

Chemical Degradation of Pentachlorophenol Contaminated Soil with Fenton-Like Oxidation Using Nano Zero-Valent Iron

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Abstract: Fenton-like processes are applicable to treatments of all organic pollutants, including chlorinated hydrocarbon, BTEX (benzene, toluene, ethylbenzene and xylene), PAHs (polycyclic aromatic hydrocarbons), phenols, esters, and pesticides. Moreover, Fenton-like processes are more effective with low costs and toxicity. This research used chemical reduction methods to prepare and synthesize nano zero-valent iron (nano-ZVI), while conducting a batch test to examine the pentachlorophenol (PCP) degradation efficiency of contaminated soil by adopting Fenton-like processes (which add hydrogen peroxide to nano-ZVI) to treat three PCP-contaminated soil samples.

First, the analyses of the three soil samples indicate that Al_2O_3 and Fe_2O_3 account for a considerable portion in the chemical composition of the soil samples. This result also shows that the soil samples all feature small granules, large specific surface areas, and surfactants that are located higher than ordinary oxidized irons on the surface. Using ZVIs of various wt% as catalysts, this study applied H_2O_2 of three concentrations to the three PCP-contaminated soil (1000 mg/kg) samples, respectively, to study their PCP degradation efficiency. The result shows that under higher concentrations of H_2O_2 , the degradation efficiency of PCP increases as the concentrations of wt% ZVI and the number of hydroxyl groups ($\bullet OH$) increase. Finally, this study explored how Fenton-like processes influence PCP contaminated soils by applying $CaCO_3$ of different wt% to the processes. The outcomes indicate that the more $CaCO_3$ that is added, the higher the PCP degradation efficiency of contaminated soils because the dichlorination rate of PCP increases when $CaCO_3$ sediments and releases CO_3^{2-} into the water, which enables ZVI to remove PCP in the soils faster. The research findings offer an effective and novel approach to contaminated soil treatment; these can serve as references for government departments concerned when it comes to soil restoration.

Keywords: Pentachlorophenol, BTEX, Fenton-like, nano zero-valent iron

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I. Introduction

Advanced Oxidation Processes (AOPs) involve the generation of reactive oxygen species using a combination of strong oxidants such as H_2O_2 , O_3 , and catalysts by completely mineralizing the biodegradable compounds and the degradation of non-biodegradable organic pollutants (Babu Ponnusami and Muthukumar, 2014, Malakootian et al., 2015). The AOPs are an attractive option due to the usage of environmentally friendly chemicals and their high efficiency for the removal of persistent and synthetic organic compounds with short treatment times (Moreira et al., 2017). Some of the most popular AOPs are Fenton's reaction, Photo-Fenton, Sono-Fenton, Electro-Fenton, electrochemical oxidation, TiO_2 photocatalysis, advanced ozonolysis, cavitation, and Fenton-like reaction (Wang et al., 2016), among others. In the Fenton reaction, the formation of hydroxyl radicals is the main event accomplished by different processes: (1) homogeneous Fenton process, involving iron salts and an oxidant under an acid medium; (2) heterogeneous Fenton process, involving a solid catalyst and oxidant ('Fenton-like catalyst'); (3) photo reduction of Fe(III) to Fe(II) by ultrasound and UV ('photo-Fenton and sono-Fenton processes', respectively) (Cheng et al., 2018). Heterogeneous Fenton-like processes by solid catalysts (iron or other transition metals) have been applied over a wide pH range; reduce hydroxide precipitation and possibly facilitate solid/liquid phase separation (Munoz et al., 2015). Recently, an innovative treatment method based on heterogeneous Fenton-like catalysis oxidant activation has been researched as an alternative to conventional methods of the AOPs (Han et al., 2017).

