ#101 corresponding to Pd loadings of 0.005%, 0.01%, 0.02%, 0.05% and 0.1% were 20.3%, 33.8%, 40.7%, 48.2% and 57.8%, respectively. The results demonstrated that higher Pd loading is favorable for the dechlorination of BZ#101.

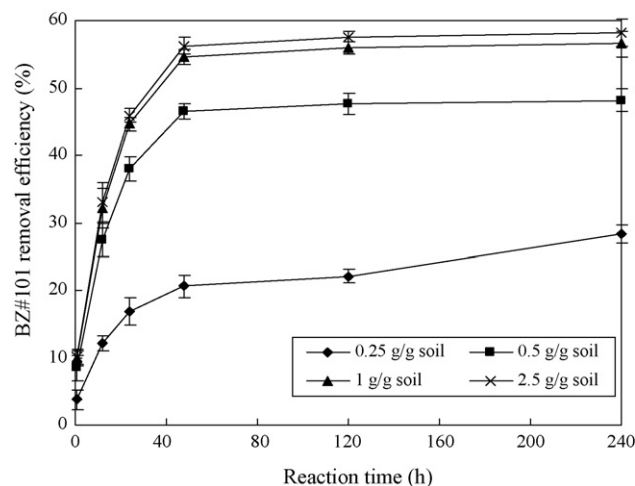


Fig. 3. Effect of added amounts of Pd/Fe on the removal efficiency of BZ#101: C₀ = 50 mg/kg, Pd loading = 0.05%, T = 25 °C, pH 6.9.

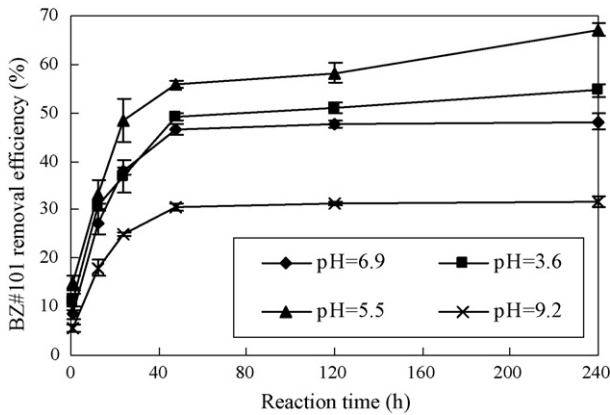


Fig. 4. Effect of initial pH on the removal efficiency of BZ#101: $C_0 = 50 \text{ mg/kg}$, Pd loading = 0.05%, Pd/Fe powder = 0.5 g/g soil, $T = 25^\circ\text{C}$.

We suggest that the promotion effect of palladium on the dechlorination of BZ#101 occurs for two reasons—catalytic functions of palladium surface and galvanic cell effects of the bimetallic system. Palladium could promote dechlorination reactions through the formation of strong Pd–Cl bonds, thereby accelerating the dissociation of chlorinated hydrocarbons [21]. We can thus assume that same process takes place for BZ#101. Furthermore, the hydrogen gas produced during reaction process is adsorbed on palladium and dissociated into atomic H, one of the strongest reductants for the dechlorination reactions. The presence of the less active palladium on the iron surface certainly creates many galvanic cells, in which iron acts as the anode and palladium, cathode. The electrons transferred from iron to palladium are contributed to the chlorine atoms to form chloride ions [22–24].

It is therefore presumed that the dechlorination of BZ#101 by Pd/Fe probably occurs on the palladium surface. BZ#101 molecules are adsorbed on the palladium surface through forming the strong Pd–Cl bonds. The H atoms, formed on the palladium surface, and the electrons, released from iron, move to the Cl atoms. Thus BZ#101 is dechlorinated and BZ#17 is produced.

