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STUDY TO EVALUATE THE REMOVAL EFFICIENCY OF 2,4-D AND 2,4,5-T IN CONTAMINATED SOIL BY ZERO-VALENT IRON NANOPARTICLES

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Abstract

In this study 2,4-Dichlorophenoxy-acetic acid (2,4-D) and 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) in contaminated soil were removed using zero-valence iron nanoparticle material (nZVI), which was prepared by liquid phase reduction method. The nZVI contains 50% 10-20 nm particles and about 86.38% Fe. Soil samples were taken at four sites, with 2,4-D and 2,4,5-T contents of 4.83 - 87.98 ppm and 6.25 - 148.38 ppm, respectively. The sample with the highest concentration and the sample mixed from 4 samples taken at different points were used. With the ratio of nZVI:(2,4-D and 2,4,5-T) is 1:1 (w/w), the amount of polyacrylamid (PAA) of 0.01% and pH 3.0, the removal efficiency increased with time and depended on the initial contents. After 84 day-reaction, the content of 2,4-D and 2,4,5-T decreased from 87.98 to 10.68 and from 148.38 to 29.37 ppm, respectively for highest content samples. For mixed samples, these values were respectively from 39.31 to 3.53 and from 67.85 to 8.48 ppm. The removal efficiency of 2,4-D and 2,4,5-T obtained over 90 and 87.5%, respectively. During the reaction process, 2,4-D and 2,4,5-T were absorbed onto the surface of nZVI, where they were decomposed into 2,4-DCP and 2,4,5-TCP, then further dechlorinated to less toxic compounds e.g. parachlorophenon, phenon and benzene. The nZVI is considered as promising material to remove chlorine-containing organic compounds in soil environment.

Key words: contaminated soil, 2,4-D, 2,4,5-T, nanoparticle material, zero-valence iron

1. Introduction

2,4-D and 2,4,5-T are chlorinated organic compounds (COCs) hydrolyzed from 2,4-D and 2,4,5-T n-butyl esters, known as Orange agent. Among chlorophenoxy herbicides, 2,4-D and 2,4,5-T are commonly used in agriculture worldwide, for weed control of maize and cereal crops, and forestry [1-3]. 2,4-D and 2,4,5-T compounds are persistent chlorine-containing organic pollutants that persist for a relatively long time in the soil environment (a half-life of about 1-6 months and 1 month for 2,4,5-T and 2,4-D, respectively. However, in practice, the half-life is highly dependent on the composition, properties of the soil, climatic conditions, etc. [4].

2,4-D và 2,4,5-T contamination in the soil has been much concerned by scientists and governments [5, 6]. 2,4-D và 2,4,5-T is difficult to decompose, persistient relatively long in the soil, causing very severe consequences for human health, nature and the environment [7, 8].

Currently, several methods have been used to treat Orange agent in the soil such as: isolation [9], thermal incineration decomposition [10], soil washing [11], oxidation [10], thermal de-sorption [11] and biological methods . Each method has been found its advantages and disadvantages [11].

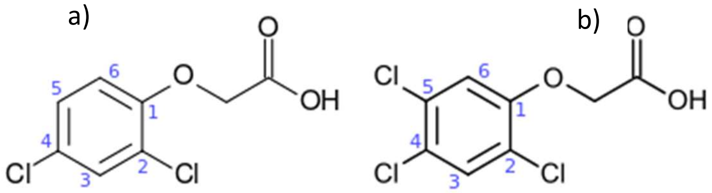


Figure 1. Molecular structure of 2,4-D (a) and 2,4,5-T (b)

Recently, the use of nano zero valent iron (nZVI) for the treatment of persistent COCs in water and soil has been widely studied [12-15], however, researches on the compounds of 2,4-D and 2,4,5-T are very limited. In addition, nZVI materials are low-cost and environmental friendly. Compared to large-sized Fe° particles, nZVI particles provide a larger surface area with high surface activity. Because of their small size, nZVIs can be injected and transported easily in porous media. nZVIs have been successfully used for transformation and detoxification of common environmental pollutants including COCs and pesticides [16]. nZVI has $E^\circ_{Fe2+/Fe^\circ} = -0.44V$, that has a strong reduction and is capable of reducing COCs like 2,4-D and 2,4,5-T by reductive dehalogenation in anaerobic environments [17]. In an aerobic environment, O_2 is present, the reaction occurs similarly a Fenton process.

