

Degradation of pentachlorophenol with zero-valence iron coupled with microwave energy

Chih-Ju Jou*

Department of Safety, Health and Environmental Engineering, National Kaohsiung First University of Science and Technology, Kaohsiung, Taiwan, ROC

Received 10 October 2006; received in revised form 13 July 2007; accepted 13 July 2007
Available online 18 July 2007

Abstract

The objective of this research is to study the degradation of pentachlorophenol with zero-valence iron (Fe^0) coupled with the use of microwave energy. The sample containing 1000 mg/L PCP solution was dosed with 0.5 g Fe^0 and then subject to 700 W microwave energy for 10 s; 85% pentachlorophenol was noted to be removed. If the microwave treatment time was increased to 30 s, the pentachlorophenol removal efficiency exceeded 99% with end products including H_2O , CO_2 , HCl, etc. Using Fe^0 as a medium, the microwave treatment is made an efficient method for degrading pentachlorophenol. The time needed to achieve a satisfactory treatment is also reduced leading to significant savings of energy consumption to make this method cost-effective. Since this technology applies Fe^0 , which is amenable to natural environment, to speed up the decomposition of an industrial solvent, it is not only cost-effective but also environmental friendly for the industry to pursue sustainable development.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Microwave; Induced; Zero-valence iron; Pentachlorophenol

1. Introduction

Pentachlorophenol (PCP) may pollute surface water and groundwater or be released to the atmosphere due to improper waste disposal and/or use as ingredients of pesticides [1,2]. It may be accumulated in living organisms via food chain to cause gene mutation or even death. PCP that exists in soil or surface water may be decomposed by microorganisms through de-chlorination reduction processes into 2,3,4,5-tetrachlorophenol, 2,3,5,6-tetrachlorophenol, 2,3,4,6-tetrachlorophenol, 2,4,5-trichlorophenol, 2,3,5-trichlorophenol, etc. However, traditional biological treatment methods are not effective in removing these biologically recalcitrant and toxic substances.

Most of the current research on treating industrial chlorine-containing substances concentrates on using the Fenton or photo-catalytic processes to oxidize PCP [3–5], applying various reagents to adsorb PCP [6,7], using microorganisms to decom-

pose and to mineralize PCP into harmless substances [8,9], or even utilizing the heat process to desorb chlorine-containing substance [7,10]. All the aforementioned methods may have decent results but they may also have many shortcomings. For example, incinerating chlorine-containing substances may produce strong acids that corrode the furnace thus making this method expensive in addition to releasing toxic chlorine-containing by-products. Additionally, organic substances that contain high chlorine content are toxic and recalcitrant to make the biological treatment methods ineffective.

Zero-valence iron serves as a donor of electrons (reducing agent); it easily releases electrons to form oxidative Fe ions that are capable of reducing various pollutants. Hence, it has been widely applied for treating groundwater polluted by halogen-containing organic substances. For example, the studies using Fe^0 to decompose and de-chlorinate trichloroethylene, tetrachloroethylene, carbon tetrachloride and pentachlorophenol and using filters filled with iron powder to remove Trichloroethylene from groundwater have shown satisfactory results [11,12]. However, the microwave-based technology has a great potential for treating chlorine-containing substances. Using a dielectric medium to absorb the microwave to produce heat directly inside

* Tel.: +886 7 601 1000x2316; fax: +886 7 601 1061.
E-mail address: george@ccms.nkfust.edu.tw.

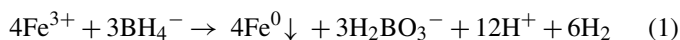
the medium, the heat transfer into the media from an external heat source is eliminated thus greatly raising the energy utilization efficiency. Comparing with the traditional thermal or catalytic oxidation method, the microwave-based treatment takes shorter time to reach higher reaction temperature [13,14]. Results presented in literature have shown that the microwave treatment is rapid and efficient to decompose and de-chlorinate organic substance [15–20].

The zero-valence iron absorbs MW energy to induce electronic vibration and the friction among molecules leads to the generation of thermal energy from MW energy thus raising the iron molecular temperature to assist PCP pyrolysis. Using the highly active but environment-friendly metal, Fe⁰, is expected to raise the efficiency and cost-effectiveness of the microwave treatment.

