Dechlorination of 3-Chlorobiphenyl by nZVI Particles Prepared in the Presence of 20 kHz Ultrasonic Irradiation

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Abstract: Nanoscale zero-Valent Iron (nZVI) particles were prepared in the presence of 20 kHz ultrasonic irradiation in order to enhance disparity and reactivity and simultaneously avoid agglomeration. Dechlorination of 3-chlorobiphenyl (3-Cl BP) by nZVI particles was investigated to understand its feasibility for an in situ remediation of contaminated groundwater. Experimental results showed that the induction of ultrasound during the preparation of nZVI further enhanced the removal efficiency of 3-Cl BP, meanwhile the Biphenyl (BP) formation rates increased obviously. The dechlorination rate was dependent on various factors including nZVI dosage, reaction temperature and initial pH values. The degradation of 3-Cl BP followed pseudo-first-order kinetics reaction.

Keywords: 3-Chlorobiphenyl (3-Cl BP), dechlorination, kinetics, nanoscale Zero-Valent Iron (nZVI), ultrasound

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 (O'brien *et al.*, 2005). The high stability, low aqueous solubility and high organic affinity of PCBs make them difficult to treat (Choi *et al.*, 2009; Borja *et al.*, 2005). This raises an urgent need for efficient reductive dechlorination methods to eliminate chloroaromatics from both concentrated industrial effluents and diluted polluted groundwater.

Many physical, chemical and biological remediation technologies have been proposed, including dredging, landfilling, incineration, biodecomposition, in *situ* capping and electrochemical degradation (Choi *et al.*, 2009; Borja *et al.*, 2005; Murphy *et al.*, 2006; Agarwal *et al.*, 2007b; Wiegel and Wu, 2000). Among them, 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 (Agarwal *et al.*, 2007a; Fang and Al-Abed, 2007). Previous studies have reported that the reductive dechlorination of chlorinated organic compounds by nZVI particles involves (Zhang *et al.*, 2010; Zhou *et al.*, 2010; Lowry and Reinhard, 2001):

- Chlorinated organic compounds in solution diffuse to nZVI particles surface and adsorb in the surface of nZVI particles

- The adsorbed chlorinated organic compounds takes reductive reaction under the influence of nZVI particles
- The organic compounds of reaction desorb from nZVI particles and diffuse to the bulk solution.

These results imply that the reductive reactions occur by electron transfer at the iron surface (Sayles *et al.*, 1997). Therefore, it is important to enhance the nZVI surface properties, such as surface tension, specific surface area, particles diameter, disparity and so on.

In order to obtain the stabilized and high reactive nZVI particles and decrease their agglomeration and accumulation in the effluent, ultrasound is applied to the preparation of nZVI particles. Acoustic cavitation can increase the surface area of the reactive solids and decrease particle diameter by causing particles to rupture (Zhang *et al.*, 2006; Suslick *et al.*, 1996). Herein, we report an efficient method of preparing nZVI particles with the help of ultrasound for better disparity and also avoiding the agglomeration. 3-chlorobiphenyl (3-Cl BP) was selected as a model compound due to its abundance in the contaminated groundwater. Meanwhile, other influential factors on 3-Cl BP reductive dechlorination, such as nZVI particles dosage, reaction temperature and initial pH values, were also investigated.

EXPERIMENTAL SECTION

Chemicals: 3-chlorobiphenyl (chemically pure, or AP grade) and biphenyl (CP grade) were purchased from the J&K Chemical Reagent Co., Ltd., China, $FeSO_4 \cdot 7H_2O$ (AR grade), $NaBH_4$ (AR grade)

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purchased from Tianjin Chemical Reagent Research Institute. All chemicals were used as received without further purification. 3-Cl BP is dissolved in a methanol/deoxygenated deionized water solution (50:50, *V/V*) and stored at 4°C. nZVI particles were synthesized immediately before use.

Experimental procedures: In the presence of 20 kHz and 150 W ultrasound, nZVI particles were prepared in a 500 mL three-necked flask under nitrogen gas. They were synthesized by drop wise addition of stoichiometric amounts of $NaBH_4$ aqueous solution into a flask containing $FeSO_4 \cdot 7H_2O$ solution simultaneously with mechanical stirring at 25°C.

