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Treatment of pentachlorophenol-contaminated soil using nano-scale zero-valent iron with hydrogen peroxide

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Abstract

This study uses nano-scale zero-valent iron with hydrogen peroxide to treat pentachlorophenol contaminates soil with the expectation to offer new and effective solution for future treatment work. The primary study indicates that the BET specific surface area of nano-scale zero-valent iron is about 34.9 m^2/g. When different content percentages of nano-scale zero-valent iron with 0, 0.2, 0.5, and 1 wt.% are added to 1% H_2O_2 for oxidation, 1 wt.% is found to give the best result to treat pentachlorophenol-contaminated soils. Among three types of sampling soils, Pianchen (Pc) series is proven to be more effective because zero-valent iron releases Fe^{2+} during oxidation. Addition of H_2O_2 promotes the generation of Fenton with $OH^{\bullet}$ and oxidation–reduction reaction. Due to the dual mechanism, the phenol compounds that are otherwise difficult to be removed are now effectively treated. This study also indicates that when 5% of calcium carbonate is added for 40 h, the decay rate on pentachlorophenol of Chengchun (Cf) series soil is from 37% to 78%, and Pianchen (Pc) series is from 43% to 76%. The result of treatment of pentachlorophenol-contaminated soil using the added calcium carbonate is a new treatment method and serves as the reference for future on-site treatment.

Keywords: Pentachlorophenol; Nanocomposite; Zero-valent iron; Oxidation

1. Introduction

The treatment of contaminated soil includes physical, chemical and biological methods; chemical treatment method makes use of chemicals to remove pollutants in the contaminated soil or convert the chemical structure of compounds into those with lower toxicity or no toxicity. These treatment methods include the use of Fenton, Fenton-like, and zero-valent iron, the advantages of fewer limitation and time saving suitable for treatment sites with time emergency feature. Fenton-like oxidation makes use of Fenton agent to activate with hydrogen peroxide to generate iron with hydroxyl free radical, which replaces natural iron and oxidized minerals (such as zero-valent iron and goethite) to participate in the catalysis and the reaction is similar to that of Fenton. Iron is one of the metals with the richest amount on the earth. In recent years, zero-valent iron has been widely applied to the treatment of contamination because of its easy accessibility, effective degradation of pollutants, generation of very little waste and second-time pollutants.

In recent years, zero-valent iron has been intensively studied for its ability to reduce organic pollutants [1–4] and nitrate [5]. Elemental iron (Fe^0) and dissolved Fe^{2+} form a redox couple that has a standard reduction potential of 0.440 V [2]. Elemental iron is regarded as a suitable donor of electrons for the in-situ remediation of contaminated groundwater and soil [2,4]. Zero-valent iron has been used for the reduction of halogenated organic compounds [1], nitroaromatic. In recent years, zero-valent iron has been intensively studied for its ability to reduce organic pollutants [1–4] and nitrate [5]. Wang and Zhang [8] directly pressed nano-iron particle and Pd/Fe particle under the earth surface through gravity or pressure used for effective treatment of halogenated organic compounds (HOCs) such as trichloroethene (TCE) or polychlorinated biphenyl (PCB).

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 [9]. Even though use of pentachlorophenol is severely

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restricted both in the USA and Europe, the US EPA has listed PCP as a priority pollutant, due to its slow and incomplete biodegradation [10–12], it can be found in surface, groundwaters and in soils [9,13–16]. Besides, recent studies indicate that even at low dose levels, PCP can exert synergistic effects when mixed with other aquatic pollutants such as cadmium, copper, ammonium and polycyclic aromatic hydrocarbons [17,18].

The purpose of this study is to use nano-technology to combine chemical oxidation treatment method and the method to add calcium carbonate to treat soil contaminated with pentachlorophenol (PCP) with two different categories of properties, and the test is carried out in two parts: (1) using Fenton (nano-iron plus hydrogen peroxide) to treat PCP-contaminated soil; (2) adding calcium carbonate to Fenton system to treat PCP-contaminated soil to address the related feasibility and economic effectiveness and compare the removal results of PCP in the contaminated soil. It is expected to offer the new, effective and timely treatment of contaminated soil for the reference of on-site application.