There are many methods of nZVI synthesis such as: Milling [16], noble gas sputtering [18], laser ablation [19], liquid-phase reduction [20], chemical reduction [16], pyrolysis method [21], etc. In this study, nZVIs were synthesized by liquid-phase reduction method - a common chemical method, from iron salt (III) chloride, $NaBH_4$ as a source of reducing substances, with the addition of PAA to prevent their cluster and enhance stability..

2. Experimental method

2.1. Chemicals and reagents

The chemicals used are $FeCl_3$ (96%), $NaBH_4$ (98%), PAA, NaOH, NH_4OH, Na_2SO_4, NaN_3, HCl, HNO_3, CH_3COOH, n-Hexan, C_2H_5OH, axetonitril (ACN); 2,4-D và 2,4,5-T 99,9 % of Sigma - Aldrich, Germany; nitrogen gas 99.999%. Humic acid is separated from peat with a buffer solution using sodium priophotphat and NaOH with pH =13, shaken overnight, then filtered for solution and collected humic acid by precipitation with H_2SO_4 1N at 80°C. Buffer solutions of amonium acetate pH 3; 4; 5 and 7 are prepared from the solutions NH_4OH 0,2 N and CH_3COOH 0,2 N.

Soil samples

Soil samples SS1; SS2; SS3 and SS4 were taken at different locations at the South of Vietnam. Sampling site coordinates (SS1): 100 58.216" N 106048.346" E; (SS2): 10057.712" N 106048.857" E; (SS3): 10057.725"N 106048.84" E; (SS4): 10057.740" N 106048.823" E. Samples were taken at depths from 0 to 2.5 m according to TCVN 7538-2:2005. SS5 sample is the mixing pattern of the above samples.

Synthesis of nZVI material

nZVI material was prepared by the liquid-phase reduction method according to Wang and Zhang [22] using $NaBH_4$ 1.6 M, $FeCl_3$ 1.0 M, with the addition of PAA 0.01% without O_2 presence (using N_2 gas). Take 100 ml of $NaBH_4$ solution into a heat-resistant beaker, add 5 ml of PAA solution, stir the solution at 500 rpm, drop 50 ml of $FeCl_3$ solution at 5ml/min to the beaker containing $NaBH_4$ solution, then continue stirring for about 20 minutes to remove all H_2 gas. The product is centrifugated at 4000 rpm in 20 minutes, separated and washed 3 times with ethanol that has been expelled oxygen with N_2 gas, then dried in the N_2 gas at 60°C for 3 hours. The product is preserved in a sealed container under room temperature.

Characterization of iron nanoparticles

Particle size and composition of nZVI material were analyzed by SEM (Nova nano SEM), TEM (Philip CM20 FEG Lorentz), EDS (Jeol 5410) and XRD (D8-Advance).

2,4-D and 2,4,5-T degradation experiment

Soil samples SS4 and SS5 (1.0 kg each) were annealed with suspension: 250 ml buffer solution, pH 3, 20 ml PAA solution (0.01%) with 236 mg/kg and 117 mg/kg nZVI for SS4 and SS5 samples, respectively, in plastic trays. The sample is mixed equally with homogenizer 2 minutes/time/day. Samples were taken after 1; 4; 8 and 12 weeks to analyze the 2,4-D; 2,4-DCP; 2,4,5-T; 2,4,5-TCP and intermediate products.

Analysis methods

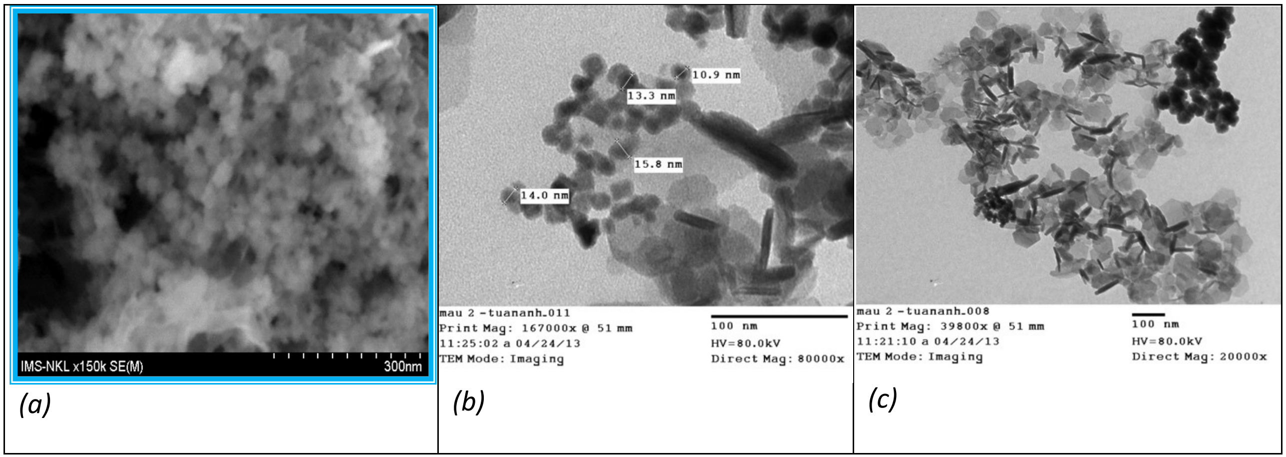
Physical and chemical parameters of soil samples (pH, humic acid content, CEC, texture composition, 2,4-D; 2,4,5-T, 2,4-DCP and 2,4,5-TCP) were analyzed according to the standard analysis method. The analysis was carried out on GC-MS, Agilent Technology 6890N/5973i; HPLC, Agilent Technology, model 1100; UV-VIS Optizen 2120 UV.