2. Materials and methods

2.1. Materials

In this research, 0.045 M FeCl₃·6H₂O (SHOWA, 97%) and 0.25 M NaBH₄ (Lancaster, 98%) were mixed to proceed with the chemical reaction leading to the production of zero-valence Fe⁰ according to the chemical reaction shown as [21]:



The resulting Fe⁰ particles have diameters between 60 and 80 nm with 33.36 m²/g specific surface area as determined using the BET method (Beckman Co., SA-300). Solid PCP (90%, Lancaster Co., UK) was used in this study; the 1000 ppm PCP acetone solution was prepared by adding 49.45 mg solid PCP into 25 mL analytical grade acetone. Further, a fixed volume of 25 mL acetone was used in all subsequent extraction of remaining PCP after the treatment for being consistent.

2.2. Experimental device and procedure

The schematic diagram in Fig. 1 shows the laboratory setup for conducting the microwave energy enhanced degradation. A modified household microwave oven (SAMPO Co., frequency 2.45 GHz, max power 750 W) was used for generating the microwave energy. The column reactor that holds the sample is made of low-energy loss and heat-resistant (up to 700 °C) amber boron-silica glass with screw cap that has Teflon lining, the boron-silica glass column reactor was installed in the microwave oven. After filling the test sample in the reactor, a layer of activated carbon was placed on top of the Fe⁰-PCP to adsorb the un-reacted PCP and end products that may escape with the tail gas for quantitative analyses.

With the MW power output fixed at 700 W, three sets of samples were prepared to contain 0.1, 0.3 and 0.5 g Fe⁰, respectively. The catalyst was placed on top of the 1000 ppm PCP layer directly and the prepared samples were treated with an array of 350, 490 and 700 W for various durations, e.g. 0, 10, 20, . . . , 60 s. At the end of the heating period, 25 mL acetone was added as the

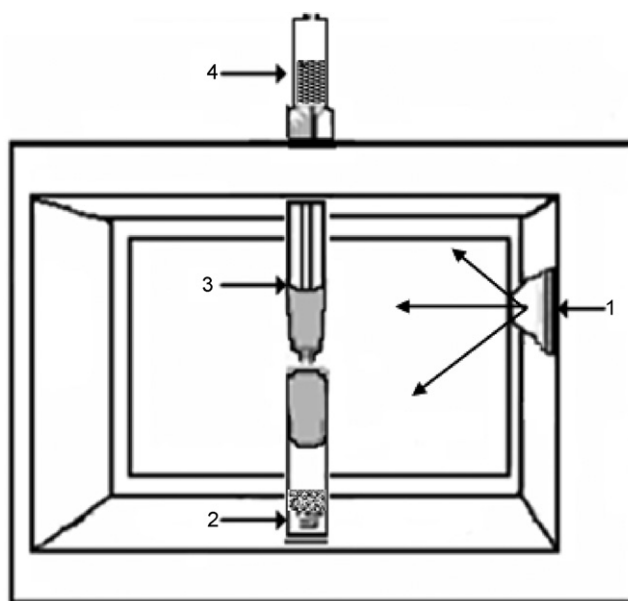


Fig. 1. Schematic diagram of the microwave reactor system. (1) MW generator, (2) zero-valence Fe⁰ particles and 1000 ppm PCP, (3) boron-silica glass column reactor, and (4) granular activated carbon.

extracting solvent. After shaking in an ultrasonic wave shaker for 5 min, the solvent was collected for analyses.

2.3. Analysis

Qualitative analyses was done with a HP 6890 gas chromatography (GC) coupled with an HP 5973 mass selective detector (MSD) and a capillary column (HP-5MS, 30 m × 0.25 mm × 0.25 μm) was used for the identification of intermediates and degradation products. The carrier gas (He) flow rate was at 1.5 mL/min (constant flow). The oven temperature was programmed from 70 to 260 °C (hold for 5 min) at a ramp rate of 30 °C/min. The GC injector temperature was 250 °C and MSD injector temperature was 320 °C.

