

Efficiency of Nanoscale Zero Valent Iron in Soil Washing System for Removal of Trinitrotoluene

Rachain Kosanlavit and Waraporn Jiamjitpanich

Abstract—This research aimed to investigate the applications of nanoscale zero valent iron particles (nZVI) in soil washing method to remediate or degrade TNT in the contaminated soil sample. The soil washing reactor was used in this study to determine TNT remediation in slurry soil with nZVI. TNT contaminated soil was divided into two sets. The first one was only washed with milli-Q water (1:2 w/v) and the other one was added with nZVI particles (250/1 nZVI/TNT ratio) before washing with milli-Q water. The reaction times in this experiment were varied between 0-100 minutes. The results of the experiment without added nZVI particles demonstrated that TNT removal efficiency was slightly increased with a maximal value of 11.89% at the time point of 100 minutes. In comparison, it was considerably increased up to 78.86% TNT removal efficiency of slurry soil in the experiment with added nZVI particles at the time point of 50 minutes before it was relatively constant afterward. In this study, the concentrations (mg/kg) of 2-ADNT and 4-ADNT as TNT metabolites in soil and wash water were also analyzed and presented. The results showed that the concentrations of 2-ADNT and 4-ADNT were found in washed soil in the system with added nZVI higher than those without added nZVI. It was possibly due to degradability of nZVI. The highest concentration was about 2 mg/kg of 2-ADNT in soil of washing system with nZVI at 40 minutes. Overall, the TNT metabolite formation showed quite fluctuation with a rapid increase in the first 40 minutes after that it was dropped. Meanwhile, there was no detection of 2-ADNT and 4-ADNT concentrations in wash water in both with and without added nZVI particles.

Index Terms—Soil washing system, Trinitrotoluene (TNT), Nanoscale Zero Valent Iron (nZVI), Removal efficiency.

I. INTRODUCTION

Soil washing technology is a technique of physicochemical process to separate and remove the contaminants which may be organic and inorganic substances including radioactive and hazardous materials. The effectiveness of soil washing technology is known that it partly depends on the types of soil.

Contaminants absorbed onto fine soil particles are separated from bulk soil in an aqueous-based system on the basis of particle size. The wash water may be augmented with a basic leaching agent, surfactant, pH adjustment, or chelating agent to help remove organics and heavy metals

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[1]. Normally, the simple method of soil washing is useful and more effective in case of the coarse soil (sand and gravel particles) that has a size of 63 micrometer or larger. Whereas, soil washing of contaminants in the fine soil (clay and silt particles) which is less than 63 micrometer of size [2] should be carried out in combination with other essential technologies to remove the contaminants from the fine soil such as incineration, heating, scrubbing, biological treatments or nanotechnology. Incineration is widely used as a method for the elimination of toxic contaminated materials. However, incineration of the contaminants is rather expensive which generates air emission and noise problems.

Trinitrotoluene (TNT) is 2-methyl-1,3,5-trinitrobenzene (Chemical formula $C_7H_5N_3O_6$) in IUPAC name. It is also called 2,4,6-trinitrotoluene. TNT is found as a contaminant in soil and water where TNT is used in military training site or battlefield. TNT is occasionally used for industrial purposes. This toxic substance may be left as a contaminant in environment for years [3]. Generally, TNT-contaminated soil is found in mixed soil which soil particles vary in size. The effective treatment of TNT-contaminated soil needs to be sought out to remove TNT from the soil.

With this regards, the researchers have increasingly focused on nanotechnology such as using zero-valent iron metal (nZVI) as a remediation tool to treat the contaminated environments [4]. More recently, researches on the remediation of TNT include the assessment of zero valent iron (Fe^0) or ferrous iron (Fe^{2+}) to transform TNT and other nitroaromatic and nitramine compounds to less hazardous or more biodegradable products [5]. The metallic iron is inexpensive, non-toxic, and already common in the environment and serves as a strong reductant. It makes the targeted chemicals become less toxic or non-toxic products. The advantages of this technology include the added flexibility to inject iron to the subsurface at multiple locations and at great depth. Moreover, nanoscale iron particles increase reaction rates from 500 to 1000 times higher than that of conventional granular iron filing remediation systems [6].

Thus, it was rational to use the combined process between soil washing technique and nanotechnology (by adding nano-particles) to enhance the efficiency of soil washing technique. This research aimed to investigate the efficiency of nZVI to remediate or degrade TNT in the contaminated soil samples. The effects of reaction times were also determined.

II. MATERIALS

A. Chemicals

The chemical stocks of 2,4,6-trinitrotoluene (TNT), 2-amino-4,6-dinitrotoluene (2-ADNT) and 4-amino-2,6-dinitrotoluene (4-ADNT) (99.90% purity at 1000 mg/L concentration) were purchased from SUPELCO Co., USA.