3. Results and discusions

3.1.nZVI material

3.1.1. SEM and TEM images of nZVI

As can be seen in Figure 2, in the TEM image Fe^0 nano-forming product are flattened, cluster particles, with some long rod-shaped particles. Over 95% of the particles are smaller than 100 nm, about 50% of the particles are between 11 and 20 nm in size.



(a) *(b)* *(c)*

Figure 2. SEM image (a) và TEM image (b, c) of Fe^0 nano

In the presence of PAA - a polymer cations, and due to stirring, Fe^0 particles were evenly distributed and dispersed. The amount of Fe^{3+} ions introduced into the solution reacts slowly to avoid colloidal production and the amount of generated H_2 gas is sufficient to immediately react with Fe^{3+}. Therefore, the obtained product, nZVI, is quite even in small size, about 11-20 nm. Compared to other authors' products such as Duc Le [23] and Xiao-qin Li's et al. [24], Fe^0 nano products formed by this method have smaller particle sizes.

3.1.2. *Energy-Dispersive X-Ray spectroscopy of nZVI*

EDX spectrum of nZVI showed that Fe and oxygen elements account for 86.38 and 10.07% by mass, respectively. The O content in the sample is high because the synthesis and stored processes, oxygen from the air may contact and react with Fe^0 to form FeO and Fe_2O_3 according to the following reaction:

$$Fe + O_2 \rightarrow FeO \qquad (1)$$

$$FeO + O_2 \rightarrow Fe_2O_3 \qquad (2)$$

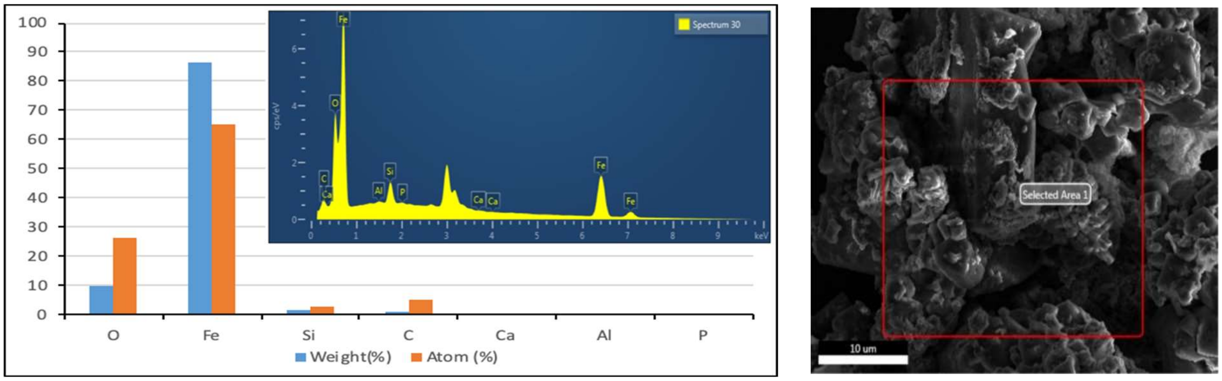


Figure 3. EDX spectrum of nZVI material

In addition, impurity compounds, such as SiO_3^{2-}, PO_4^{3-} were also found in the original raw material. At the same time, during the material synthesis, PAA with amid group [-C(=O)-N], acting as dispersing substance, was added to protect the nanomaterials. When washing the material with water and absolute alcohol, PAA still adhere to the surface of the nZVI material, it increases the content of O and C in the sample. With the nano-product obtained shows that the synthetic Fe^0 nanoparticles are perfectly agreed with Xiao qin Li [24].