3.2.2. Effect of Pd/Fe dosage on dechlorination of BZ#101

The effect of Pd/Fe dosage is one of the major factors that affect the removal efficiency as shown in Fig. 3. Fig. 3 shows BZ#101 removal efficiency as a function of time by various Pd/Fe doses from 0.25 g/g soil to 2.5 g/g soil with a mixing speed of 150 rpm. From experimental data, the removal efficiency by Pd/Fe dosage of

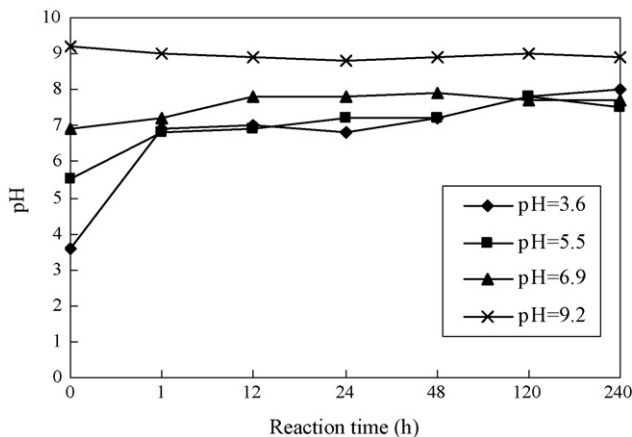


Fig. 5. The variation of pH value with time at the different initial pH conditions.

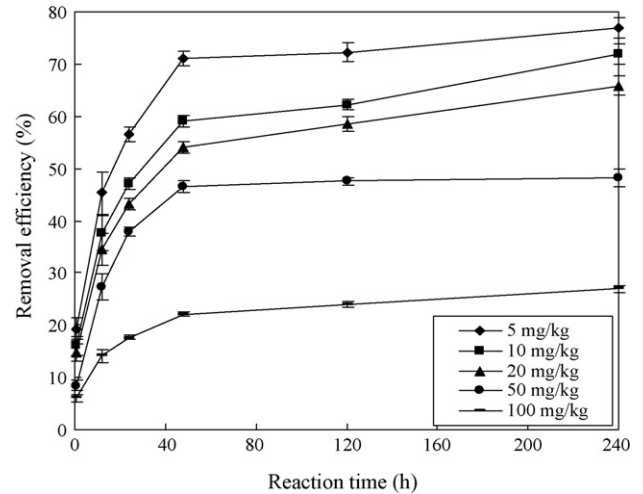


Fig. 6. Effect of initial concentration on the removal efficiency of BZ#101, Pd loading = 0.05%, Pd/Fe powder = 0.5 g/g soil, $T = 25^\circ\text{C}$, pH 6.9.

0.25 g/g soil, 0.5 g/g soil, 1 g/g soil, and 2.5 g/g soil reached 28.3%, 48.2%, 56.5%, and 58.2%, respectively. The results show that the removal efficiency of BZ#101 was dependent on Pd/Fe dosage and the removal efficiency increased with the increase of Pd/Fe dosage. Increase of the dosage of Pd/Fe particles speeded up substantially the initial reaction, whereby BZ#101 collides with the greater number of active surface sites of iron particles and the greater area of adsorptive Pd sites. The larger amount of Pd/Fe catalyst relative to the amount of chlorine to be removed allows for more complete reaction before passivation of the surface occurs.

3.2.3. Effect of initial soil pH on dechlorination of BZ#101

The experiments were conducted under various pH conditions, which were adjusted by dilute oxalic acid solution or aqueous ammonia. Without adjustment, the pH value for the reaction was 6.9. The results are shown in Fig. 4. The removal efficiency of BZ#101 increased more rapidly at pH 5.5 than in other pH conditions. The results demonstrated that weak acid condition favors the dechlorination of BZ#101. In weak acid conditions such as pH 5.5, the

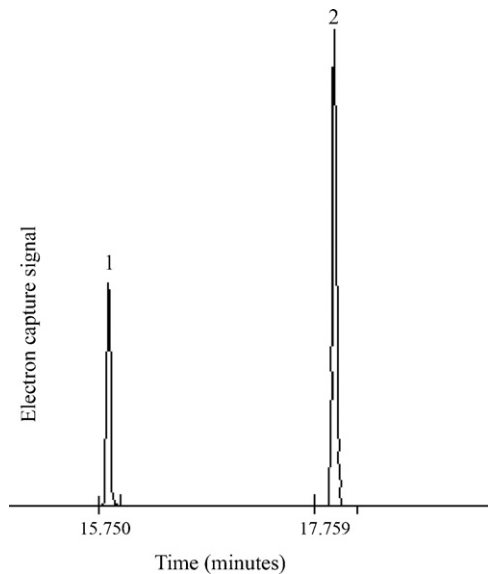


Fig. 7. Representative gas chromatograms of reaction solution after 48 h: Peak 1, BZ#17 and Peak 2, BZ#101.

