

## Treatment of Chlorpyrifos Pesticide in Water Using Nano Scales Zero Valent Iron (nZVI)

Abdul-jabbar Abbas Ali    Ahmed Khudair Hassan    Hassan Fadhil Mohammed  
Essa Abed Salih

Ministry of Science and Technology / Environmental and Water – hazard. Treatment  
Technology Center

Baghdad – Iraq

E-mail: [abd\\_045@yahoo.com](mailto:abd_045@yahoo.com)

### Abstract

This study deals with degradation efficiency of chlorpyrifos by nano zerovalent iron (nZVI) for effective remediation of water contaminated with chlorinated pesticide. We prepared the nZVI and the effects of pH, time and iron dosage on chlorpyrifos degradation were studied. Chlorpyrifos degradation percentage was increased with increasing nZVI treatment amount and reaction time. The experimental results showed that chlorpyrifos was completely removed by nZVI, chlorpyrifos solution at 25 mg/L was efficiency removed by nZVI within 6 hours, at initial solution pH 3, nZVI dose of 500 mg/L. These results suggested that nZVI could be effectively applied to degradation of chlorpyrifos pesticides in the aqueous environments.

**Key Words:** Degradation of Chlorpyrifos Pesticides and Nano Zero Valent Iron (nZVI).

### معالجة مبيد الكلوربيرفوس في المياه باستخدام الحديد النانوي صفري التكافؤ

عبد الجبار عباس علي    أحمد خضير حسان    حسن فاضل محمد    عيسى عبد صالح

وزارة العلوم والتكنولوجيا / دائرة البيئة والمياه - مركز تكنولوجيا معالجة الملوثات

بغداد/العراق

### الخلاصة

تتعامل هذه الدراسة مع كفاءة الازالة لمبيد الكلوربيرفوس باستخدام الحديد النانوي صفري التكافؤ (nZVI) لمعالجة المياه الملوثة بهذا المبيد العضوي الكلوري اذ تم تحضير الحديد النانوي صفري التكافؤ ومن ثم دراسة الظروف المثلى لتفكك مبيد الكلوربيرفوس من الدالة الحامضية والزمن و كمية الحديد النانوي المضافة. لوحظ من خلال النتائج المستحصلة بان نسبة التفكك للمبيد تزداد كلما ازدادت كمية الحديد النانوي المضافة وكذلك مع زيادة زمن التفاعل. وظهرت نتائج البحث ازالة كاملة لمبيد الكلوربيرفوس عند تركيز 25 ملغم/لتر عند اضافة 500 ملغم/لتر من الحديد النانوي وعند دالة حامضية تساوي 3 ولمدة زمنية مقدارها 6 ساعات. ان الدراسة بينت من خلال النتائج المستحصلة بانه يمكن انحلال المبيد الكلوربيرفوس عند استخدام الحديد النانوي وبكفاءة عالية جداً.  
**الكلمات المفتاحية:** تفكك مبيد الكلوربيرفوس و الحديد النانوي صفري التكافؤ.

## Introduction

Chlorpyrifos (IUPAC name: *O,O*-diethyl *O*-3,5,6-trichloropyridin-2-yl phosphorothioate) is an organophosphorus insecticide which is one of the most widely-used active ingredients in agricultural insect control in the world because of their acute toxicity to insect pests and short persistence after application (Kulkarni *et al.*, 2000). Chlorpyrifos is formulated into various products such as Dursban, Bestban and Teragard, etc.

Chlorpyrifos has been of a great concern due to persistence, toxicity and accumulation in soils and ground waters (Hossain *et al.*, 2013). A new approach has been developed recently to solve some problems of surface and ground water contamination by the use of nano Zero Valent Iron (nZVI) which is a powerful reducing agent, non-toxic and relatively inexpensive. Many studies have shown that a wide variety of toxic contaminants, such as chlorinated organic substances (Kim *et al.*, 2008; Kim and Carraway, 2003), removal of antibiotic metronidazole (Fang *et al.*, 2011a), polybrominated diphenyl ethers (PBDEs) (Fang *et al.*, 2011b), nitro compounds (Bandstra *et al.*, 2005), azo dye (Moon *et al.*, 2011), heavy metals (Liu and Lo, 2011) and so on, could be rapidly degraded by nZVI. Meanwhile, an increasing number of field tests in pilot- and full-scale remediation sites have been implemented by using nZVI (Wei, *et al.*, 2010).