3.1.3 XRD spectrum of nZVI

The X-ray diffraction spectrum of nZVI showed that between 2-theta from 20-90°, characteristic peaks were appeared, with 2-theta at 44.90°. These peaks have a very high intensity which characterizes the cubic crystals of Fe^0 nano. In addition, two scattered peaks at 2-theta points are 65.22° and 82.50° with smaller intensity, characterizing mesh crystals. Thus, Fe^0 nano is major content in the obtained material, apart from that, there are also other Fe compounds like FeO or Fe_2O_3. However, their contents are insignificant (see Figure 4). This is consistent with the results of analysis by EDS (Figure 3) and many other authors [24].

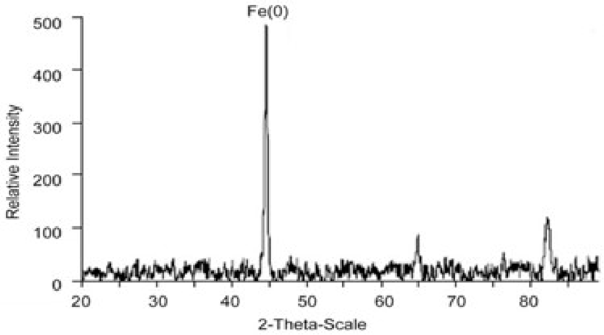


Figure 4. XRD spectrum of nZVI material

3.2.The physical and physical properties of Orange agent in contaminated soil in studied areas

It is observed that there are quite significant differences in the physio-mechanical composition of soil samples, especially the content of 2,4-D and 2,4,5-T (see Table 1 and 2). In addition, 2,4-dichlorophenol (2,4-DCP) and 2,4,5-trichlorophenol (2,4,5-TCP) found presence in soil samples that are the products of 2,4-D and 2,4,5-T hydrolysis by microorganisms and other factors [25, 26].

Table 1. Basic composition of in 2,4-DCP and 2,4,5-TCP contaminated soil in studied areas

Sample	pH	Soil texture, %				A.humic+ A.fulvic (%C)	A.humic (%C)	CEC soil (me/100 g)	CEC clay (me/100g)
		Coarse sand	Fine sand	Limon	Clay				
SS1	5.4	48.92	24.92	4.78	21.38	0.030	0.004	4.32	5.96
SS2	5.7	21.77	43.75	4.56	29.92	0.030	0.004	7.68	10.78
SS3	5.6	17.10	41.30	7.56	34.04	0.090	0.008	9.92	14.84
SS4	5.8	12.91	46.03	4.80	36.26	0.080	0.007	9.28	13.95
SS5	5.6	37.73	29.35	7.20	25.72	0.065	0.006	7.52	10.46

Table 2. 2,4-DCP, 2,4,5-TCP content and some elements in contaminated soil in studied areas

Samples	Average contents (n=6)			
	2,4-D (ppm)	2,4,5-T (ppm)	2,4-DCP (ppm)	2,4,5-TCP (ppm)
SS1	10.76 ± 0.07	16.15 ± 0.12	0.37 ± 0.02	0.79 ± 0.03
SS2	41.82 ± 0.29	92.74 ± 0.25	0.43 ± 0.20	18.52 ± 0.26
SS3	4.83 ± 0.09	6.25 ± 0.10	0.42 ± 0.02	1.35 ± 0.05
SS4	87.98 ± 1.00	148.38 ± 0.95	0.14 ± 0.01	11.85 ± 0.50

SS5	39.31 ± 0.57	78.61 ± 0.66	0.356 ± 0.01	8.23 ± 0.21

The lowest and highest content of 2,4-D is 4.83 and 87.98 ppm, respectively for for the SS3 and SS4 samples (Table 2). For 2,4,5-T, these values were 6.25 and 148.37 ppm also for the SS3 and SS4 samples. Even, over time, there is movement and decomposition by microorganisms, absorption of plants, hydrolysing and decomposition by other substances [25, 26], the concentration of these pollutants is still very high.

The content of 2,4-DCP and 2,4,5-TCP found much lower than that of the 2,4-D and 2,4,5-T compounds in the same soil samples. The appearance of 2,4-DCP and 2,4,5-TCP in soil samples was probably due to the activity of 2,4-D and 2,4,5-T hydrolysed microorganisms [1, 25, 27].

