



Catalytic Degradation of Pentachlorophenol Contaminated Soil using Nano Zero-Valent Iron Catalyst

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ABSTRACT

Pentachlorophenol (PCP) was widely applied in the industrial or agricultural sector in the early days. After long-term abusive use of PCP, the soil became contaminated. PCP is considered an “environmental hormone” in terms of toxicity identification; alkali-chlorine plants in Southern Taiwan are those most polluted by PCP. This study first discussed the results of functional group identification using Fourier-transform infrared spectroscopy (FT-IR) performed on three test soils. Next, it used the self-synthesized nano zero-valent iron to observe its particle size distribution with a field emission scanning electron microscope (FM-SEM). Furthermore, it conducted catalytic degradation reaction on three test soils contaminated by PCP, to which different percentages of the zero-valent iron by weight (wt%) were added, in order to explore the degradation efficiency of the zero-valent iron over PCP.

Regarding the degradation efficiency of four different percentages of the zero-valent iron by weight (wt%) over PCP in soil, the experimental results suggest that there are slight differences in the degradation efficiency of different percentages of the zero-valent iron by weight over soil contaminated by PCP at room temperature; the reaction rate and degradation efficiency of the zero-valent iron over PCP in soil increase as the amount of added zero-valent iron increases. This is largely because the oxidation reaction between the zero-valent iron and PCP in soil is more significant, while more electrons are released, when the content of the zero-valent iron increases and the zero-valent iron reacts with the pollutant. Meanwhile, electrons received by test soils relatively increase the reaction between these soils and PCP in soil; they also replace the original ligands in soil, which enables the effective degradation of concentrations of PCP in soil. Currently, the zero-valent iron has been extensively applied to environmental pollution remediation, which is especially effective for remediation of soil and groundwater pollution control sites and restoration work.

Key words: pentachlorophenol, nanozero-valent iron, FT-IR, contaminated soil

INTRODUCTION

Pentachlorophenol (PCP) is a well-known organochlorine compound mainly used as a general herbicide, pesticide and wood preservative, as well as an insecticide and broad-spectrum biocide. PCP is an organo-chlorine compound (C_6HCl_5O) used mainly as a fungicide. Its salt, sodium pentachlorophenate ($C_6Cl_5NaO-NaPCP$), is used for similar purposes and readily degrades to PCP [1]. The ester, pentachlorophenyllaurate (PCPL), is also used. All three substances are toxic, persistent and liable to bioaccumulate, although PCPL is less toxic by an order of magnitude. They need to be considered together. Priority was given to PCP in the 1992 OSPAR Action Plan, and it was therefore included in 1998 in the OSPAR List of Chemicals for Priority Action [2].

Iron (Fe)-based materials possess remarkable potential for the remediation of soil aquifers, groundwater and cyanobacterial blooms [3-5]. Numerous in-situ applications of zero-valent iron (ZVI) nanoparticles have proved a powerful tool in the clean-up of chlorinated ethenes and toxic metal ions due to their high reductive capacity [6-7]. Further, emerging particulate materials containing Fe as Fe(0), Fe(II) and Fe(III), where the Fe species act as reductants or sorbents for metals and metalloids, have been used successfully in microbiological contaminant degradation or as heterogeneous Fenton catalysts [3, 8-9].

The overall impact of materials containing Fe(0) on aquatic ecosystems (introduced intentionally or accidentally) remains questionable [3]. Other nanomaterials also have the potential to seriously affect aquatic microorganisms such as microalgae, primary producers that play a key role in healthy ecosystems [10]. While iron is an essential nutrient in small

amounts, increased loading of Fe(II)/Fe(III) ions can rapidly accumulate in the cells of aquatic organisms, resulting in oxidative stress due to the generation of oxide and hydroxide radicals via the Fenton reaction [11-12]. Moreover, ZVI particles show a strong affinity for cell surfaces; thus, they have the potential to physically damage bacterial or algal cells [13].

This study used self-synthesized zero-valent iron to conduct catalytic degradation reaction on three test soils contaminated by PCP, to which different percentages of the zero-valent iron by weight (wt%) were added, in order to explore the degradation efficiency of the zero-valent iron over PCP in soil. It is hoped that this study can provide effective new ways to tackle soil pollution, and which can be used as a reference for applications of soil restoration in the future.

2. MATERIALS AND METHODS

2.1. Sources of test soils

This study selects Taiwanese soils with three different categories of properties as the sampling soil sample.