In heterogeneous Fenton process, iron salts, were adsorbed onto the surface of supported catalysts, and in a suitable aqueous medium; the reduction-oxidation reactions between Fe(II)/Fe(III) take place in the presence of hydrogen peroxide which promote the formation of reactive components such as ($\bullet OH$) and hydroperoxyl ($\bullet OOH$) radicals [Daud and Hameed, 2010]. The radicals generated by the decomposition of hydrogen peroxide can oxidize organic compounds adsorbed over the catalyst or degrade soluble organic

compounds in the vicinity of active iron ions present at both the catalyst surface and in the bulk liquid phase. Thus, the Fe(III)/Fe(II) complex formed on the surface of support can react with H₂O₂ thus allowing iron ions to participate in the Fenton catalytic cycle (Sum et al., 2007). The Fenton process completely destroys contaminants and breaks them down into harmless compounds, such as carbon dioxide, water, and inorganic salts. However, its applications are limited due to the generation of excessive amounts of ferric hydroxide sludge that requires additional separation process and disposal (Masomboon et al., 2011).

This research used chemical reduction methods to prepare and synthesize nano-ZVI, while conducting a batch test to examine the PCP degradation efficiency of contaminated soil by adopting Fenton-like processes (which add hydrogen peroxide to nano-ZVI) to treat three PCP-contaminated soil samples. The research findings offer an effective and novel approach to contaminated soil treatment; these can serve as references for the prevention and control of soil pollution, as well as soil restoration, in the future.

II. 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 mudstone.

(3) Pianchenshi 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 Preparation of pentachlorophenol contaminated soil

Take 4 g of PCP and add it to a 1000 ml mixed solution of acetone and n-Hexane to create a PCP stock solution with a concentration of 4000 mg/L. Add 250 ml of the stock solution to 1 kg of each of the three soil samples. Shake the soil samples for 2 h at room temperature, so they can be mixed thoroughly with the solution. After leaving the mixture for 2 d, the PCP-contaminated soil with a concentration of 1000 mg/kg can be obtained.

2.3.3 Analysis of the chemical composition of the three soil samples

An analysis of the chemical composition of the soil samples can help in examining their chemical content, including free elements and elements that appear in crystal form. From the data obtained, researchers can estimate the proportion of each chemical element when it forms oxide. The procedure for the analysis is as follows: Place 0.1 g of soil from each of the three soil samples in a polytetrafluoroethylene cup. Add 1.5 ml of aqua regia and 2.5 ml of hydrofluoric acid (HF) to the cups, respectively, and then heat the soil inside the cups at 110°C for 2 h. After the soil cools down, add 25 ml of boric acid to the soil and heat the soil again (without exceeding the boiling point) for 10 to 15 min so that sediments can be completely depleted. Run the soil solution through filters and add deionized water until the total volume reaches 100 ml, and then test the chemical composition of the three soil samples with inductively coupled plasma atomic emission spectroscopy (ICP-OES).

2.4 Testing the use of ZVI and chemical oxidation reaction on PCP-contaminated soil samples

2.4.1 Adding ZVI of different wt% and H₂O₂ of various concentrations (Fenton-like)

Take 4.0 g of soil from each of the three soil samples, and examine how Fenton-like processes, with the use of ZVI, affect PCP degradation efficiency under the following conditions: adding H₂O₂ of five concentrations (3%, 2%, and 1%) and ZVI of five different wt% (0.1 wt%, 0.2 wt%, 0.5 wt%, and 1 wt%), respectively.

2.4.2 Adding different concentrations of CaCO₃ to Fenton-like processes

Take 4.0 g of soil from each of the three soil samples, and examine how Fenton-like systems affect PCP degradation efficiency under the following conditions: adding 1% H₂O₂, 0.1 wt% ZVI, and CaCO₃ of three different concentrations (5 wt%, 10 wt%, and 20 wt%), respectively.