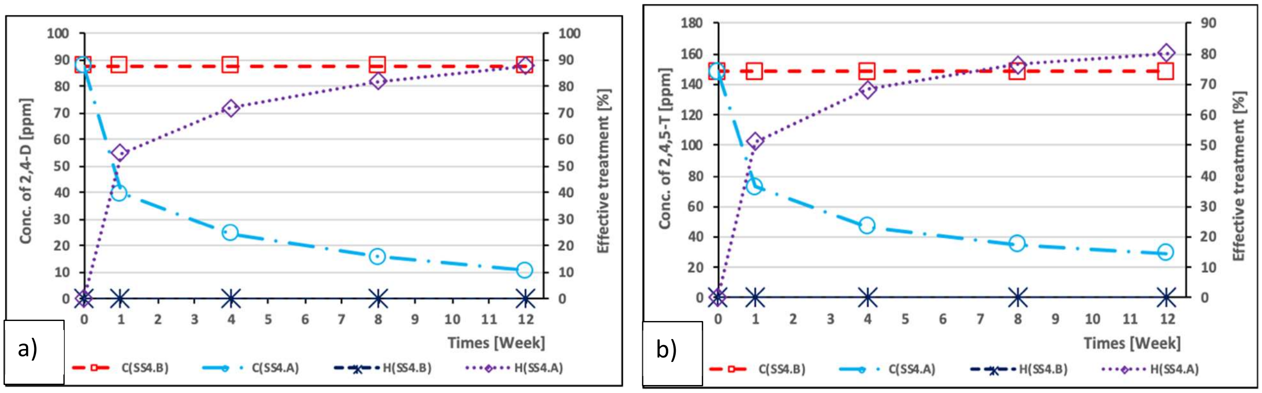
From the analysis results, SS4 and SS5, were selected for futher study as SS4 has the highest Orange agent content and mixed SS5 is representing for all sampling sites.

3.3.The 2,4-D and 2,4,5-T removal efficiency by nZVI

Figure 6 and 7 showed a decrease in concentration and removal efficiency of 2,4-D and 2,4,5-T in 2 soil samples in studied areas using 236 and 117 mg nZVI per kg soil respectively with SS4 and SS5, corresponding with the ratio of nZVI: 2,4-D and 2,4,5-T is 1:1(w/w), after 1, 4, 8 and 12 weeks.

The removal efficiency increases from the 1st to 12th week, which is significantly increased in the 1st week and slowly increased for the following weeks. After the 1st week, the decline of 2,4-D was 54.91 and 59.78%, of 2,4,5-T was 51.09 and 53.61% for SS4 and SS5 samples, respectively. When extending the incubation period, the content of 2,4-D and 2,4,5-T substances in both trials continues to decrease. By the 12th week, the decline of 2,4-D reached 87.86 and 91.03%, of 2,4,5-T reached 80.20 and 87.5% for the SS4 and SS5 samples, respectively. From the obtained data it is showed that under the same conditions, the removal efficiency of 2,4-D is higher than that of 2,4,5-T and in the SS5 sample is higher than the SS4 sample. Meanwhile, in the sample control their content is unchanged from the original (inputs).

This is probably due to the persistent and stable of 2,4-D and 2,4,5-T. Therefore, in treated soils, nZVIs are clearly the cause of the deterioration of 2,4-D and 2,4,5-T.



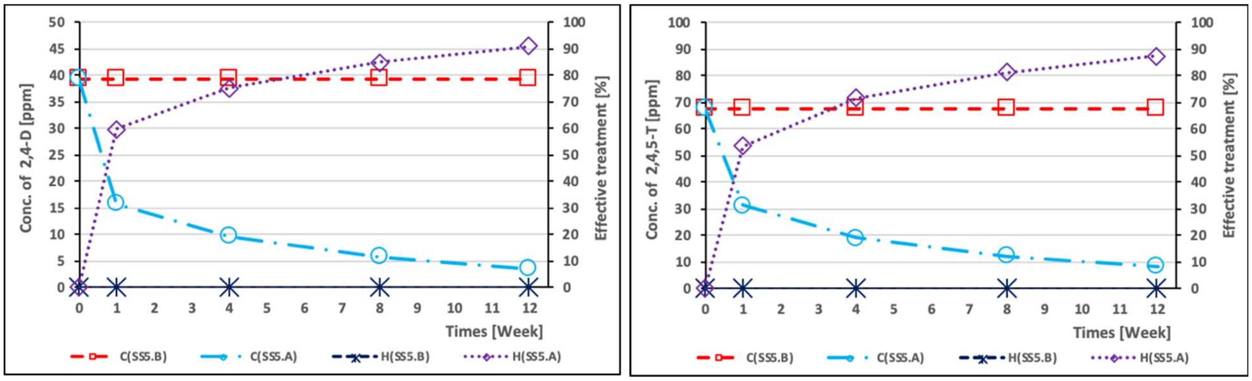


Figure 6. Removal efficiency of 2,4-D in SS4 (a); 2,4,5-T in SS4 (b); 2,4-D in SS5 (c) and 2,4,5-T in SS5 (d)