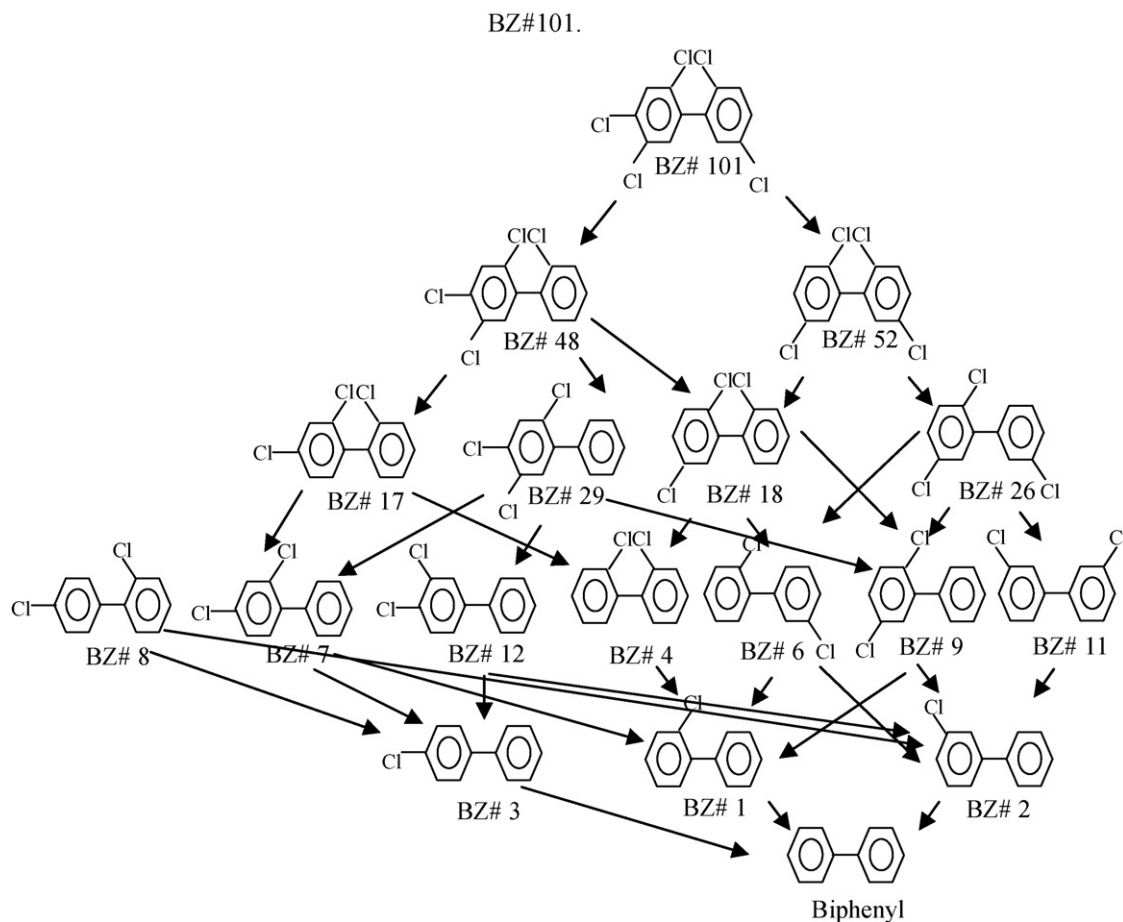


Fig. 8. Possible reduction pathways of BZ#101.

amount of H^+ is sufficient to produce H_2 through the corrosion of iron, thus the reduction of BZ#101 progresses more readily. However, at lower pH value of 3.6, more intensive corrosion of iron could result in the loss of Pd, and inhibition of the reaction as the surface becomes covered by H_2 becomes apparent at the lower pH. Therefore, pH 3.6 is not the most suitable for BZ#101 dechlorination, as was also found in Wei et al. [22] experiment.