2. Experiments

2.1. Materials

This study selects Taiwanese soil with two 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. Pollutant for testing

The major pollutant used in this study is pentachlorophenol (PCP) (98% purification manufactured by Merck, GR grade) and PCP concentration in the soil is conducted in GC–MS qualitative and quantitative analysis.

2.3. Preparation of nano-zero-valent iron

The wet-chemical precipitation reaction [8] is adopted for making zero-valent iron: add $FeCl_3{\cdot}6H_2O$ solution to the solution of $NaBH_4$ to form sedimentation of Fe^0 (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:

$$Fe(H_2O)_6{}^{3+} + 3BH_4{}^- + 3H_2O \rightarrow Fe^0{}_\downarrow + 3B(OH)_3 + 10.5H_2 \quad (1)$$

2.4. 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.

2.5. The measurement of the specific surface area

This study uses surface area analyzer (SA 3100, Beckman oulter) to measure the specific surface area of the sampling soils and zero-valent iron catalyst.

2.6. Nature decay rate

Prepare contaminated soil with 0.1 wt.% in the reaction through and simulate the decay of pentachlorophenol. Take the individual samples on days 2, 5, 8, 13, 21 and 31, and extract with hexane and acetone (1:1 v/v) before analyzing the absorptive amount of pentachlorophenol in GC–MS analysis.

2.7. Kinetic absorption test

Weight proper sampling soil and use solvent of butane and ketone (1:1 v/v) at a concentration level of 1000 mg/kg to prepare synthesized pentachlorophenol-contaminated soil and to stir for 2 h at room temperature and place still. Take the individual samples after 0.16, 0.33, 0.5, 1, 2, 4, 8, 12, 24, 32, 48 and 72 h and then use hexane and acetone (1:1 v/v) to extract for the analysis of pentachlorophenol concentration analysis.

2.8. Field emission-scanning electron microscope (SEM) analysis

With a scanning electron microscope (SEM), this study observes the size of each 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.

3. Results and discussion

3.1. SEM analysis of zero-valent iron

Fig. 1 shows the structure of zero-valent iron. From Fig. 1(a) and (b), we know that the diameter of zero-valent iron is between 10 and 90 nm. Compared to the previous result [8], the size of zero-valent iron of this study is even smaller and the structure more uniform.

3.2. The analysis results of soil properties

This study selects Tk, Cf and Pc series soils for experiment. The texture of soil and the level of organic content will affect the experiment results and the analysis of soil properties of the three series soils is listed on Table 1. The texture from the roughest to the finest ones is Cf, Pc and Tk. The samples of Pc series soil have shown higher amount of organic content, 2.56%; in

Table 1
Property analysis of sampling soils

Soil	Moisture rate (%)	pH	CEC (cmol/kg)	Granular size			Texture	Organic compounds	Calcium carbonate
				Sand (%)	Silt (%)	Clay (%)			
Tk	4.56	8.25	14.43	2.4	53.4	44.2	SiC	1.61	4.72
Cf	1.33	6.12	9.55	46.7	46.9	6.4	L	0.98	3.47
Pc	2.51	4.03	16.58	20.3	32.5	47.2	C	2.56	2.81

terms of pH, the Tk series soil has the highest pH value of 8.25 due to its formation, the more contents of calcareous material in geographic structure, and calcareous concretion in bottom soil. The Pc series soil belongs to acid oxidized soil and has the high degree of weathering due to the weather conditions of high temperature, rain, and obvious dry and wet seasons. Also because the series soil contains more free iron oxides, the color appears to be brick red and minerals are washed away, so the soil shows strong acid response with pH value of 4.03. The pH value of the Cf series soil is 6.12.