- (1) Taikang series (Tk): Taiwanese clay soil evolved from the sedimentary material from the recent time is wind-eroded sand shale deposit of alluvial soil.
- (2) Chengchung series (Cf): this is the youngest alluvial soil in Taiwan area evolved from wind-eroded sandstone and shale on the mountain area of West Taiwan mixed with mud stone.
- (3) Pianchen series (Pc): it is long evolved laterite soil and is the most significant soil representative sample with the largest distribution area in Taiwan.

2.2. Fourier-transfer infrared spectrometer- Function Group Authentication

A Fourier-transfer infrared spectrometer (FT-IR) is adopted for analysis to make use of the movement or vibration of molecular structure to absorb radiation with the same frequency. The fingerprint area and Eigen-area of FT-IR are used for determination of the homeotype substitution of clay catalyst and the existence of organic molecules.

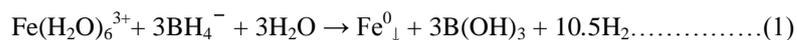
The test soils and KBr powder are placed in the oven separately to dry for 48 h, and then mixed in a 1:10 ratio, before being ground in an agate mortar. An oil presser using a pressure of 10 tons is used to produce a transparent sheet which is then scanned from 4000 cm^{-1} to 400 cm^{-1} for analysis on the spectrometer.

2.3. Field emission scanning electron microscope (FE-SEM) analysis of zero-valent iron

With a scanning electron microscope (SEM), this study observes the size of zero-valent iron and its distribution. The model in use is JEOL-6330, and its emitting energy comes from the field emission filament with high space and energy resolution.

2.4. Preparation of nano zero-valent iron

In this study, the wet-chemical precipitation reaction is adopted for making zero-valent iron: add $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution to the solution of NaBH_4 to form sedimentation of Fe0 (note the rise of temperature and reaction during the synthesis process) and then freeze and dry out synthesized nano zero-valent iron and preserve with nitrogen. This formula is as follows:



2.5. Preparation of pentachlorophenol contaminated soil

Use pretreated soil (dry out, break, ground and screen) as sample soil to prepare pentachlorophenol contaminated soil at the concentration level of 1000 mg/kg and then use hexane and acetone (1:1 v/v) as the solvent to stir for 2 h and place still for 2 days for further study.

3. RESULTS AND DISCUSSION

3.1. Results of test soils FT-IR analysis

Figures 1-3 show the results of an FT-IR analysis on the three test soils (Tk, Cf and Pc series). As shown in the figures, the three test soils have broad-OH telescopic vibration absorption peaks in the following wavenumber section: 3704~2985 cm^{-1} due to isomorphic substitution in a tetrahedral or octahedral layer. After making an inference using the fingerprint area in FT-IR, a further reading was done using the Eigen area, which suggests the occurrence of -OH telescopic vibration between 3000~3800 cm^{-1} . In particular, broad absorption peaks occur in the following wavenumber section: 3600~ 3700 cm^{-1} , which result from the replacement of silicon within the tetrahedron by aluminum. Furthermore, many significant and complex wave crests occur in the following wavenumber sections: 600~1000 cm^{-1} and 1620~1640 cm^{-1} ; they represent strong Si-O bonds within the silicate mineral and H-O-H telescopic vibration absorption peaks, respectively.