Fig. 5 shows the variation in the pH values with time at the different initial pH conditions. As the initial pH values were 3.6, 5.5 and 6.9, the pH values increased to between 7 and 7.8 after 1 h, then the changes were small until the end of reaction. The change in pH value was small at initial pH value of 9.2.

3.2.4. Effect of initial concentration of BZ#101 on dechlorination of BZ#101

Five initial concentrations of BZ#101 in soil (i.e., 5 mg/kg, 10 mg/kg, 20 mg/kg, 50 mg/kg and 100 mg/kg) were studied in the experiments. Fig. 6 shows that the BZ#101 removal efficiency decreased when the initial concentrations increased during the same reaction period. The final removal efficiency of BZ#101 at different treatment levels were 76.9%, 71.9%, 65.9%, 48.2%, and 26.9%, respectively.

3.3. Dechlorination of BZ#101 and kinetics

The results of Section 3.2 showed that the BZ#101 could be dechlorinated by Pd/Fe bimetal system. The only product observed from the reduction of BZ#101 was BZ#17, identified in a hexane extract of the reaction mixture by comparison of retention times

with a standard BZ#17 solution (Fig. 7). These results show that the dechlorination of BZ#101 occurs in soil, the chlorine atoms being replaced by hydrogen atoms to yield lower chlorine-substituted counterparts. The exclusive formation of BZ#17 shows that *ortho* position chlorines are much more resistant to reductive dechlorination than the *para* and *meta* ones. This phenomenon was also observed by Yak et al. [1]. Possible reduction pathway of BZ#101 is presented in Fig. 8 [1].

The removal efficiency–time curve of BZ#101 is presented in Figs. 2–4 and 6. The removal efficiency can be expressed as the following equation:

$$\text{removal efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

where C_0 is the initial concentration of BZ#101 and C is the concentration of BZ#101 after reaction.

Previous studies [9,25,26] have shown that the rate of degradation of chlorinated solvents by Fe^0 follows a pseudo-first-order reaction with respect to contaminant concentration as depicted in Eq. (3). The pseudo-first-order equation is generally expressed as follows:

$$-\frac{dC_p}{dt} = kC_p \quad (3)$$

where k is the observed rate constant of pseudo-first-order reaction and C_p expresses the concentration of BZ#101. The rate constants can be obtained by regression of a natural log of BZ#101 concentration with respect to reaction time according to the following

Table 1
Model regression parameters for the BZ#101 removal by Pd/Fe in soil

Pd loading (%)	k^a (h^{-1})	$t_{1/2}$ (h)	R^2	BZ#101 initial concentration	k^a (h^{-1})	$t_{1/2}$ (h)	R^2
0.005	0.0044	158	0.9252	5	0.0209	33	0.9684
0.01	0.0067	103	0.8987	10	0.0145	48	0.9492
0.02	0.0065	107	0.7467	20	0.0125	55	0.942
0.05	0.0109	64	0.9159	50	0.0109	64	0.9159
0.1	0.0113	61	0.7993	100	0.0037	187	0.9055
Pd/Fe dosage (g/g soil)	k^a (h^{-1})	$t_{1/2}$ (h)	R^2	pH	k^a (h^{-1})	$t_{1/2}$ (h)	R^2
0.5	0.0039	178	0.886	3.6	0.0111	62	0.9438
1	0.0109	64	0.9159	5.5	0.0137	51	0.9156
2	0.014	50	0.9276	6.9	0.0109	64	0.9159
5	0.0147	47	0.9301	9.2	0.0062	112	0.8963

R^2 is the linearity of the data fitting.

^a 95% confidence interval was provided for all the values of first-order rate constant.

equation:

$$\ln \frac{C_p}{C_{p0}} = -kt \quad (4)$$

where C_{p0} is the initial concentration of BZ#101.