3.3. The measurement result of specific surface scale

This study uses BET liquid nitrogen method to analyze the specific surface area of sampling soils and zero-valent iron

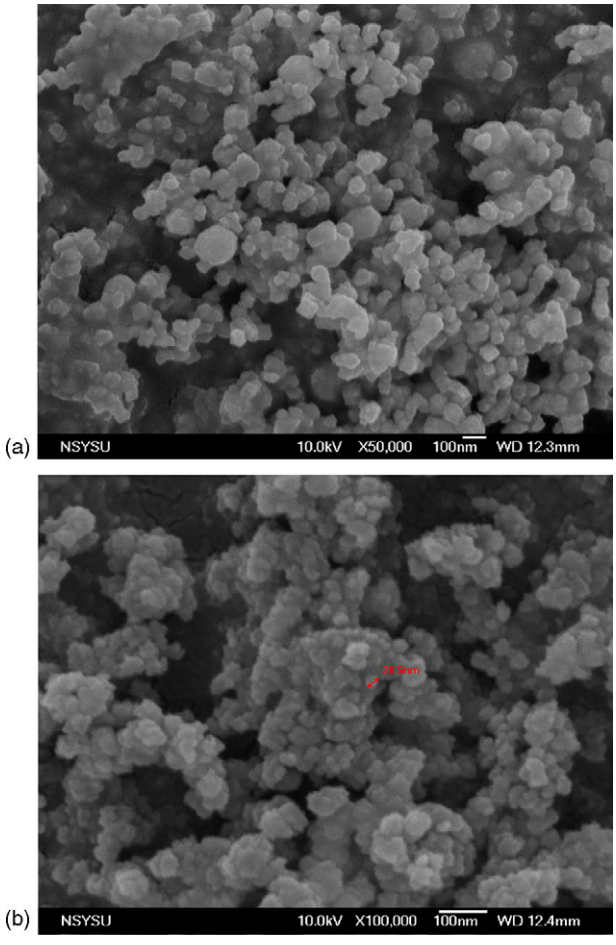

Fig. 1. (a) SEM analysis of zero-valent iron (×50,000). (b) SEM analysis of zero-valent iron (×100,000).

Table 2
Specific surface area of sampling soil

Soil	Specific surface area (m^2/g)
Tk	24.509
Cf	8.367
Pc	39.095

shown as in Table 2. The coarse texture of the Cf series soil has the smaller specific surface area, about 8.367 m^2/g; the fine texture of the Pc series soil has higher specific area of 39.095 m^2/g; surface Tk consisting of silty clay is about 24.509 m^2/g. In regard to nano-metal, nano-scale zero-valent iron has a specific surface area of 30.9 m^2/g. Wang and Zhang [8] used chemically synthesized method to compose nano-scale zero-valent iron and treat organic compounds such as vinyl chrolide, the BET surface scale was found about 33.5 m^2/g, nearly 37.2 times that of the synthesized nano-scale zero-valent iron (<10 μm), equivalent to 0.9 m^2/g.

3.4. The measurement results of free iron, manganese, and amorphous iron

Iron oxide goes through different soil formation and weathering conditions to form iron oxygen mineral at various levels of crystallization. The amorphous iron belongs to the low-crystallization part of free iron, so free iron is able to show the total content of iron. The ferro-oxygen mineral with high level of crystallization can promote the catalysis. Table 3 indicates that the Pc series soil has higher content of free iron, reaching 16.68 g/kg; the Cf has lower content of 4.32 g/kg. Due to its fine texture, the Pc series soil has higher content of free iron than the Cf series soil; as soil with fine texture has a more completed function of weathering, enabling the washing out of iron and the formation of free iron, it is likely to have higher content of free iron. On the other hand, the Tk series soil has the higher content of free manganese reaching 0.45 g/kg and the amorphous iron is about the range of 1–3 g/kg; therefore, Cf is the higher.