Iron has the capacity to degrade many halogenous hydrocarbon compounds such as carbon tetrachloride, trichloroethane, trichloroethylene and some pesticides (Hossain *et al.*, 2013). Chlorpyrifos use has been prohibited since 2001 in the U.S and some

countries, but which still continues use in Iraq.

The aim of this work is to study the possibility of pesticide elimination by reduction with nZVI. The pesticide choosed for this study is chlorpyrifos because it is not quickly biodegraded and is widely used in the agricultural productivity in Iraq.

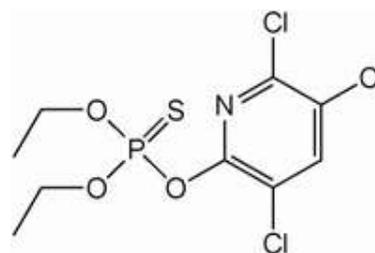
## Materials and Methods

### Chemicals

Chlorpyrifos (purity > 99.9%) was purchased from Sigma-Aldrich (U.S.A). Commercial grade Chlorpyrifos (Dursban 20% EC) was obtained from Dow Agro sciences, Jordan. Ferrous sulfate heptahydrate (FeSO<sub>4</sub>.7H<sub>2</sub>O) and Sodium borohydride (NaBH<sub>4</sub>) were obtained from BDH (England). Ethanol, methanol and other used solvents were of analytical grade. Aqueous solutions were made with de-ionized water. The main physical and chemical characteristics of chlorpyrifos are listed in Table 1.

**Table (1) Physical and Chemical Characteristics of Chlorpyrifos.**

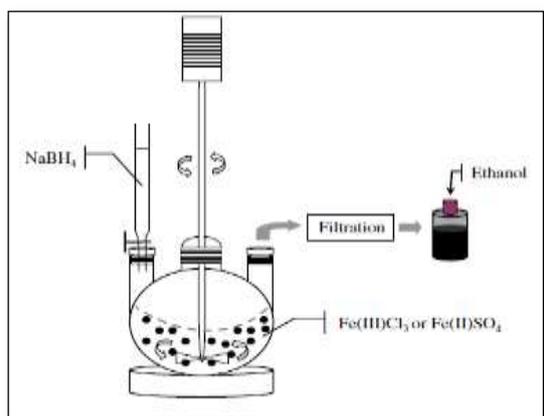
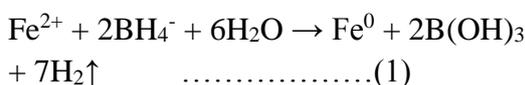
<b>Molecular formula</b>	<b>C<sub>9</sub>H<sub>11</sub>Cl<sub>3</sub>NO<sub>3</sub>PS</b>
<b>Molar mass</b>	350.59 g/mol
<b>Density</b>	1.398 g/cm <sup>3</sup> (43.5 °C)
<b>Melting point</b>	(41-42) °C
<b>Solubility in water</b>	2 mg/L (25 °C)
<b>log P</b>	4.96 (octanol/water)



**Figure (1) Chemical Structure of Chlorpyrifos**

### Preparations of nZVI Particles

Nanoscale zero-valent iron (nZVI) particles can be prepared in aqueous solutions via the reduction of ferrous ion with sodium borohydride (Sun *et al.*, 2005). The preparation of iron nanoparticles was conducted in a flask reactor with three open necks as illustrated in Figure 2. The central neck was housed with a tunable mechanical stirrer at 300 rpm. Slow addition of the borohydride was introduced to reduce ferrous ion ( $\text{Fe}^{2+}$ ) to zero-valent iron ( $\text{Fe}^0$ ), according to the following reaction:



**Figure (2) Experimental Setup for nZVI Particle Synthesis.**

Typically, 1:1 volume ratio of  $\text{NaBH}_4$  (0.2 M) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (0.05 M) were vigorously mixed in the flask reactor for additional 30 min after the titration. The complete reduction of 0.05 mol  $\text{Fe}^{2+}$  requires only 0.0375 mol of  $\text{BH}_4^-$ . The excessive borohydride (0.2M) was applied to accelerate the preparation reaction. The generated iron particles were harvested with vacuum filtration and stabilized with a large volume of

deionized water to wash, and at the end, with diluted ethanol with water (20%). For storage, our experience suggests that maintaining a thin layer of ethanol on the top of iron particles can help preserve the nanoparticles.