III. Results and discussion

3.1.3 Analysis of oxides of different elements in the composition of the three soil samples

Table 1 shows the results of the analysis of the chemical composition of the three soil samples. Table 4.4 indicates that Al₂O₃ and Fe₂O₃ take up a considerable share in the composition. Fe₂O₃ and Al₂O₃ take up 28.81% and 12.98% of the composition of Pc series soil, a type of oxisol, respectively. This suggests that Pc series soil has the highest content of Fe and Al oxides among the three soil samples; the total content of Al₂O₃ and Fe₂O₃ in the soil is over 40%. Also, Cf series soil contains less Fe and Al oxides than Pc series soil and Tk

series soil, but has more silicon oxide than the other two (SiO₂ takes up to 80.72%). Similar to other soil samples, Al₂O₃ and Fe₂O₃ take up a considerable share in the total content of metal oxides in Cf series soil, with Al₂O₃ taking up 10.09% and Fe₂O₃ taking up 5.14%, respectively, as shown in Table 1. However, compared with the Tk series soil and Pc series soil, which have higher total contents of metal oxides, the total content of Fe and Al oxides in the sand-shale calcareous alluvial soil of the Cf series soil is closer to that of the total content of other oxides.

Table 1. The ratios of oxides of different elements in the composition of the three soil samples

	Fe	Al	Si	Pb	Ni	Cr	Na
	----- % -----						
Tk	10.9700	17.1930	67.9140	0.00373	0.01464	0.018000	2.20160
Pc	28.8190	12.9820	54.5600	0.00000	0.61835	0.271545	1.82569
Cf	5.14440	10.0900	80.7210	0.03659	0.03042	0.016730	2.92773

3.2 The use of ZVI and chemical oxidation on the degradation of PCP in contaminated soil

3.2.1 Adding H₂O₂ of five concentrations to PCP-contaminated soil samples at room temperature without adding ZVI

Figs. 1-3 present the degradation efficiency of PCP (1000 mg/kg) of the three soil samples after adding H₂O₂ of five different concentrations and reacting for 5h, 24h, 48h, 72h, and 96 hat room temperature without adding ZVI. Since ZVI was not used as the catalyst for the reaction, meaning that the only compound reacting with PCP was H₂O₂, there was no Fe²⁺ that facilitated the production of hydroxyl groups (•OH) for oxidation through hydrogen peroxide. Hence, the PCP degradation efficiency at room temperature was lower than that when ZVI was applied (Mueller et al., 2012). Moreover, Figs. 1-3 indicate that after 96 h, adding H₂O₂ of 10% concentration resulted in the highest PCP degradation efficiency, which was about 14%. The findings suggest that adding H₂O₂ without ZVI to the soil cannot effectively remove organic pollutants.

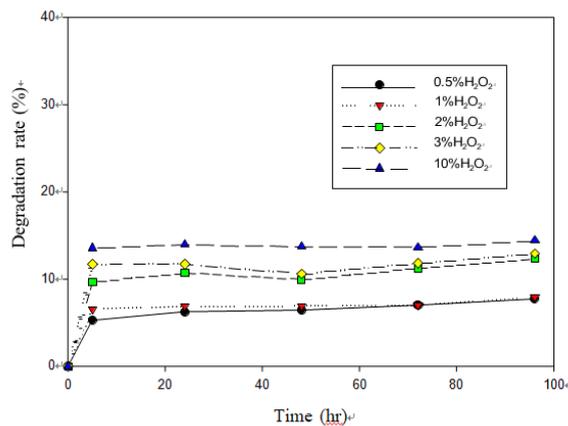


Figure 1. Changes in PCP (1000mg/kg) degradation efficiency in Tk series soil after adding H₂O₂ without ZVI at room temperature

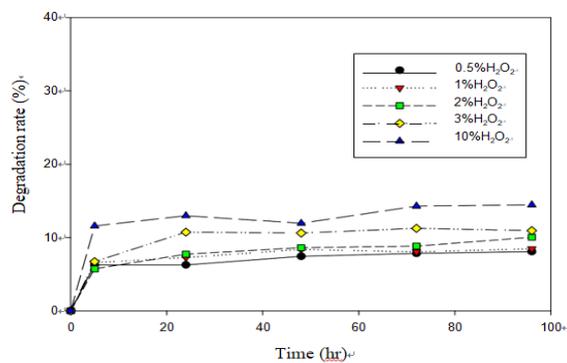


Figure 2. Changes in PCP (1000mg/kg) degradation efficiency in Cf series soil after adding H₂O₂ without ZVI at room temperature