3. Results and discussion

3.1. Influence of Fe⁰ dosages on the treatment efficiency

Fig. 2 indicates that under the microwave power of 700 W for 30 s, 0.5 g Fe⁰ can achieve more than 99.9% removal of PCP. If the Fe⁰ dosage is reduced to 0.3 g while other conditions remain unchanged, the PCP removal efficiency is reduced to 83.2% and further to 69.1% for 0.1 g Fe⁰. The microwave treatment efficiency is better with more Fe⁰ dosage applied with shorter reaction time. Thus, 0.5 g Fe⁰ was chosen as the dosage for conducting all subsequent studies.

In order to compare the effectiveness of PCP reduction using Fe⁰ with and without microwave energy induction, the reactor containing 0.5 g Fe⁰ was placed directly on the PCP layer and the prepared sample was left undisturbed for a certain period. The supernatant was then decanted to be analyzed using GC/MS. The results are shown in Fig. 3. After 75 min, the PCP reduction is seen to reach a steady level with 972 ppm PCP being removed

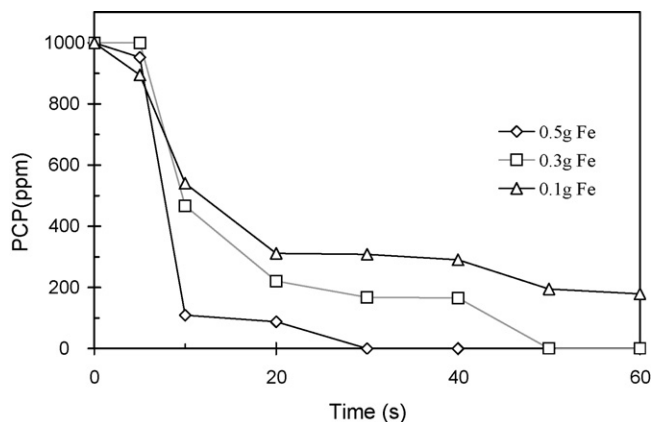


Fig. 2. Influence of Fe^0 dosage on the removal of PCP using the microwave-induced Fe^0 treatment (1000 ppm PCP and 700 W microwave energy).

by 0.5 g Fe^0 . However, the maximum PCP removal efficiency is only 3%, which is insignificant when comparing with the 99.9% obtained with the same Fe^0 dosage induced with microwave. Being induced with microwave for 30 s, Fe^0 generates heat to raise the temperature that is effective to break up the chemical bonds of PCP.

3.2. Influence of microwave energy levels

Fig. 4 shows that with the microwave energy maintained at 700, 490 and 350 W when the reaction time is reduced to 20 s, the PCP treatment removal efficiencies are 99.9% for 700 W, 89.2% for 490 W and 13.3% for 350 W. If the microwave induction time is increased to 60 s, the treatment efficiencies are 99.9% for 700 and 400 W and 91.6% for 350 W. When absorbed by the zero-valence iron, the MW energy causes the molecules to polarize leading to electronic vibration thus generating heat to raise the temperature. Hence, more MW power (350–700 W) applied causes higher Fe^0 temperature (370–540 °C) to achieve better PCP removal efficiency; the treatment time for achieving the same results will be shortened.

Fig. 4 shows the results obtained with the microwave energy maintained at 700 W. As the reaction time is concerned, about 89.1% PCP is removed at 10 s but almost 100% PCP can be

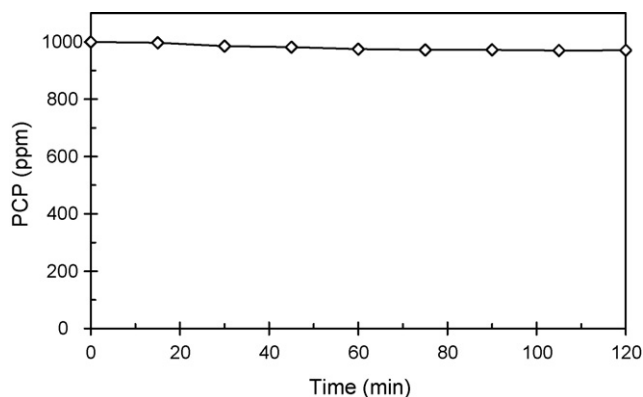


Fig. 3. PCP decomposition with Fe^0 in the absence of microwave induction (PCP 1000 ppm).