Table 3
Iron content of sampling soil

Soil	Free iron (g/kg)	Amorphous iron (g/kg)	Free magnanese (g/kg)
Tk	11.90	1.26	0.45
Cf	4.32	2.80	0.29
Pc	16.68	1.71	0.15

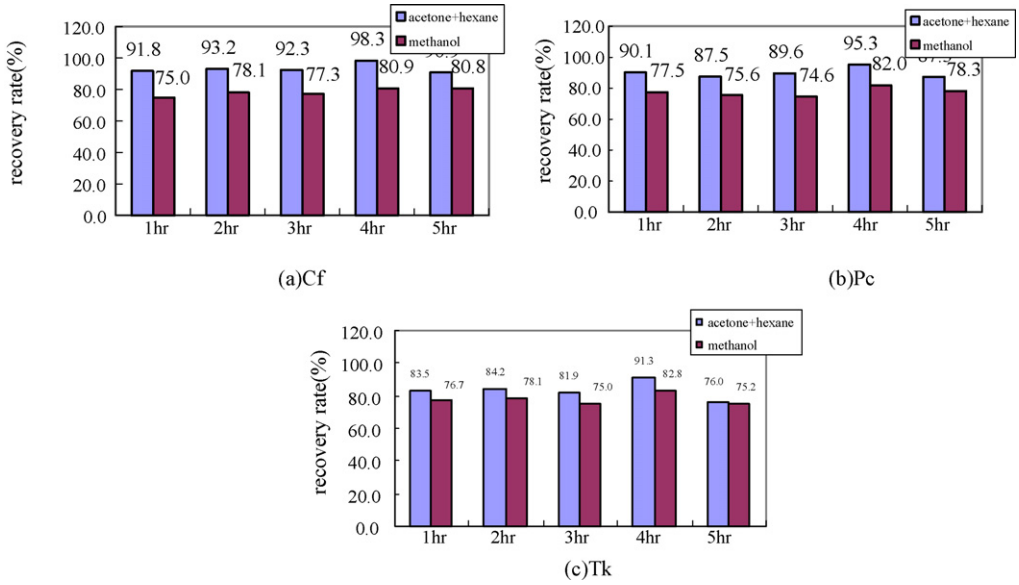

Fig. 2. Recycling rate of sampling soil.

3.5. The analysis result of recycling rate

The absorptive time of pollutants will affect the results of the desorption experiment. The longer the absorptive time, the easier it is for pollutants to be absorbed in the soil and the more difficult it is for them to be desorbed; on the contrary, the shorter the absorptive time, the easier it is for them to be extracted by the solvent. The absorptive time of 1–2 days has achieved the best result; thus, this research uses 2 days as the base to prepare the contaminated soil and then uses the vibrating desorption to extract. After extracting, separate solid and liquid at 3000 rpm centrifugal speed and take contaminated soil samples at different extracting times of 1, 2, 3, 4 and 5 h to centrifuge the top layer for GC–MS analysis. Fig. 2 indicates that the recycling rate of the Tk, the Cf and the Pc series soil within the first 4 h is more than 90%; accordingly, the best extracting time of this experiment is 4 h.

3.6. The measurement result of natural decay rate

Fig. 3 shows the three types of soils used for testing the treatment of pentachlorophenol-contaminated soil: the Cf series soil has higher decay rate of 8.8% and the Pc has lower rate of 5.2%. This is because the high content of organic material of the Pc series soil affects the decay rate. The result initially proves that the change in decay rate is determined by the soil texture and the content of organic material.

3.7. The measurement result of kinetic absorption

Fig. 4 indicates that the PCP absorption times of the three types of soils remain unstable before the first 32 h and then gradually settle down between 32 and 48 h. Therefore, the balancing absorption time of the pollutants is about 48 h and the three types of soil could be blended well.

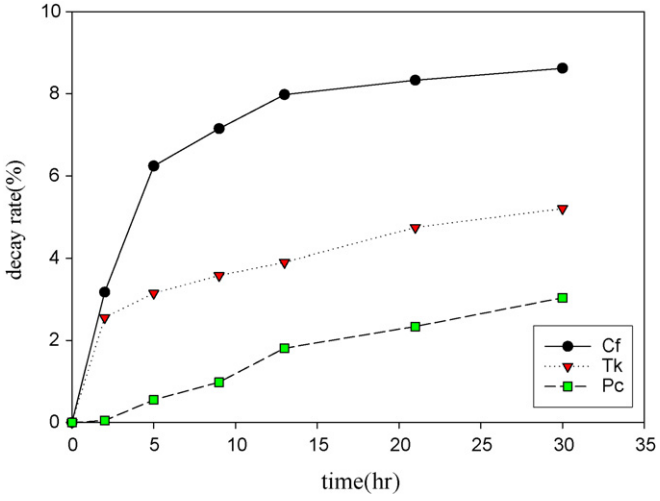

Fig. 3. Natural decay rate of pentachlorophenol in sampling soil.