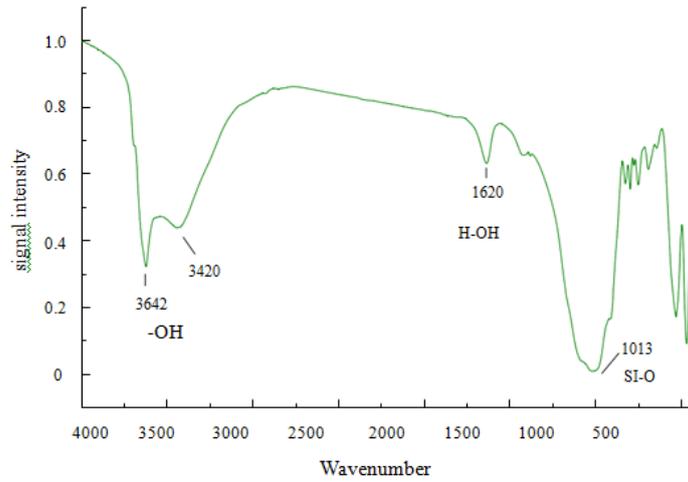


Fig. 1 FT-IR spectrum of Tk series soil

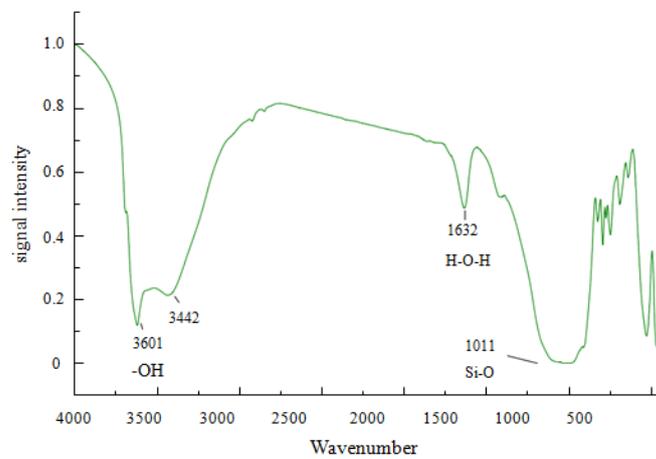


Fig. 2 FT-IR spectrum of Cf series soil

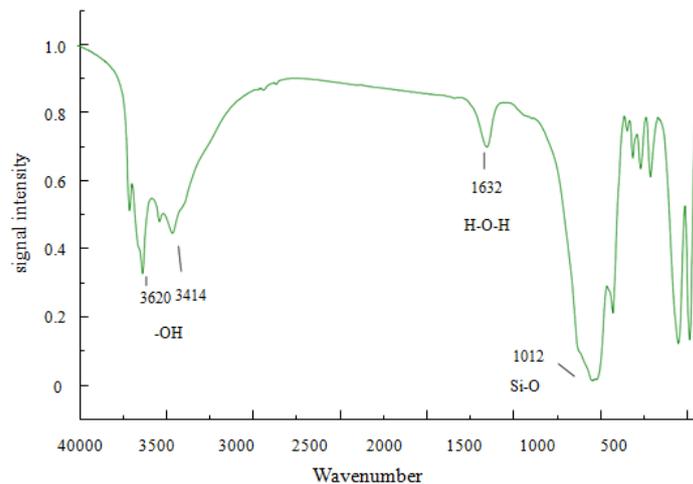


Fig. 3 FT-IR spectrum of Pc series soil

3.2. FE-SEM analysis of zero-valent iron

Figures 4-5 show the results of an FE-SEM analysis on the surface structures of nano zero-valent iron prepared by chemical reduction; observation of these surface structures was done with the magnification ratios: 50,000 and 100,000, respectively. The images in said figures clearly show that the particle size distribution of the zero-valent iron is approximately 10-90 nanometers. Compared with the zero-valent iron synthesized by Wang and Zhang [14], the synthesized zero-valent iron in this study is more even and its particle size is smaller.

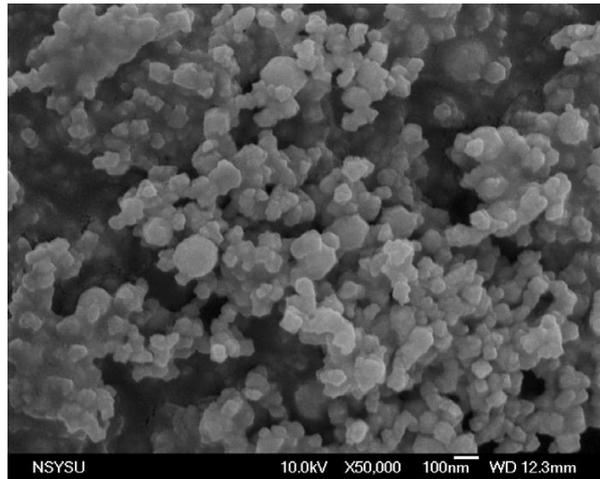


Fig. 4 FE-SEM analysis of the zero-valent iron (ratio: 50,000)

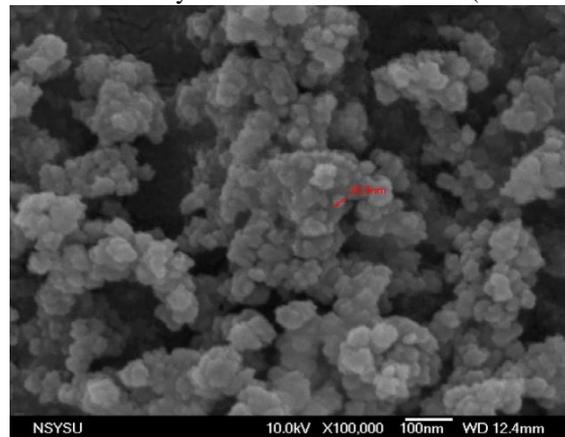


Fig. 5 FE-SEM analysis of the zero-valent iron (ratio: 100,000)