3-chlorobiphenyl (3-Cl BP) dechlorination experiments were performed in the same three-necked flask into which nZVI particles were added. 3-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 nZVI particles into 500 mL of total reaction volume. The reaction solution was stirred under nitrogen flow to simulate anaerobic environment at 25°C. Aliquots of samples were periodically collected with glass syringes and the reaction was quenched by passing through 0.22 μm polyether sulphone (PES) membrane filters.

Methods of analysis: 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 (λ = 1.5418 A°).

Organic compounds, 3-Cl BP and BP were analyzed by SHIMADZU High Performance Liquid Chromatography. C18 Column, 150 mm×4.6 mm, mobile phase: $MeOH/H_2O$ (70/30, v/v), flow rate: 1.0 mL/min, detector: UV at 243 nm, sample size: 20 μL .

RESULTS AND DISCUSSION

nZVI particles characterization: The SEM images of the fresh nZVI particles prepared in the presence of ultrasound and the reacted (after 360 min) nZVI particles prepared in presence of ultrasound are shown in Fig. 1a and b.
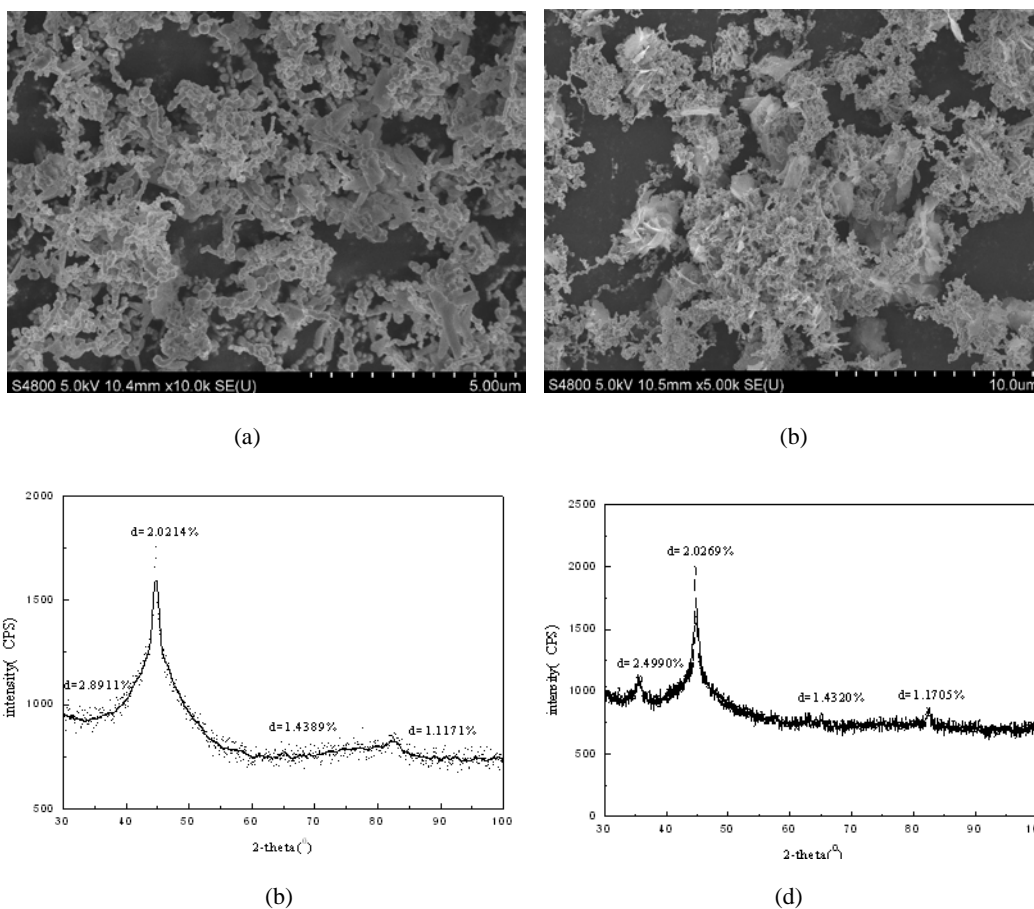

(a)

(b)

(b)

(d)