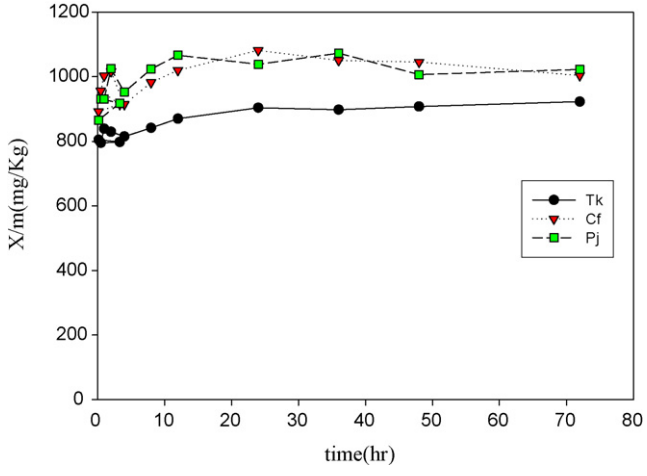

Fig. 4. Kinetic absorption model of sampling soil.

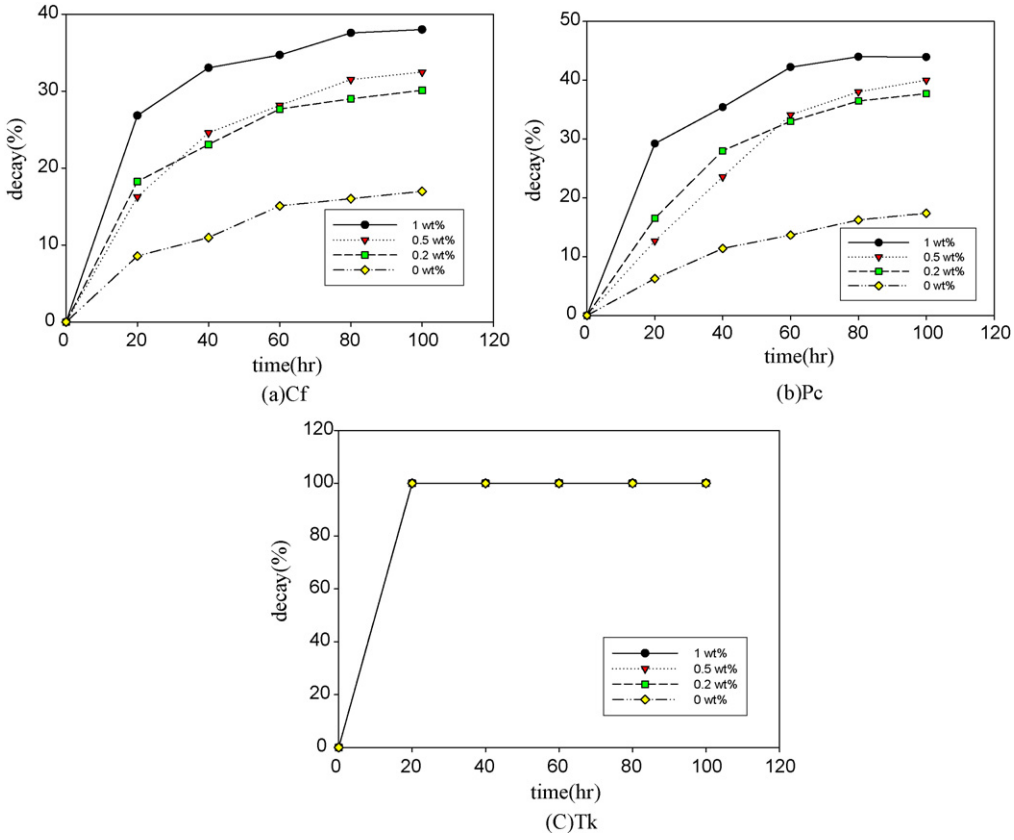

Fig. 5. The decay rate of pentachlorophenol at 1000 mg/kg when adding 1% H_2O_2 and different amount of zero-valent iron at room temperature.