The half-life is calculated using the following equation, which was derived from Eq. (4) by replacing C_p with $C_{p0}/2$.

$$t_{1/2} = \ln \frac{2}{k} = \frac{0.6931}{k} \quad (5)$$

Thus pseudo-first-order kinetics was also expected to apply to the reaction in this study. A linear relation between $-\ln C_p/C_{p0}$ and reaction time reveal that the dechlorination reaction followed approximately a pseudo-first-order process for the first 48 h of treatment time. The rate of dechlorination between 48 h and 240 h slowed significantly, and the reaction order was no longer well defined, as was also in the Yak et. al [1] experiment. With the increase of reaction time, the reaction deviated from the pseudo-first-order reaction kinetics, probably due to the formation of surface passivation layers or due to the precipitation of meta hydroxides (e.g., $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$) and metal carbonates (e.g., FeCO_3) on the surface of iron. The values of k , being a first-order rate constant and half-life are presented in Table 1. The k values increased as the Pd loading increased and BZ#101 initial concentration decreased, the related coefficient are 0.8910 and 0.9188, respectively, which reach the remarkable level ($r_{0.05} = 0.878$; $n = 3$). The k values increased as Pd/Fe dosage increased. The k value is higher at pH 5.5 than in other pH conditions.

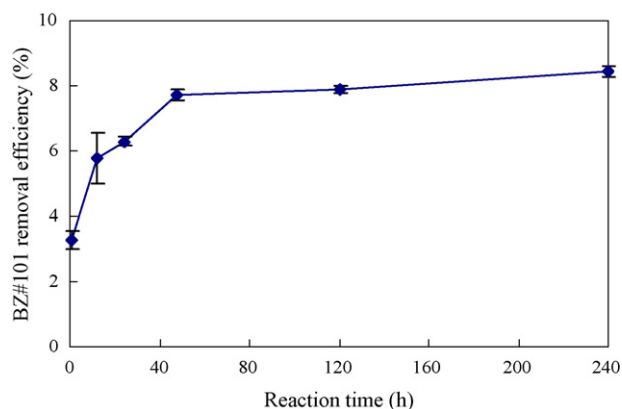


Fig. 9. The reaction of BZ#101 with un-palladised Fe: $C_0 = 50$ mg/kg, Fe powder = 0.5 g/g soil, $T = 25$ °C, pH 6.9.

3.4. Reaction of BZ#101 with un-palladised iron particles

To investigate the differences between the Pd/Fe particles and un-palladised iron particles, a batch experiment with reduced iron powders was conducted under the same experimental conditions. The result is presented in Fig. 9. After 240 h contact time, 91.6% of the parent BZ#101 remained in the solution. Our results show that the removal efficiency with un-palladised iron was much lower than with the Pd/Fe bimetal system, and this experiment also confirmed that Pd could promote dechlorination reactions.

4. Conclusions

The experimental results suggest that the Pd/Fe bimetallic complex showed substantial activity in the removal of BZ#101 from soil at ambient temperature and pressure. The removal efficiency of BZ#101 benefited from an increase in the relative amount of Pd/Fe, an increase in the loading of palladium on the catalyst, extended reaction time and weak acid condition. It was found that the removal efficiency of BZ#101 in soil could reach 48.2% after 10 days of reaction with 0.5 g/g soil of Pd/Fe (Pd loading (0.05%)) and at an initial pH of 6.9. The removal efficiency increased as the contamination level decreased, and the best removal efficiency obtained was 73.8% at a BZ#101 level of 5 mg/kg and pH 5.5. The degradation of BZ#101 catalyzed by Pd/Fe followed the pseudo-first-order kinetics. Although the amount of Pd/Fe powder use would be huge for PCB-contaminated soil remediation when this technique is applied to the field, the amount of Pd/Fe could be decreased by adjusting the pH, temperature, Pd loading, etc.

As a result of this work, a method has been demonstrated wherein the toxicity of PCB pollutants will be greatly reduced and the biodegradability will be improved when compounds such as BZ#101 are reduced to lower-substituted counterparts or biphenyl. The present finding demonstrated the flexibility of catalytic reduction approach, which could be adjusted towards the complete removal of BZ#101 in soil media at room temperature. Such method could also be considered as a potential tool for the in situ remediation of groundwater and soil contaminated with PCBs.

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