Fig. 1: (a) SEM image of fresh nZVI particles prepared in the presence of 20 kHz ultrasound, (b) SEM image of aged nZVI particles prepared in the presence of 20 kHz ultrasound (360 min), (c) XRD patterns of fresh nZVI particles prepared in the presence of 20 kHz ultrasound and (d) XRD patterns of aged nZVI

Figure 1a shows many nZVI particles aggregate to form flocks and dendrites. After 360 min of reaction, the white platelet-shaped crystals appeared on the surface of nZVI particles and fraction of the nZVI particle's diameter getting larger (Fig. 1e), suggests the formation of iron oxides resulting from iron corrosion in water. These minerals were likely composed of FeOOH or Fe_3O_4 (Zhou *et al*., 2010; Phillips *et al*., 2000; Huang and Zhang, 2006). This is generally consistent with our observation in XRD patterns. Figure 1d and e shows the XRD patterns of the fresh and the 360 min aged nZVI particles prepared in the presence of ultrasound. The XRD pattern for the fresh sample particles prepared in the presence of 20 kHz ultrasound 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 aged sample shows evidence of iron oxides, possibly Fe_3O_4 or Fe_2O_3, or their mixture. This agrees with the previous work (Wang *et al*., 2008).

Kinetic modeling of 3-Cl BP dechlorination by nZVI particles Previous studies showed that Polychlorinated Biphenyls (PCBs) were hydro-dechlorinated according to the following sequence of steps by nZVI particles (O'brien *et al*., 2005; Choi *et al*., 2009; Zhuang *et al*., 2011). In the following equations, 3-Cl BP and BP are the abbreviated forms of 3-chlorobiphenyl and biphenyl, respectively:

$$3\text{-}Cl\,BP \xrightarrow{\;k\;} BP + Cl^- \tag{1}$$
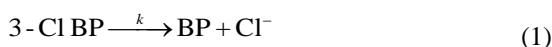
It is well established that the pseudo-first-order kinetics could be applied in the reductive dechlorination of Chlorophenols (CPs) and polychlorinated biphenyls (PCBs) by the nZVI particles if the nZVI particles dosage is excessive in the reaction (Zhang *et al*., 2010; Zhuang *et al*., 2011). Therefore, the pseudo-first order reaction kinetics was adopted to model the 3-Cl BP dechlorination by nZVI particles. The corresponding reaction rate equations for the degradation of 3-Cl BP and the accumulation of sole final product BP in the batch system are shown as follows:

$$\frac{-dC_{3-ClBP}}{dt} = kC_{3-ClBP} \tag{2}$$

$$\frac{d[BP]}{dt} = k_2 C_{3-ClBP} \tag{3}$$

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

$$\alpha_{3-ClBP} = e^{-k_1 t} \tag{4}$$

$$\alpha_{BP} = 1 - \alpha_{3-ClBP} \tag{5}$$

where, α represents the molar fraction of the subscript compound to the initial concentration of the parent compound (i.e., 3-Cl BP). Since a fraction of organic compounds were absorbed on the larger surface of nZVI particles, the actual concentration of the organic compound in aqueous phase has to be corrected. As the production of BP was step wise, equilibrium time for organic compounds absorbed onto nZVI particles was little and the total molar fraction of the organic compounds did not change, the proportion of BP in the aqueous phase can be seen as invariable, as a result, Eq. (5) can be revised as follows:

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

where, α' represents the molar fraction of the organic compounds which were adsorbed onto nZVI particles to the initial concentration of the parent compound (i.e., 3-Cl BP). 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 methods of nZVI particles, nZVI particles dosage, reaction temperature and initial pH values on the 3-Cl BP reductive dechlorination efficiency were investigated in the following experiments (Fig. 2). Meanwhile, k values in different experimental conditions were obtained and listed in Table 1.

Effects of different nZVI synthesized methods on 3-Cl BP dechlorination: Figure 2a shows reductive dechlorination of 3-Cl BP by nZVI prepared in the presence and absence of ultrasound. The concentration of 3-Cl BP decreased rapidly and the removal percentage reached 90% in 180 min and then further reached to nearly 98% in 360 min for nZVI synthesized in the presence of ultrasound. In contrast, only about 75% and 92% of the removal percentage were obtained for nZVI synthesized in the absence of ultrasound during the same reaction periods, respectively. It shows that the apparent pseudo-first-order kinetics constants k values increased obviously from 0.0072 to 0.0109/min under nZVI prepared in the absence and presence of ultrasound, respectively. Therefore, nZVI particles were prepared in the presence of 20 kHz ultrasound in the following experiments.