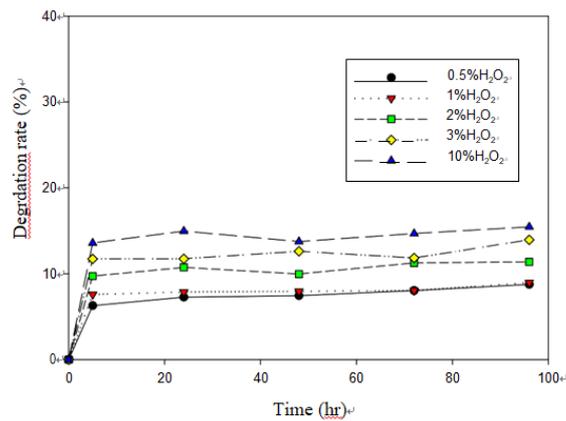
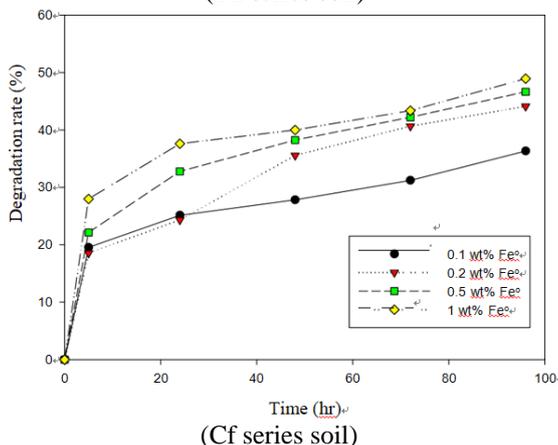
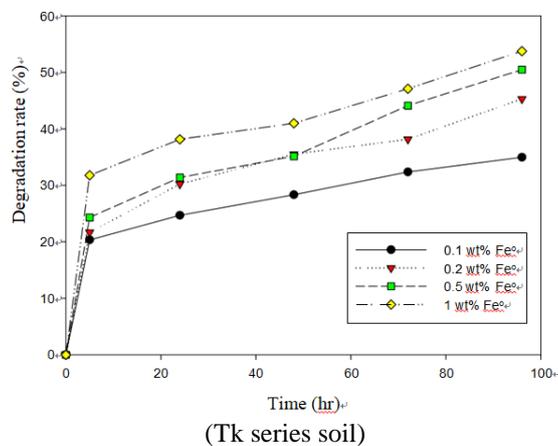


Figure 3. Changes in PCP (1000mg/kg) degradation efficiency in Pc series soil after adding H₂O₂ without ZVI at room temperature

3.2.2 Adding ZVI of different wt% and H₂O₂ of different concentrations to the three PCP-contaminated soil samples at room temperature

Figs. 4-6 present the PCP (1000 mg/kg) degradation efficiency of the three soil samples after adding H₂O₂ of three different concentrations (3%, 2%, and 1%) to the Fenton-like processes and reacting for 5h, 24h, 48h, 72h, and 96 h at room temperature with ZVI of different wt% as catalysts. Although H₂O₂ is an oxidant and cannot wholly degrade PCP, it reacts with ZVI and triggers oxidation and erosion (Cheng et al., 2018), during which time ferrous ions (Fe²⁺) are released. The ferrous ions then continue to react with H₂O₂, creating hydroxyl groups (•OH) with high oxidizing power (Han et al., 2017). Moreover, Figs. 4-6 show that under high concentrations of H₂O₂, the degradation efficiency of PCP grows as the concentrations of wt% ZVI and the number of hydroxyl groups both increase.