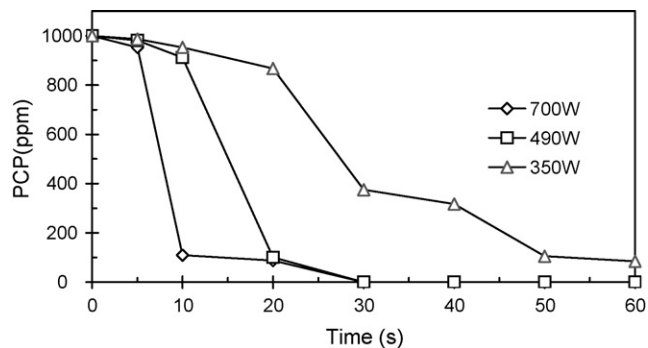


Fig. 4. Influence of microwave energy level on PCP reduction for the microwave-induced Fe^0 treatment of aqueous PCP solution (1000 ppm PCP and 0.5 g Fe^0).

removed at 30 s. The PCP removal rate is the highest for the initial 5–10 s and becomes diminished after 10 s. During the initial seconds of microwave induction, portions of Fe^0 emitting incandescent light to show the spark effect. After 10 s, the high temperature caused by the spark effect leads to changes of the Fe^0 surface thus bringing about a reduction of the surface porosity or causing the surface porosity covered by impurities. This further reduces the microwave refraction in the pores on the Fe^0 surface to yield a mild PCP removal rate.

3.3. Identification of reaction products

Analyses of the acetone that has been used to extract organic substances from the microwave-based Fe^0 treated samples show that the by-products include tetrachlorophenol and pentachlorobenzene. The Fe^0 sample that has gone through the microwave treatment is mixed with 25 mL de-ionized water and the mixture shaken in ultrasonic shaker for 5 min. The decanted supernatant is found to be acidic probably because during the process of microwave treatment, Fe^0 and PCP ($\text{C}_6\text{Cl}_5\text{OH}$) form Cl^- and Cl_2 that react with water vapor to form HCl to drop the pH.

The reactor tail gas was collected by placing 1 g granular activated carbon (GAC) in the tube that exhaust the gas from the microwave reactor to adsorb the gas emission. After the microwave induced Fe^0 treatment of PCP had been completed, the GAC was removed and mixed with 25 mL acetone; the mixture was then subject to 5 min ultrasonic shaking. The supernatant was decanted and injected into a GC/MSD for qualitative analyses of organic substances. The results show that using 700 W microwave energy for 10 s, the tail gas contains detectable CO_2 and trace amount of HCl gas. If the treatment time exceeds 10 s, the end product is only CO_2 . Thus, the observations indicate that under high temperature (520–540 °C) by Fe^0 during the microwave treatment, some chemical bonds in PCP are cleaved up to result in the formation of Cl-C or Cl^- , which react with moisture to form trace quantity of HCl.

4. Conclusion

The feasibility on using microwave-induced Fe^0 to decompose PC in aqueous solution has been studied in this research.

When the microwave energy is maintained at 700 W, a 30 s treatment time will achieve almost 100% removal efficiency. When the reaction time is increased to 20 s, the treatment efficiency is proportional to the microwave energy level applied with 700 W being superior to 490 and 350 W. If the microwave energy level is fixed, longer reaction time will result in slower PCP removal rate. This is caused by the oxidation of the Fe⁰ surface that results in alterations of the surface crystal structure and particle size leading to poor microwave refraction in the surface pores thus lowering the production of arcing light intensity. However, when the microwave reaction time is maintained at 60 s, the 350 W microwave energy may still achieve 90% PCP removal. As the cost-effectiveness of this process is concerned, the selection of a proper microwave energy level will depend to a great extent on the need for removing PCP. The final end products of microwave-induced Fe⁰ treatment of PCP consist of H₂O, CO₂ and trace amount of HCl.

The lab experimental results indicate that the microwave-induced Fe⁰ treatment is a practical method that can effectively reduce the reaction time and thus energy consumption to yield a satisfactory removal of PCP. Additionally, Fe⁰ is an environment-friendly substance and its use will eliminate the possibility to cause secondary pollution hence achieving a win-win situation in terms of environmental protection and economic development.