Effects of nZVI particles dosage on 2,4-DCP dechlorination: Effects of different nZVI particles dosage on 3-Cl BP dechlorination were explored as shown in Fig. 2b. Increasing the dosage of nZVI particles by nZVI particles prepared in the presence of ultrasound, means the larger nZVI particles surface area. The higher the nZVI particles surface area concentration is, the faster the reaction velocity. Therefore, with the elevation of the nZVI particles dosage from 3 to 7 g/L, the removal percentage of 3-Cl BP increased from 75 to 93% and the formation rate of BP increased from 68 to 84% in 240 min. The removal
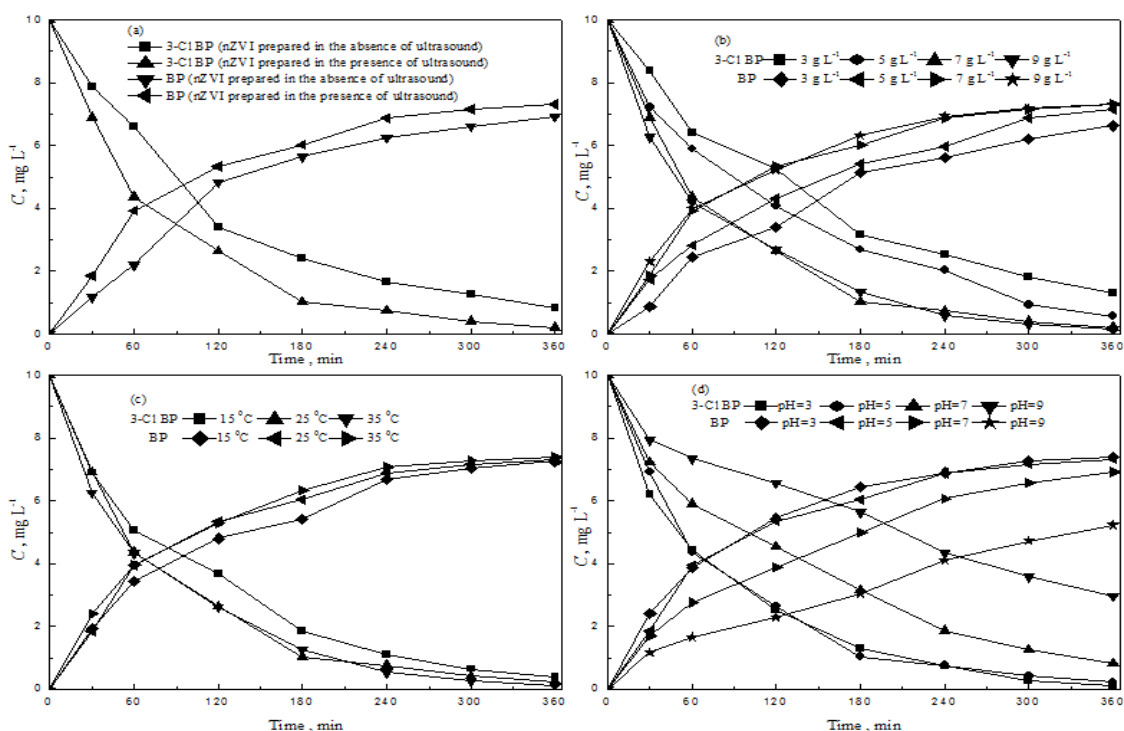
Fig. 2: (a) Effects of nZVI particles prepared methods on the 3-Cl BP dechlorination (T = 25 °C, pHin = 5.0, C3-Cl BP = 10 mg L, CnZVI = 7 g L); (b) Effects of nZVI particles dosage on the 3-Cl BP dechlorination (nZVI particles prepared in the presence of ultrasound, T=25 °C, pHin = 5.0, C3-Cl BP = 10 mg L); (c) Effects of temperature on the 3-Cl BP dechlorination (nZVI particles prepared in the presence of ultrasound, pHin = 5.0, C3-Cl BP = 10 mg L, CnZVI =7 g L); (d) Effects of initial pH on the 3-Cl BP dechlorination (nZVI particles prepared in the presence of ultrasound, T = 25 °C, C3-Cl BP = 10 mg L, CnZVI = 7 g L)