At the beginning, due to the presence of O_2 in the environment, a Fenton-type reaction to decompose 2,4-D and 2,4,5-T (equations 3 to 6) may occur, which reduced their concentration very quickly [28]. After exhaust of O_2, the concentrations of 2,4-D and 2,4,5-T and of nZVI remain high that it provides a large surface area for absorption. Therefore, 2,4-D and 2,4,5-T compounds were absorbed onto the surface of large nZVI and take place quite quickly. The mechanism of 2,4-D and 2,4,5-T compounds on the surface of nZVI to fast form the products is as follow [29-31]:

$2Fe^{\circ} + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^{-}$ (3)

$O_2 + 2H^{+} + 2e \rightarrow H_2O_2$ (4)

$Fe^{2+} + H_2O_2 \rightarrow {}^{*}OH + OH^{-} + Fe^{3+}$ (5)

${}^{*}OH + Cl_3C_6H_5OCH_2COOH \rightarrow CO_2 + H_2O + Cl^{-}$ (6)

After incubation, the amount of nZVI decreases, at the same time, there is a competitive e source from nZVI between 2,4-D and 2,4,5-T with other compounds present in the environment such as 2,4-DCP and 2,4,5-TCP etc. Besides, there is the formation of FeOOH and $Fe(OH)_3$ on the surface of nZVI, which prevents the interaction between nZVI with chlorinated pollutants such as 2,4-D and 2,4,5-T, resulting in reduction of the reaction rate [32].

Over the 12-week incubation period, the removal efficiency of 2,4-D and 2,4,5-T in the SS4 sample was always higher than that of the SS5 samples. This probably due to the influence of their physio-mechanical and chemical composition. For SS4 soil sample, the content of coarse particle was low (12.91%) and high clay (36.26%), higher total humic and fulvic content than that of SS5 (Table 1), therefore the absorption capacity of organic substances such as 2,4-D, 2,4,5-T, 2,4-DCP and 2,4,5-TCP, etc., found higher, impeding the contact of nZVI and organic compounds. In addition, the cation exchange capacity and total humic and fulvic content of the SS4 sample (9.28) are larger than that of the SS5 (7.52), which causes the content of the Fe^{2+} ion in the soil solution decreased, thereby decrease the electron donor for the reduction process [33, 34].

3.4. Products of 2,4-D and 2,4,5-T decomposition process by nZVI

3.4.1. Main products

During decomposition process, the presence of 2,4-Dichlorophenol (2,4-DCP), 2,4,5-Trichlorophenol (2,4,5-TCP), Parachlorophenol, Phenol, Benzaldehyde and Benzene were observed (figure 7). These compounds were considered as 2,4-D and 2,4,5-T conversion products.