3.3. The catalytic degradation efficiency of the zero-valent iron over PCP in soil

3.3.1 The natural degradation efficiency of PCP in soil

Figure 6 shows the results of the natural degradation of the self-prepared three test soils contaminated by PCP over PCP under natural air drying. As shown in the figure, among the three test soils, Cf series soil with a medium texture has the highest natural degradation efficiency of PCP in soil after 30 days (approximately 8.8%), while Pc series soil has the lowest (approximately 3.0%). The degradation efficiency of Tk series soil is approximately 5.2%. The research findings suggest that since Pc series soil has higher organic matter content, it has an impact on the degradation efficiency of PCP concentrations [15]. The natural degradation efficiency of PCP in soil varies along with vaporization or microbial degradation, as well as with the texture and organic matter content of the soil itself. The results of this study show that after 30 days of natural degradation, the natural degradation efficiency of PCP concentrations in the three test soils is not high.

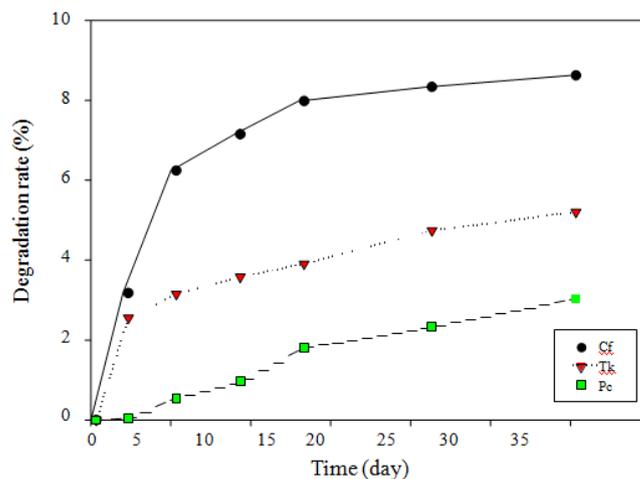


Fig. 6 The natural degradation efficiency of PCP in the three test soils

3.3.2. The degradation efficiency of different percentages of zero-valent iron by weight (wt%) over PCP in soil

Figures 7-9 show the degradation efficiency of PCP obtained by using different percentages of zero-valent iron by weight: 0.1 wt%, 0.2 wt%, 0.5 wt%, and 1 wt% to conduct catalytic reactions with the three test soils contaminated by PCP (with a concentration of 1000 mg/kg) at room temperature. The experimental results suggest that there are slight differences in the degradation efficiency of different amounts of added zero-valent iron over soil contaminated by PCP at room temperature; however, the catalytic efficiency of the zero-valent iron over PCP increases as the amount of added zero-valent iron increases. Among the three test soils, Tk and Pc series soils have higher degradation efficiency of PCP if 1 wt% of zero-valent iron is added and after approximately 95 hours of catalytic reaction. Figures 8-9 show the degradation efficiency of zero-valent iron over PCP in Cf series soil and Pc series soil at 28.21% and 30.23%, respectively. This is largely because the oxidation reaction is more significant when the zero-valent iron with more wt% reacts with PCP in soil, while more electrons are released (Adeleye et al., 2016). Meanwhile, electrons received by test soils relatively increase the reaction between these soils and PCP in soil; they also replace the original ligands in soil, which enables the effective degradation of concentrations of PCP in soil.

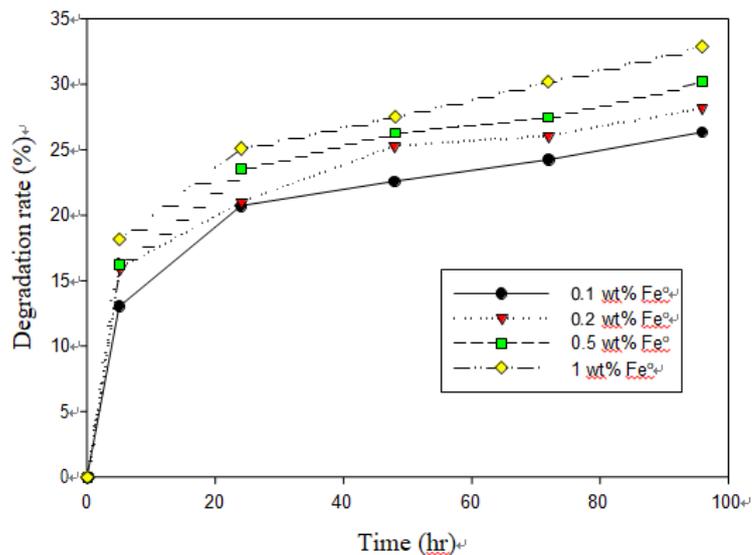


Fig. 7 The degradation efficiency of four different percentages of zero-valent iron by weight (wt%) over PCP in Tk series soil (1000 mg/kg)