### Nanoparticle Characterization

Morphological studies of the synthesized nZVI particles were carried out by using scanning electron microscope (SEM) fitted with an Energy Dispersive X-ray Analysis (EDAX) System (model TESCAN VEGA SEM microscope). Scanning Probe Microscope was used to determination of the average diameter of nZVI.

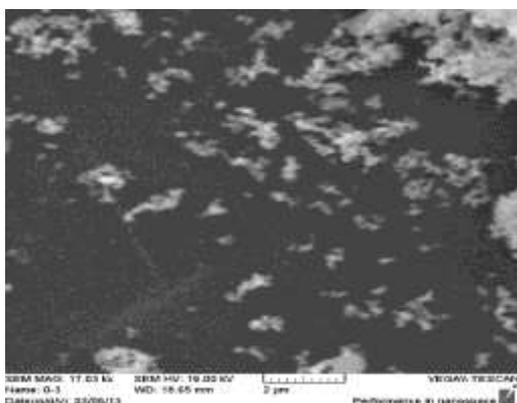
### Batch Experiments

Batch experiments were conducted in 250 mL glass bottles containing 100 mL of aqueous chlorpyrifos solution with an initial concentration of 25 mg/L and desired amount of nZVI particles was added into bottles were then fitted with Teflon cover and mixed on a rotary shaker (200 rpm) at  $30 \pm 5$  °C. At selected time intervals, 5 mL of the aqueous sample was withdrawn then filtered through a piece of membrane filter with a pore size of 0.45  $\mu\text{m}$  and then the sample was transferred into a 15 mL vial containing 5 mL of hexane for extraction of chlorpyrifos. Upon phase separation, the extract was analyzed for chlorpyrifos using GC (MOD 2010- SHIMADSU - Japan) equipped with electronic capture detection and fused silica capillary column (ZB-5 0.25 $\mu\text{m}$  film thickness) were used for this study. The GC operating conditions are as follows: initial temperature 150°C; hold 0.5 min; ramp, 50 °C/min, till 200-230°C; ramp 7.5°C/min, 230-300°C, ramp 20 °C/min, final temperature 300°C hold 5 min; injection port temperature 300°C;

detector temperature 300 °C; carrier gas helium, flow rate 1 mL/min. Control experiments (without the addition of the nanoparticles) were carried out in parallel.

### Results and Discussions

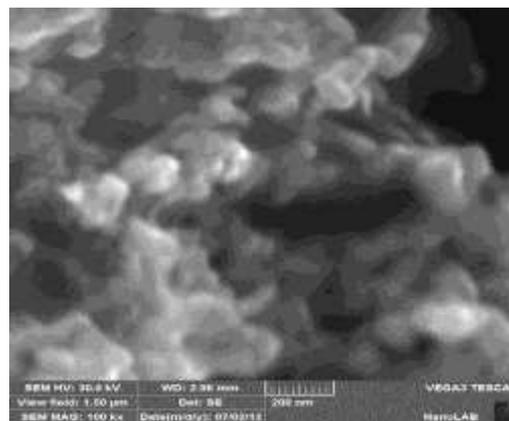
Figure 3 presents SEM images of nZVI particles. The laboratory prepared iron particles were largely spherical characteristic of particles formed in solution. A representative average single particle size is around 150–170 nm as shown in Figure 3a. A few particles had size as large as 250–350 nm, whereas most (>70%) particles were less than 250 nm. SEM images also showed that most particles formed chain-like aggregates. A size distribution (Figure 4) was calculated using Scanning Probe Microscope. The average size was around 165.6 nm.