Table 1: k values in different experimental conditions

Reaction conditions		1-a	k/min	R
nZVI prepared method	In the absence of ultrasound	0.9265	0.0072	0.9878
	In the presence of ultrasound	0.9021	0.0109	0.9928
nZVI dosage	3 g/L	0.9462	0.0055	0.9899
	5 g/L	0.9324	0.0072	0.9942
	7 g/L	0.9021	0.0109	0.9928
	9 g/L	0.8974	0.0118	0.9899
Reaction temperature	15°C	0.9091	0.0089	0.9883
	25°C	0.9021	0.0109	0.9928
	35°C	0.9090	0.0116	0.9944
Initial pH values	3	0.9047	0.0118	0.9895
	5	0.9021	0.0109	0.9928
	7	0.9216	0.0066	0.9910
	9	0.9050	0.0033	0.9893

1-a represents the molar fraction of the total organic compounds in solution; k refers the corresponding reaction rate for the disappearance of 3-Cl BP, respectively; R denotes the correlation coefficient between the experimental data can match the calculated number

percentage of 3-Cl BP and the formation rate of BP slightly increase under a dosage of nZVI particles of 7 or 9 g/L in 360 min. Meanwhile, the apparent pseudo-first-order kinetics constants k values increased from 0.0055, 0.0072 and 0.0109 to 0.0118 min, respectively as the nZVI dosage was increased from 3, 5 g, 7 to 9 g/L, respectively. Hence, the optimal nZVI dosage for 3-Cl BP dechlorination is 7 g/L.

Effects of reaction temperature: Figure 2c shows the effect of reaction temperature on the reductive dechlorination efficiency of 3-Cl BP by nZVI particles

prepared in the presence of ultrasound. The dechlorination efficiency of 3-Cl BP and the production rates of BP increased with the increase of reaction temperature. With the reaction temperature increasing from 10 to 35°C, k values increased from 0.0089 min, 0.0109 min to 0.0116 min as temperature was increased from 10, 25 to 35°C, respectively. When the reaction temperature was 25°C and 35°C, 3-Cl BP could be nearly completely reduced to BP. At higher temperature, 3-Cl BP dechlorination becomes much faster possibly due to that the mobility of 3-Cl BP from solution to nanoparticles increased at higher

temperature, or the activation energy for electron transfer or formation of a reactive surface complex increased. Where as its feasibility for an in situ remediation of contaminated groundwater, the subsequent experiments were performed at 25°C.

Effects of the initial pH value on 3-Cl BP dechlorination: Figure 2d shows the effect of different initial pH values on the reductive dechlorination of 3-Cl BP by nZVI particles prepared in the presence of ultrasound. Prior to initializing reaction all reactant solutions were adjusted to different pH values by dilution with sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) and during the reaction pH values were not adjusted. When the initial pH values increased from 3, 5, 7 to 9, the removal percentages of 3-Cl BP dropped from nearly 99, 98, 92 to 70%, respectively in 360 min. Meanwhile, the production concentration of BP dropped form 7.38 to 5.23 mg L with initial pH values increased from 3 to 9 in the same reaction period. Low pH favors more iron surface available for reaction with the chlorinated molecules or at least promote the corrosion rate, leading to release of chloride ions. In addition, k values dropped from 0.0118, 0.0109, 0.0066 to 0.0033 min, respectively as the initial pH values was increased from 3, 5 and 7 to 9. Therefore, the presence of H^+ largely enhances the 3-Cl BP reductive dechlorination efficiency and the BP formation rates.

CONCLUSION

Our experimental results suggest that the nZVI particles synthesized method in presence of ultrasound was a better technique to enhance the disparity and reactivity. In the reductive dechlorination of 3-Cl BP, the dechlorination efficiency was dependent on a number of factors including nZVI particles availability, reaction temperatures and initial pH values. The degradation of 3-Cl BP followed pseudo-first-order kinetics reaction and the apparent pseudo- first-order kinetics constants were obtained.