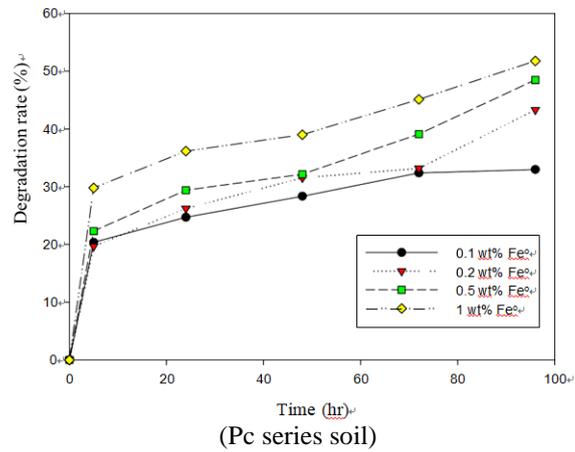
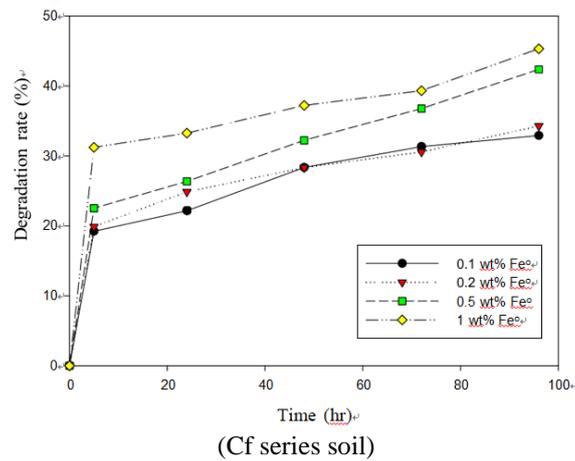
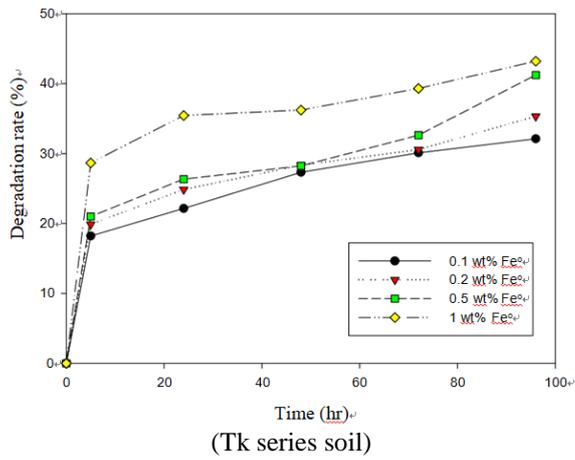


Figure 4. PCP (1000mg/kg) degradation efficiency of contaminated soil after applying ZVI of different wt% and 3% H₂O₂ at room temperature