(a)

[Figure (3) particles had size as large as 250–350 nm

Figure 3(a & b)



(b)

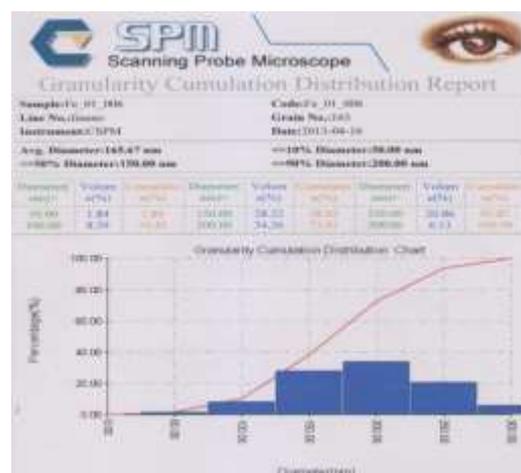


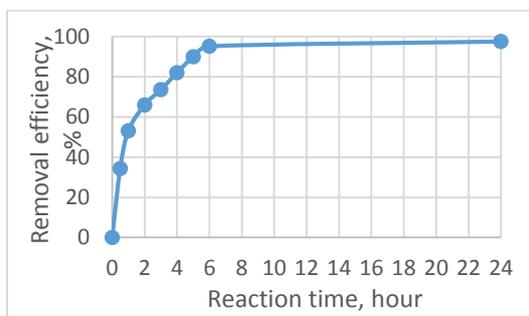
Figure (4) Particle Size Distribution (PSD) of nZVI Particles Using Scanning Probe Microscope

### Degradation of Chlorpyrifos by nZVI Particles

#### Effect of Reaction Time

As was shown in the Figure 5, with increasing reaction time, the removal efficiency of chlorpyrifos increased with fixed amounts of nZVI particles 500 mg/L at pH=3. The removal efficiency increased from 53 % to 90% at 1 and 5 hours, respectively. This phenomenon can be explained by the fact that the degradation process of the contaminant by Fe-based nanoparticles is an interface reaction. Therefore, for the first 5 hours of reaction, the degradation speed of chlorpyrifos in the solution was rapid

and, as the reaction proceeded, the gradual oxidation on the surface of nZVI formed a passivated layer, which covered some reaction sites. This may led to the decrease in the removal efficiency after 5 hours of reaction.

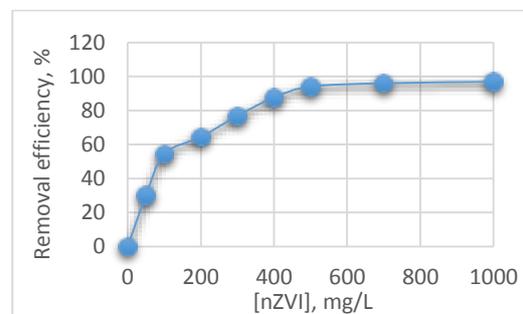


**Figure (5) Effect of Various Reaction Time on Chlorpyrifos Degradation Potential of nZVI; (Chlorpyrifos) = 25 mg/L; (nZVI) = 500 mg/L; pH= 3.**

#### Effect of nZVI Particle Addition

The residual concentration of chlorpyrifos decreased as the amount of nZVI increased. At 6 h, the removal efficiency of 500mg/L nZVI was about 94%, which was 1.9 higher than that at 100 mg/L nZVI, 1.46 times higher than that at 200 mg/L nZVI, and 1.1 times higher than that at 400mg/L nZVI as shown in Figure 6. On the other hand, the removal efficiency of 1000 and 500 mg/L was 94% and 98 % respectively, therefore they are seemed equal. Some researchers have shown (Noubactep *et al.*, 2012) (Zhang *et al.*, 2009) (Wang and Zhang, 1997) that both the absorption and removal in the degradation system of the nano metal solution occurred on the surface of the nano metal, such that the specific surface area of the nano metal was an important factor for the removal of the contaminant. When the specific surface area of the nanoparticles was bigger, there were more corresponding reactive

sites, and the absorption and removal abilities were stronger. Accordingly, the increasing amount of nano metals added meant the addition of more reactive sites, thereby improving the efficiency of removal.