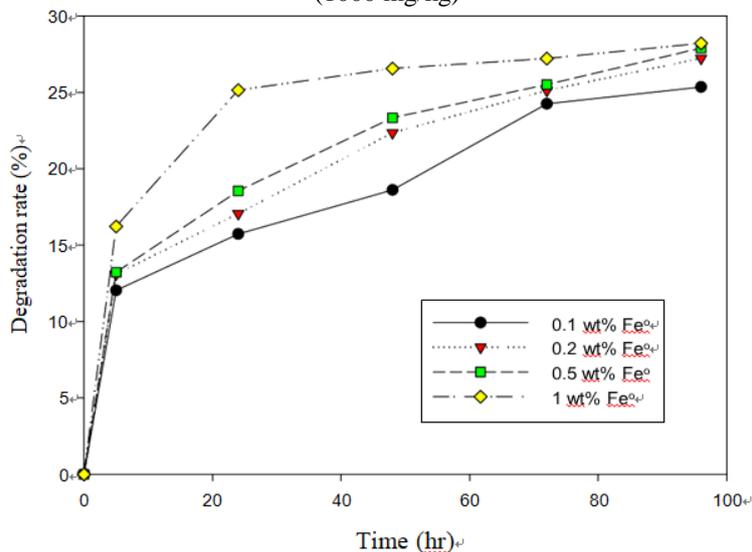


Fig. 8 The degradation efficiency of four different percentages of zero-valent iron by weight (wt%) over PCP in Cf series soil (1000 mg/kg)

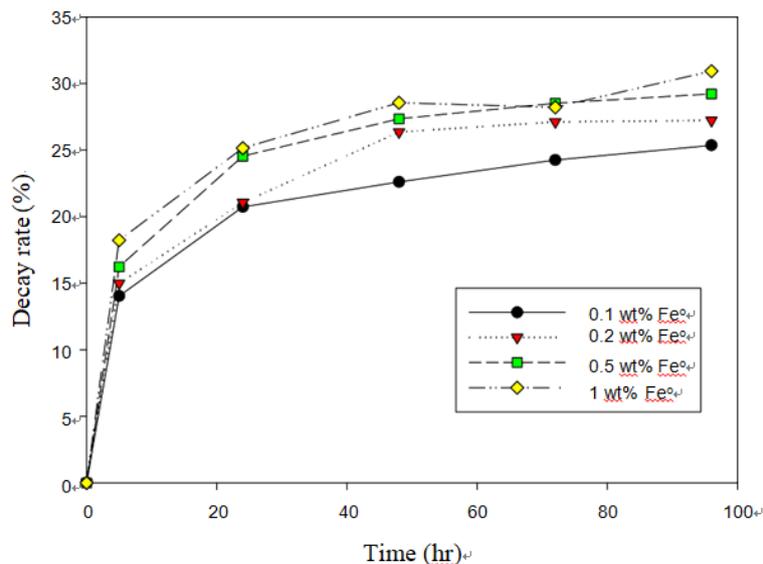


Fig. 9 The degradation efficiency of four different percentages of zero-valent iron by weight (wt%) over PCP in Pc series soil (1000 mg/kg)

4. CONCLUSION

Using the self-synthesized nano zero-valent iron, this study first discussed the results of functional group identification using Fourier-transform infrared spectroscopy (FT-IR) performed on three test soils. Next, it explored the particle size distribution of zero-valent iron using a field emission scanning electron microscope (FM-SEM). Furthermore, it conducted catalytic degradation reaction on three test soils contaminated by PCP, to which different percentages of the zero-valent iron by weight (wt%) were added, in order to explore the degradation efficiency of the zero-valent iron over PCP.

An observation of the self-synthesized zero-valent iron using the FM-SEM with the magnification ratios: 50,000 and 100,000, respectively, clearly shows that the zero-valent iron's particles are more even, with size distribution approximately 10-90 nanometers; this means that the zero-valent iron has nanoscale properties. A comparison of catalytic reactions between different percentages of zero-valent iron by weight: 0.1 wt%, 0.2 wt%, 0.5 wt%, and 1 wt% and the three test soils contaminated by PCP suggests that the oxidation reaction is more significant when the zero-valent iron with more wt% reacts with PCP in soil, while more electrons are released. Meanwhile, electrons received by test soils relatively increase the reaction between these soils and PCP in soil; they also replace the original ligands in soil, which enables the effective degradation of concentrations of PCP in soil.

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