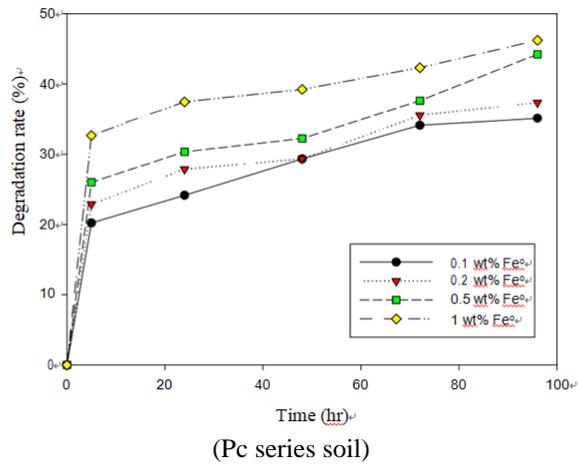
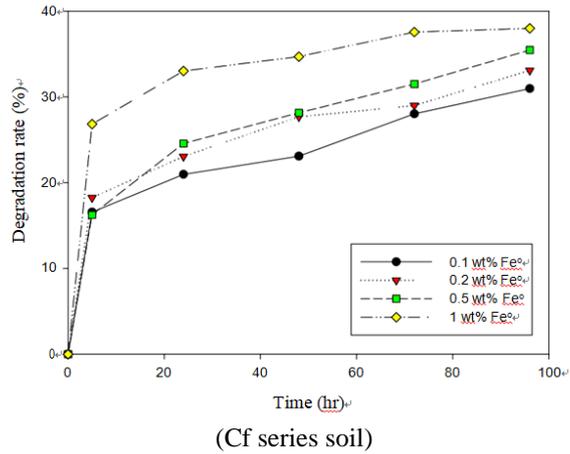
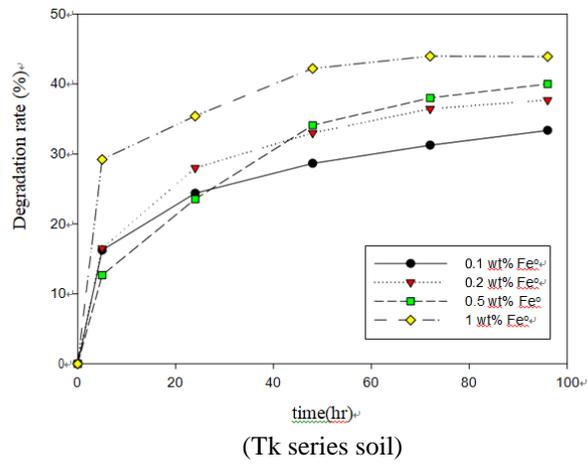


Figure 5. PCP (1000mg/kg) degradation efficiency of contaminated soil after applying ZVI different wt% and 2% H₂O₂at room temperature



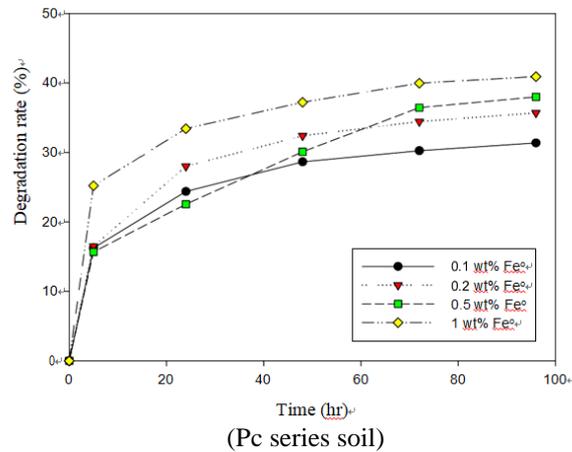
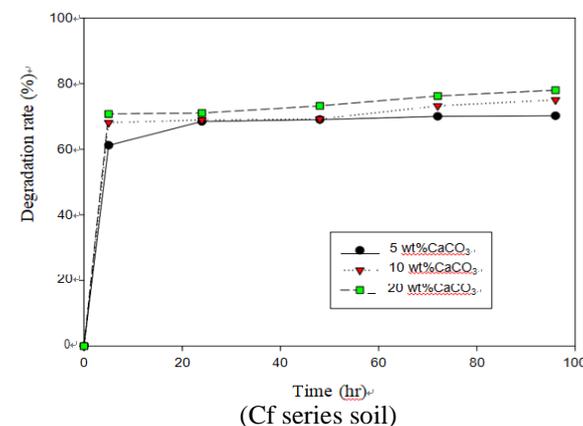
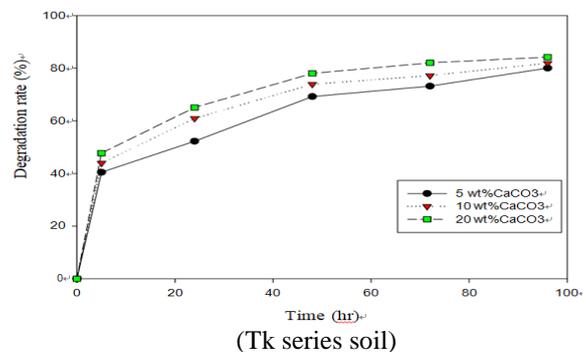