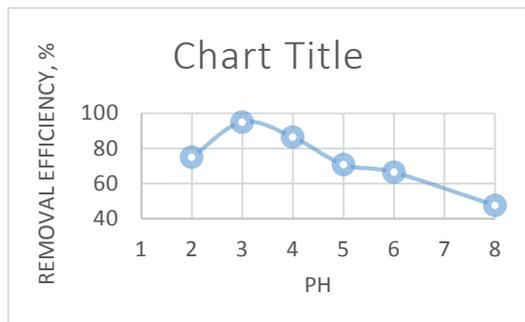


**Figure (6) Effect of Various Concentration of nZVI on Chlorpyrifos Degradation; (Chlorpyrifos) = 25 mg/L; Time = 6 h; pH= 3.**

#### Effect of pH

The aqueous pH had major effect on the removal efficiency of chlorpyrifos, when the initial pH values were 2, 3, 4, 5, 6, and 8, the removal efficiencies of chlorpyrifos were approximately 75, 95, 86.4, 70.8, 66.4, and 47.6% after a reaction of 6 h as shown in Figure 7. The removal efficiency of chlorpyrifos increased with a decrease in the pH up to 3. The nZVI process was more effective in degradation chlorpyrifos under acidic conditions. In other words, the more acidic the solution, the more rapid degradation of chlorpyrifos occurred with more  $H^+$  in the solution, the reaction occurred more easily and the reaction constant was high. However, when the initial pH was 2, the chlorpyrifos degradation rate decreased (Kusic *et al.*, 2007).The possible reasons may be attributed to: (1) at lower pH values less than 3, the iron corrosion could be accelerated, producing enough hydrogen (or hydrogen atoms), which were in favor of hydrogenation reaction (Zhang

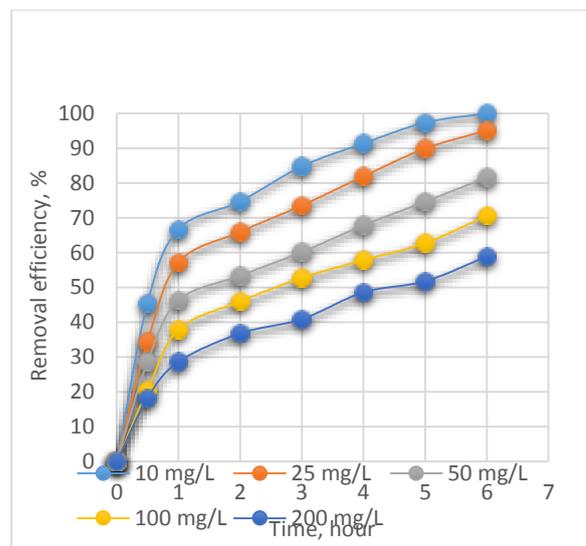
*et al.*, 2006). (2) Iron corrosion in solution of pH higher than 5 tends to form a passive film of iron hydroxide on the iron surface, which inhibits further reaction (Jovanovic *et al.*, 2005).



**Figure (7) Effect of pH on Chlorpyrifos Degradation; (Chlorpyrifos)=25 mg/L; (nZVI) = 500 mg/L; Time = 6 h.**

### Effect of Initial Chlorpyrifos Concentration

The effect of initial chlorpyrifos concentration on the reaction rate was evaluated using various initial concentrations of 10, 25, 50, 100 and 200 mg/L of chlorpyrifos, and the results were shown in Figure 8. The removal efficiency of chlorpyrifos for these different initial concentrations after 6 hour reaction were 99.0%, 95.2%, 81.7, 70.7 and 58.9%, respectively. Moreover, the removal efficiency of chlorpyrifos decreased as the initial concentration increased, (Fang *et al.*, 2011a) suggested when fixed number of reactive sites, the competitive adsorption would affect the adsorption and degradation of contaminants on the surface of nanoparticles, and further reduce the reaction rate.



**Figure (8) Effects of Variations in Initial Chlorpyrifos Concentration on The Removal Efficiency of Chlorpyrifos; (nZVI) = 500 mg/L; pH= 3.**

### Conclusions

The reduction by nano zerovalent iron (nZVI) is chemical process that can be applied to treat contaminated water in order to eliminate pollutants, especially hazardous compounds such as pesticide. In this work, the effectiveness of the nZVI in chlorpyrifos spiked water disinfection was studied. The results have shown the removal percentage of polluted samples attained 100% of chlorpyrifos solution at 25 mg/L was efficiency removed by nZVI within 6 hours, at initial solution pH 3, nZVI dose of 500 mg/L.