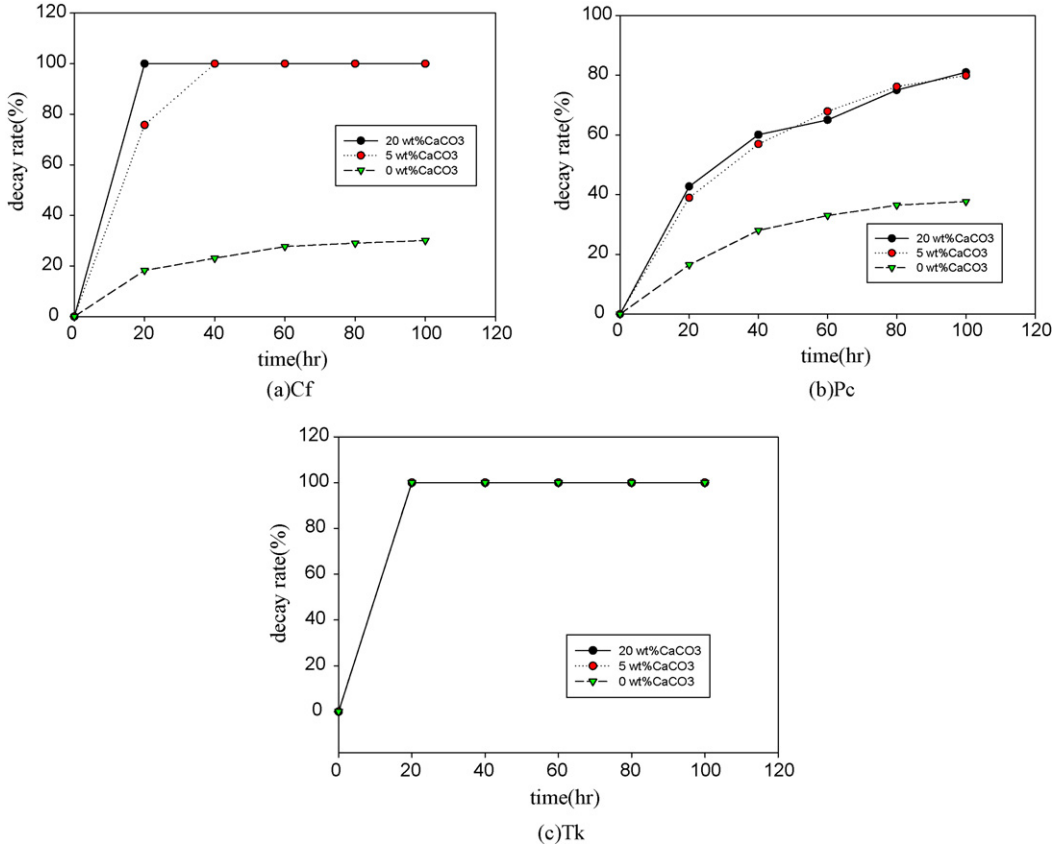

Fig. 6. The decay rate of pentachlorophenol at1000 mg/kg when adding 1% H_2O_2 and different amount of calcium carbonate at room temperature.

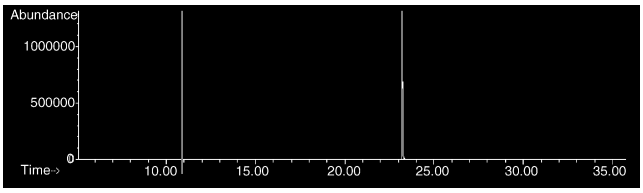

Fig. 7. GC–MS schematic diagram of pentachlorophenol-contaminated soil at 1000 mg/kg (Pc series soil) before Treatment.