Figure 6. PCP (1000mg/kg) degradation efficiency of contaminated soil after applying ZVI of different wt% and 1% H₂O₂ at room temperature

3.2.3 PCP degradation efficiency of three soil samples after applying CaCO₃ of various wt% to Fenton-like processes

Fig. 7 shows changes in PCP degradation efficiency of the three soil samples after adding 1 wt% H₂O₂, 0.1 wt% ZVI, and CaCO₃ of different wt% (5 wt%, 10 wt%, and 20 wt%) to the Fenton-like processes. The findings suggest that adding CaCO₃ to the Fenton-like processes can effectively increase PCP degradation efficiency. As shown in Fig. 7, the PCP degradation efficiency of the Tk series soil reached 78% after adding 5 wt% CaCO₃ to the Fenton-like processes and reacting for 96 h. The PCP degradation efficiency of Cf series soil and Pc series soil also reached 70% and 65%, respectively. Moreover, when tested on different soil samples, the Fenton-like processes involving alarger amount of CaCO₃ resulted in higher PCP degradation efficiency. The PCP degradation efficiency of the Tk series soil (3.47%), characterized by higher CO₃²⁻ content, is higher than that of the Cf series soil (3.15%) and the Pc series soil (2.81%) because the dichlorination of PCP intensifies when CaCO₃ becomes sedimented and CO₃²⁻ isreleased into the water; this can help ZVI remove PCP in the soil faster, thus increasing the PCP degradation efficiency (Kober et al., 2002; Klausen et al., 2003).



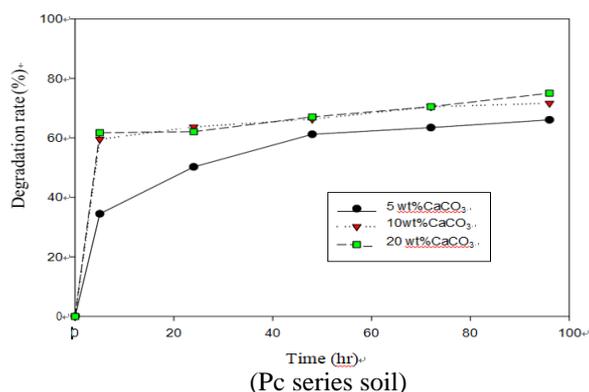


Figure 7.PCP (1000mg/kg) degradation efficiency of contaminated soil after applying 0.1 wt% ZVI, 1wt% H₂O₂, and 5 wt% CaCO₃ at room temperature

IV. Conclusion

This research applied synthesized ZVI to Fenton-like processes for treating three PCP-contaminated soil samples, aiming to examine the degradation efficiency of PCP. First, this study finds that both Al₂O₃ and Fe₂O₃ took up more than 40% of the composition of all the three soil samples. Second, the results of the PCP degradation efficiency after applying H₂O₂ of five concentrations without using ZVI show that the PCP degradation efficiency was lower at room temperature than that when ZVI was applied. Since ZVI was not used as the catalyst for the reaction, the only compound reacting with PCP was H₂O₂, i.e., there was no Fe²⁺ that facilitated the production of hydroxyl groups (•OH) for oxidation through hydrogen peroxide. Lastly, in terms of the PCP degradation efficiency after applying CaCO₃ of various wt% to the Fenton-like processes, this research finds that the higher the amount of CaCO₃ that is added, the higher the PCP degradation efficiency because the dichlorination rate of PCP grows when CaCO₃ become sedimented. Besides, CO₃²⁻ in the water can help ZVI remove PCP faster, thus increasing the PCP degradation efficiency. ZVI has been widely applied to various aspects of environmental remediation and is especially useful for the remediation and restoration of soil and underground water pollution control sites.

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