References

- [1] P.H. Howard, Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Pesticides, Lewis Publishers, 1991, pp. 559–569.
- [2] D. Mackay, W.Y. Shiu, K.C. Ma, Illustrated Handbook of Physical–Chemical Properties and Environmental Fate for Organic Chemicals, Oxygen Nitrogen and Sulfur Containing Compounds, Lewis Publishers, 1995, pp. 377–384.
- [3] M.A. Engwall, J.J. Pignatello, D. Grasso, Degradation and detoxification of the wood preservative creosote and pentachlorophenol in water by the photo-Fenton reaction, *Water Res.* 33 (1999) 1151–1158.
- [4] M.M. Higarashi, W.F. Jardim, Photocatalytic treatment of pesticide-contaminated soil using solar light and titanium dioxide, *Am. Lab.* 32 (2000) 25–26.
- [5] T.F.F. Ho, J.R. Bolton, Toxicity changes during UV treatment of pentachlorophenol in dilute aqueous solution, *Water Res.* 32 (1998) 489–497.
- [6] X. Fang, Y. He, J. Liu, J. Wu, Oxidative decomposition of 138 pentachlorophenol in aqueous solution, *Radiat. Phys. Chem.* 53 (1998) 411–415.
- [7] S.D. Lambert, N.J.D. Gaham, C.J. Sollars, G.D. Fowler, Evaluation of inorganic adsorbents for the removal of problematic textile dyes and pesticides, *Water Sci. Technol.* 36 (1997) 173–180.
- [8] S.J.T. Pollard, S.E. Hrudey, P.M. Fedorak, Bioremediation of petroleum and creosote-soils: a review of constraints, *Waste Manage. Res.* 12 (1994) 173–194.
- [9] D.M. Hicks, F. Curtin, R. Hicks, In situ bioremediation of soil and groundwater contaminated with petroleum hydrocarbons, in: *Water Environ. Federation, Proceedings of 65th Annual Conference & Exposition, 1992*, pp. 305–312.
- [10] M.J. Kanters, R. Louw, Slow combustion of pentachlorophenol in toluene, *Chemosphere* 33 (1996) 1889–1896.
- [11] Y.H. Kim, E.R. Carraway, Dechlorination of pentachlorophenol by zero-valent iron and modified zero-valent irons, *Environ. Sci. Technol.* 34 (2000) 2014–2017.
- [12] S.F. O'Hannesin, R.W. Gillham, J.L. Vogan, TCE degradation in groundwater using zero-valent iron, *Am. Chem. Soc. Extend. Abstr. Ind. Eng. Chem. Div. 20* (1995) 55–58.
- [13] H.M. Kingston, L.B. Jassie, Introduction to Microwave Sample Preparation, Washington, DC, 1988, pp. 7–13.
- [14] D.A. Jones, T.P. Lelyveld, S.D. Mavrofidis, S.W. Kingman, N.J. Miles, Microwave heating applications in environmental engineering—a review, *Resour. Conserv. Recycl.* 34 (2002) 75–90.
- [15] C.J. Jou, Application of activated carbon in microwave radiation field to treat trichloroethylene, *Carbon* 36 (1998) 1643–1648.
- [16] C.J. Jou, H.S. Tai, Application of granulated activated carbon packed-bed reactor in microwave radiation field to treat BTX, *Chemosphere* 37 (1998) 685–698.
- [17] C.J. Jou, H.S. Tai, Application of granulated activated carbon packed-bed reactor in microwave radiation field to treat phenol, *Chemosphere* 38 (1999) 2667–2680.
- [18] P.M. Coss, C.Y. Cha, Microwave regeneration of activated carbon used for the removal of solvents from vented air, *J. Air Manage.* 50 (2000) 529–535.
- [19] T. Uslu, U. Atalay, Microwave heating of coal for enhanced magnetic removal of pyrite, *Fuel Process. Technol.* 85 (2003) 21–29.
- [20] C.J. Jou, An efficient technology to treat heavy metal-lead-contaminated soil by microwave radiation, *J. Environ. Manage.* 78 (2006) 1–4.
- [21] H.L. Lien, W.X. Zhang, Nanoscale iron particles for complete reduction of chlorinated ethenes, *Colloid Surf. A* 191 (2001) 97–105.