### References

- Bandstra, J. Z.;** Miehr, R.; Johnson, R. L. and Tratnyek, P.G. (2005) Reduction of 2,4,6-Trinitrotoluene by Iron Metal: Kinetic Controls on Product Distributions in Batch Experiments. *Environ. Sci. Technol.*, 39, 230–238.
- Fang, Z.;** Chen, J.; Qiu, X.; Qiu, X.; Cheng, W. and Zhu, L. (2011a) Effective Removal of Antibiotic Metronidazole from Water by Nanoscale Zero-valent Iron Particles, *Desalination*, 268, 60–67.
- Fang, Z.;** Qiu, X.; Chen, J. and Qiu, X. (2011b) Degradation of The

- Polybrominated Diphenyl Ethers by Nanoscale Zero-valent Metallic Particles Prepared from Steel Pickling Waste Liquor, *Desalination*, 267, 34–41.
- Hossain, M. S.;** Fakhruddin, A. N. M.; Chowdhury, M. A. Z. and Alam, M. K. (2013) Degradation of Chlorpyrifos, An Organophosphorus Insecticide in Aqueous Solution with Gamma Irradiation and Natural Sunlight, *Journal of Environmental Chemical Engineering*, 1, 270–274.
- Jovanovic, G. N.;** Plazl, P. Z.; Sakrittichai, P. and Al-Khaldi, K. (2005) Dechlorination of *p*-chlorophenol in a Microreactor with Bimetallic Pd/Fe Catalyst, *Ind. Eng. Chem. Res.*, 44, 5099–5106.
- Kim, H.;** Hong, H. J.; Lee, Y. J.; Shin, H. J. and Yang, J. W. (2008) Degradation of Trichloroethylene by Zero-valent Iron Immobilized in Cationic Exchange Membrane, *Desalination*, 223, 212–220.
- Kim, Y. H. and** Carraway, E. R. (2003) Reductive Dechlorination of TCE by Zero Valent Bimetals, *Environ. Technol.*, 24, 69–75.
- Kulkarni, A. R.;** Soppimath, K. S.; Dave, A. M.; Metha, M.H. and Aminabhavi, T.M. (2000) Solubility Study of Hazardous Pesticide (Chlorpyrifos) by Gas Chromatography, *J. Hazard. Mater. A*, 80, 9–13.
- Kusic, H.;** Bozic, A. L. and Koprivanac, N. (2007) Fenton Type Processes for Minimization of Organic Content in Coloured Wastewaters: Part I: Processes Optimization, *Dyes and Pigments*, 74, 380–387.
- Liu, T. and** Lo, I. M. C. (2011) Influences of Humic Acid on Cr(VI) Removal by Zero-valent Iron from Groundwater with Various Constituents: Implication for Long-term PRB Performance, *Water Air Soil Pollut.*, 216, 473–483.
- Moon, B. H.;** Park, Y. B. and Park, K. H. (2011) Fenton Oxidation of Orange II by Pre-reduction Using Nanoscale Zero-valent Iron, *Desalination*, 268, 249–252.
- Noubactep, C.;** Caré, S. and Crane, R. (2012) Nanoscale Metallic Iron for Environmental Remediation: Prospects and Limitations, *Water Air Soil Pollut.*, 223, 1363–1382.
- Sun, Y. P.;** Li, X. Q.; Cao, J.; Zhang, W. X. and Wang, H. P. (2006) Characterization of Zero-valent Iron Nanoparticles, *Advances in Colloid and Interface Science*, 120, 47–56.
- Wang, C. B. and** Zhang, W.X. (1997) Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs, *Environ. Sci. Technol.*, 31, 2154–2156.
- Wei, Y. T.;** Wu, S. C.; Chou, C. M.; Che, C.H.; Tsai, S. M. and Lien, H. L. (2010) Influence of Nanoscale Zero-valent Iron on Geochemical Properties of Groundwater and Vinyl Chloride Degradation: A Field Case Study, *Water Res.*, 44, 131–140.
- Zhang, W. H.;** Quan, X.; Wang, J. X.; Zhang, Z. Y. and Chen, S. (2006) Rapid and Complete Dechlorination of PCP in Aqueous Solution Using Ni-Fe Nanoparticles Under Assistance of Ultrasound, *Chemosphere*, 65, 58–64.
- Zhang, Z.;** Cissoko, N.; Wo, J. and Xu, X. (2009) Factors Influencing The Dechlorination of 2,4-dichlorophenol by Ni-Fe Nanoparticles in The Presence of Humic Acid, *J. Hazard. Mater.*, 165, 78–86.