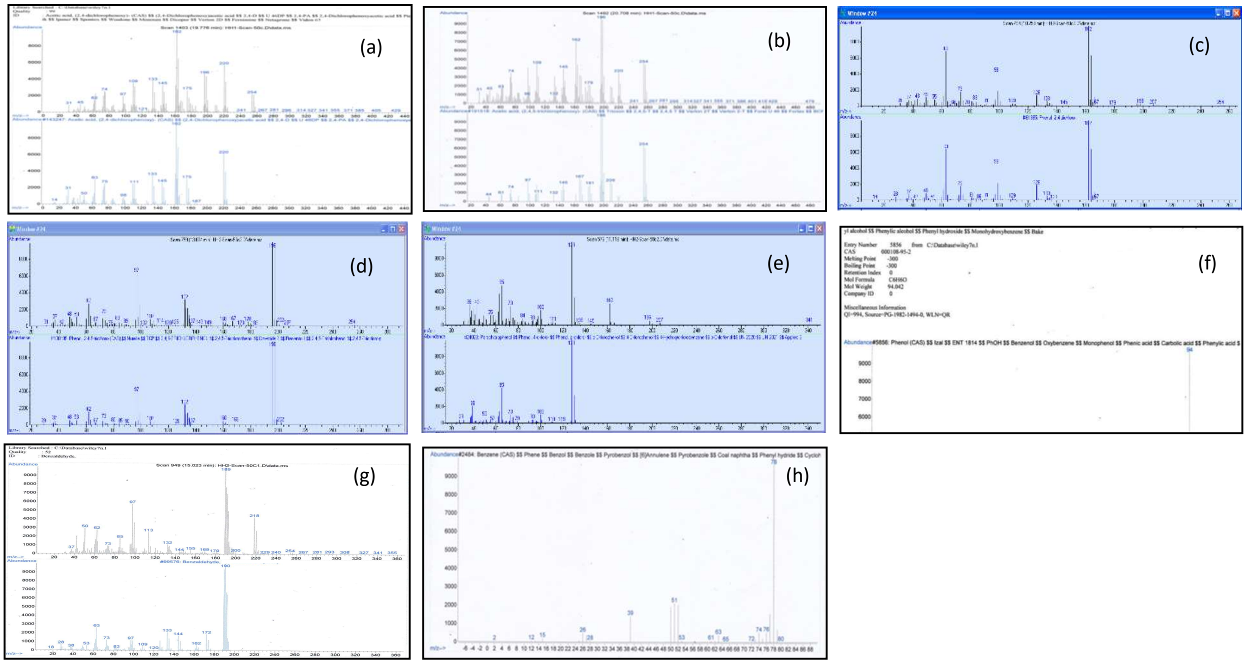


Figure 7. Mass spectrum of organic compounds generated during 2,4-D and 2,4,5-T decomposition process

The conversion process in the presence of nZVI can be taken as follows with the initially formation of 2,4-DCP and 2,4,5-TCP:

$$Fe^{\circ} + 2H^{+} \rightarrow Fe^{2+} + 2H^{\circ} \quad (7)$$

$$Fe^{\circ} \rightarrow Fe^{2+} + 2e \quad (8)$$

$$Fe^{2+} \rightarrow Fe^{3+} + e \quad (9)$$

$$Cl_2C_6H_3OCH_2COOH + 2H^{+} + 2e \rightarrow Cl_2C_6H_3OH + CH_3COOH \quad (10)$$

$$Cl_3C_6H_2OCH_2COOH + 2H^{+} + 2e \rightarrow Cl_3C_6H_2OH + CH_3COOH \quad (11)$$

2,4-DCP và 2,4,5-TCP then continued to be de-chlorinate as below reactions:

$Cl_3C_6H_2OH + H^\circ + e \rightarrow Cl_2C_6H_3OH + Cl^-$ (12)

$Cl_2C_6H_3OH + H^\circ + e \rightarrow ClC_6H_4OH + Cl^-$ (13)

$ClC_6H_4OH + H^\circ + e \rightarrow C_6H_5OH + Cl^-$ (14)

$C_6H_5OH + H^\circ + e \rightarrow C_6H_6 + OH^-$ (15)

In anaerobic environments, phenol is the product of de-chlorination and CH_3COOH is formed during hydrolytic process of 2,4-D and 2,4,5-T and from added ammonium acetate buffer solution, which is reduced by Fe^0 to form phenyl and carbonyl radicals:

$C_6H_5OH + Fe^\circ + H^+ \rightarrow {}^*C_6H_5 + H_2O$ (16)

$CH_3COOH + Fe^\circ + 3H^+ \rightarrow CH_4 + {}^*CHO + H_2O$ (17)

$^*C_6H_5$ and $^*CHO$ radicals will react very quickly to form benzaldehyde:

$^*C_6H_5 + {}^*CHO \rightarrow C_5H_5CHO$ (18)

In both experiments, along with the significant decrease of 2,4-D and 2,4,5-T contents, it is observed a sharp increase in the content of 2,4-DCP and 2,4,5-TCP in the first week, then gradually decreasing in the following weeks. For 2 control experiments (no nZVI present) content of 2,4-D substances; 2,4,5-T; 2,4-DCP and 2,4,5-TCP kept unchanged throughout 12-week incubation period (see Figure 8).