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REFERENCES

Agarwal, S., S.R. Al-Abed and D.D. Dionysiou, 2007a. Enhanced corrosion-based Pd/Mg bimetallic systems for dechlorination of PCBs. Environ. Sci. Technol., 41: 3722-3727.

Agarwal, S., S.R. Al-Abed and D.D. Dionysiou, 2007b. In situ technologies for reclamation of PCB-contaminated sediments: Current challenges and research thrust areas. J. Environ. Eng., 133: 1075-1078.

Borja, J., D.M. Taleon, J. Auresenia and S. Gallardo, 2005. Polychlorinated biphenyls and their biodegradation. Process Biochem., 49: 1999-2013.

Choi, H., S. Agarwal and S.R. Al-Abed, 2009. Adsorption and simultaneous dechlorination of PCBs on GAC/Fe/Pd: Mechanistic aspects and reactive capping barrier concept. Environ. Sci. Technol., 43: 488-493.

Fang, Y. and S.R. Al-Abed, 2007. Partitioning, desorption and dechlorination of a PCB congener in sediment slurry supernatants. Environ. Sci. Technol., 41: 6253-6258.

Huang, Y.H. and T.C. Zhang, 2006. Reduction of nitrobenzene and formation of corrosion coatings in zerovalent iron systems. Water Res., 40: 3075-3082.

Lowry, G.V. and M. Reinhard, 2001. Pd-catalyzed TCE dechlorination in water: Effect of [H_2](aq) and H_2-utilizing competitive solutes on the TCE dechlorination rate and product distribution. Environ. Sci. Technol., 35: 696-702.

Murphy, P., A. Marquette, D.D. Reible and G.V. Lowry, 2006. Predicting the performance of activated carbon-, coke- and soil-amended thin layer sediment caps. J. Environ. Eng., 132: 787-794.

O'brien, C.P., M.C. Thies and D.A. Bruce, 2005. Supercritical water oxidation of the PCB congener 2-chlorobiphenyl in methanol solutions: A kinetic analysis. Environ. Sci. Technol., 39: 6839-6844.

Phillips, D.H., B. Gu, D.B. Watson, Y. Roh, L. Liang and S.Y. Lee, 2000. Performance evaluation of a zerovalent iron reactive barrier: Mineralogical characteristics. Environ. Sci. Technol., 34: 4169-4176.

Sayles, G.D., G. You, M.X. Wang and M.J. Kupferle, 1997. DDT, DDD and DDE dechlorination by zero-valent iron. Environ. Sci. Technol., 31: 3448-3454.

Suslick, K.S., M. Fang and T. Hyeon, 1996. Sono-chemical synthesis of iron colloids. J. Am. Chem. Soc., 118: 11960-11961.

Wang, X.Y., C. Chen, H.L. Liu and J. Ma, 2008. Preparation and characterization of PAA/PVDF membrane-immobilized Pd/Fe nanoparticles for dechlorination of trichloroacetic acid. Water Res., 42: 4656-4664.

Wiegel, J. and Q. Wu, 2000. Microbial reductive dehalogenation of polychlorinated biphenyls. FEMS Microbiol. Ecol., 32: 1-15.

Zhang, W.H., X. Quan, J.X. Wang, Z.Y. Zhang and S. Chen, 2006. Rapid and complete dechlorination of PCP in aqueous solution using Ni-Fe nanoparticles under assistance of ultrasound. Chemosphere, 65: 58-64.

Zhang, Z., Q.H. Shen, N. Cissoko, J.J. Wo and X.H. Xu, 2010. Catalytic dechlorination of 2, 4-dichlorophenol by Pd/Fe bimetallic nanoparticles in the presence of humic acid. J. Hazard. Mat., 182: 252-258.

Zhuang, Y., A.L. Seyfferth, Y. Masue-Slowey, S. Fendorf and R.G. Luthy, 2011. Dehalogenation of polybrominated diphenyl ethers and polychlorinated biphenyl by bimetallic, impregnated and nanoscale zerovalent iron. Environ. Sci. Technol., 45: 4896-4903.

Zhou, T., Y.Z. Li and T.T. Lim, 2010. Catalytic hydrodechlorination of chlorophenols by Pd/Fe nanoparticles: Comparisons with other bimetallic systems, kinetics and mechanism. Sep. Purif. Technol., 76: 206-214.