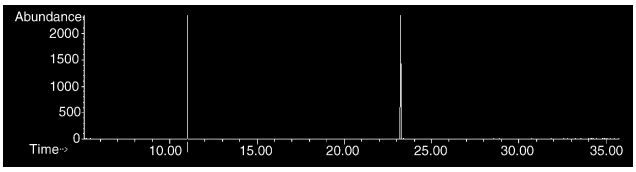

Fig. 8. GC–MS schematic diagram of pentachlorophenol-contaminated soil at 1000 mg/kg (Pc series soil) after treatment.

3.8. Measuring result of chemical oxidation method

This study prepares two types of PCP-contaminated Tk, Cf and Pc series soil at 1000 mg/kg and adding 0, 0.2, 0.5 and 1 wt.% of nano-scale zero-valent iron to initiate oxidation with 1% of H_2O_2 (shown in Fig. 5). The result indicates that at room temperature there is only minor change in the decay rate of pentachlorophenol-contaminated soil shown when adding different amounts of nano-scale zero-valent iron. But along with the increase in the amount of nano-scale zero-valent iron added, the increase in the reaction rate and the removal rate is shown mainly because of the increase in released Fe^{2+} dissolved due to the oxidation and erosion and the enhancement of $OH^{\bullet}$ generated by the catalysis of Fe^{2+}. Among these three types of soils, the Tk and Pc series soils have the better results. It is assumed that the Tk series contain a large amount of carbonate. When adding nano-scale zero-valent iron at room temperature to promote catalysis with hydrogen peroxide, the initial reaction temperature increases dramatically. It is expected to be beneficial to oxidation. On day 4, the decay rate of the Pc and Cf series soils reaches 43% and 37%, respectively. The Pc has a slightly higher decay rate than the Cf. This is because the Pc has a higher content of ferrooxygen mineral which helps to initiate oxidation reaction. Thus, under the same conditions, the Pc series soil work has better removal rate of pentachlorophenol than Cf.

This experiment under the conditions of 1% H_2O_2 and 0.2 wt.% nano-scale zero-valent iron adds different content of calcium carbonate (0, 5 and 20 wt.%) to promote reaction (shown in Fig. 6). The result indicates that the reaction rate and the removal efficiency of pentachlorophenol increase with the increase in the calcium carbonate content. Especially, when the Cf and Tk series are added with 5 wt.% and 20% of carbonate after 96 h reaction time, the removal rate is about 79% and 80%.

Before the treatment of H_2O_2, the strength of pentachlorophenol-contaminated Pc series soil has reached 1×10^6 PA in GC–MS analysis (Fig. 7). When treated with 1% H_2O_2 along with Fe^0 of 0.2 wt.% and 5 wt.% of calcium carbonate, the concentration level of pentachlorophenol is reduced to 2×10^4 PA showing the effectiveness in the removal of pentachlorophenol pollutants (Fig. 8).

The initial finding concludes that adding calcium carbonate to treat pentachlorophenol helps to treat the contaminated soil at the low hydrogen peroxide level. It reduces both the use of hydrogen peroxide and the treatment costs. This treatment, adding calcium carbonate in pentachlorophenol-contaminated soil, is a new and revolutionary method and serves as the reference for on-site application.

4. Conclusion

The primary study shows that synthesized nano-scale zero-valent iron has a BET surface area of 34.9 m^2/g. When adding different amounts of nano-scale zero-valent iron (0, 0.2, 0.5 and 1 wt.%) and 1% H_2O_2 to initiate oxidation, 1 wt.% of zero-valent iron gains the best treatment result for the pentachlorophenol-contaminated soil at 1000 mg/kg. Among the three types of series soils, the Tk and Pc give the better results. In terms of adding 5% of calcium carbonate for 40 h, the decay rate of pentachlorophenol of Chengchun (Cf) series soil is from 37% to 81% and that of Pianchen (Pc) series is from 41% to 75%. This treatment, adding calcium carbonate in pentachlorophenol-contaminated soil, is a new and revolutionary method and serves as the reference for on-site application.

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