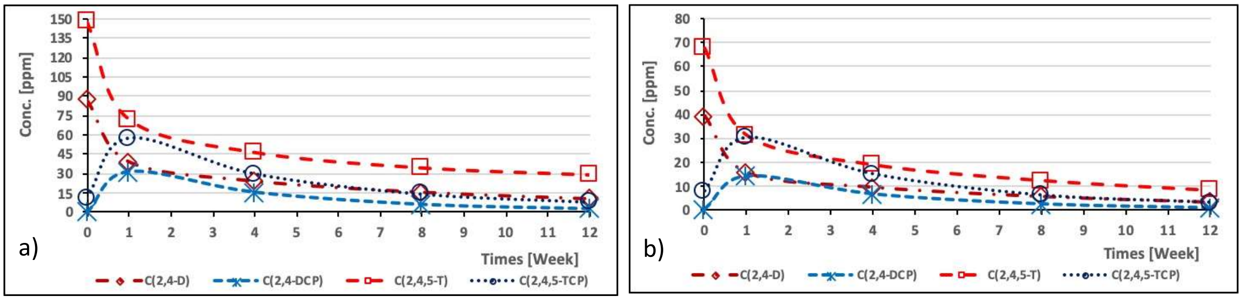


Figure 8. Variation of 2,4-D; 2,4,5-T; 2,4-DCP and 2,4,5-TCP contents during treatment: SS4 (a) and SS5 (b)

From the experimental data, after the 1st week of incubation, 2,4-DCP content increased from 0.141 to 31.46 ppm and from 0.356 to 14.57 ppm for the SS4 and SS5 samples, respectively. Meanwhile, the content of 2,4,5-TCP increased from 11.84 to 57.82 ppm and from 8.227 to 30.76 ppm for the SS4 and SS5 experiments which is higher than 2,4-DCP. After the 4th weeks of incubation, the content of 2,4-DCP and 2,4,5-TCP decreases to about 50% compared to the first week. When the incubation period reached to week 12, in both experiments, the content of 2,4-

DCP was slightly higher than at the initial and the content of the remaining 2,4,5-TCP was lower than the initial.

The reason may be because at the 1st week, 2,4-D and 2,4,5-T content were much higher than 2,4-DCP and 2,4,5-TCP, nZVI absorption is proportional to the content of COCs. After exhaust of O_2, due to the large amount of reactants, the conversion is mainly of 2,4-D and 2,4,5-T compounds on the surface of nZVI to fast form 2,4-DCP and 2,4,5-TCP (Equations 11 to 15). Simultaneously, this process is reduction of 2,4-DCP and 2,4,5-TCP products (Equations 16 to 19). However, at this stage 2,4-DCP and 2,4,5-TCP products are formed more than 2,4-DCP and 2,4,5-TCP are reduced. After one week of incubation, the remaining 2,4-D, 2,4,5-T content is equivalent to 2,4-DCP and 2,4,5-TCP (Figure 8).

Over time, the amount of nZVI decreases, the absorption surface decreases, and at the same time there is an e-source competition (from nZVI) between organic substances [32]. As findings, the content of compounds 2,4-D, 2,4,5-T, 2,4-DCP and 2,4,5-TCP kept decreasing, however, the content of 2,4-DCP and 2,4,5-TCP is observed lower throughout the incubation period from 1 to 12 weeks. This confirms that 2,4-DCP and 2,4,5-TCP decomposition is easier than 2,4-D and 2,4,5-T conversion. Dechlorination of 2,4,5-TCP molecules by nZVI takes place similarly to chlorine containing aromatic organic compounds, such as lindane, to form fewer chlorine containing molecules and final product is benzene [35].

In addition, during incubation, the total content of 2,4-D and 2,4-DCP; 2,4,5-T and 2,4,5-TCP are all decreased over time. This can be explained that under research conditions, formed compounds, such as parachlorophenol or phenol, continue to react with Fe^{3+} to form complexes, or be adsorbed on clay particles, humic compounds and other components present in the soil [30].

$$3C_6H_5OH + Fe^{3+} \rightarrow [Fe(C_6H_5O)_3] \qquad (19)$$

4. Conclusions

nZVI was prepared by liquid phase reduction method in the presence of PAA and used to remove 2,4-D and 2,4,5-T in the soil at some areas in the South of Vietnam. nZVI acts as a reducing agent, while providing a large surface area for the absorption of COCs. The processes take place on the surface of nZVI in an anaerobic medium in 4 stages: the first is the absorption of COCs such as 2,4-D, 2,4,5-T and H^+ from the liquid phase to the surface of nZVI, then conversion them into 2,4-DCP and 2,4,5-TCP and then dechlorinate into intermediate products and finally into benzene. Finally, the products are diffused out of the solid phase surface to the solution (liquid phase). With the presence of oxygen, the adsorption of molecules and ions on the surface of nZVI material that followed fenton reaction and final products are CO_2 and H_2O.

The formed products from anaerobic processes are non-toxic or less toxicity. Some products, such as phenol, can react with Fe^{3+} to precipitate or in immobile form when adsorbed on clay particles or humic acid in the soil. nZVI is a material with highly potential application in many fields. It also opens new directions in the treatment of persistent organic compounds in general and particularly in orange agent compounds.

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