B. Soil Washing Reactor

The reactor for soil washing technique was designed in order to study TNT remediation in contaminated soil with nZVI particles as shown in Fig. 1. The reactor was a batch system which was used to study the applications of nZVI to remediate or degrade TNT and its metabolites present in the contaminated water and soil samples. Two sets of batch reactors were designed for two treatments, one for TNT-contaminated soil that was washed with milli-Q water only (without added nZVI particles) and the other one for TNT-contaminated soil that was washed with milli-Q water and the added nZVI particles (250/1 nZVI/TNT ratio). The reactor had a cylindrical shape with diameter and height of 30 cm and 50 cm, respectively. The reactor was able to contain TNT-contaminated slurry soil with capacity of 10 liters. Mixing motor was installed to mix slurry soil and nanoparticles at 150 rpm. Slurry soil was prepared by mixing between soil sample and water in 1:2 w/v ratio.

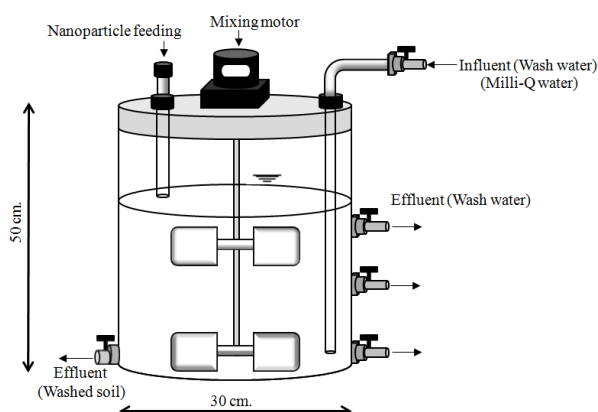


Fig. 1. Schematic representation of the soil washing reactor.

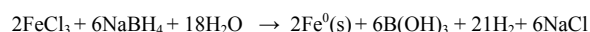
C. Artificial Contaminated Soil Preparation

The collected soil were air-dried at room temperature (25°C) for 3-4 days, ground and sieved to obtain the soil with a particle size of less than 2 mm for later experiments [4]-[7]. The TNT stock solution was added to the prepared soil samples with the appropriate amount that resulted in an initial concentration of 20 mg/kg. Then, the soil samples were allowed to stand for at least one hour in the dark at 20 °C, as stated in previous reports [8], [9] to obtain an initial TNT concentration of 20 mg/kg [4]-[7]. Milli-Q water was then added and it became slurry before using in the later experiments. Minimum volume with 10 L of water and 5 kg of soil was prepared.

III. NANOSCALE ZERO VALENT IRON SYNTHESIS

Sodium borohydride (NaBH₄) and iron (III) chloride (FeCl₃) were used for synthesis of nZVI particles under a nitrogen gas purged reactor. This procedure was carried out

as described by Wang and Zhang (1997) [6], Jiamjitrpanich *et al.* (2010) [9], Sun *et al.* (2007) [10], Choe *et al.* (2001) [11], and Jiamjitrpanich *et al.* (2012) [12], [13], according to equation as follows [14]:



IV. METHODOLOGY

In this study, 5 kg of the prepared soil samples (ground and sieved to obtain a 2 mm of soil size) were mixed with TNT stock solution and incubated soil to stand for at least one hour to obtain an initial TNT concentration of 20 mg/kg. After that, 10 liters of milli-Q water were added to the prepared soil to form slurry soil before using in the experiments. Dosages, reaction time, and other conditions followed the optimal conditions that were demonstrated by Jiamjitrpanich *et al.* (2010) [9] at the laboratory scale study.

In this experiment, the milli-Q water was used as a washer in the soil washing system. Two sets of batch reactors were designed for two treatments. The first one was conducted for TNT-contaminated soil without added nZVI particles. This was washed with milli-Q (1:2 w/v) which was called slurry. The other one was conducted for TNT-contaminated soil with added nZVI particles (250/1 nZVI/TNT ratio) before washing with milli-Q. The optimal ratio of nZVI/TNT in soil was 250/1 (w/w) at 20 minutes at the room temperature as reported in the previous study [9]. The reaction times in this experiment were designed to 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 minutes. At each time point, TNT concentration and TNT residue concentrations in soil and wash water were determined by GC-ECD. Then, the calculation was performed to obtain TNT removal efficiency (%) and TNT washout efficiency (%). Moreover, the concentrations (mg/kg) of 2-ADNT and 4-ADNT as TNT metabolites in soil and wash water were also analyzed and presented.

V. ANALYTICAL METHOD OF TNT AND ITS METABOLITES IN WATER AND SOIL

TNT and its metabolites were analyzed by GC-ECD (Hewlett Packard 5890 series II, USA.) following U.S.EPA method 8095 [15]. This method provides GC-ECD conditions with HP-5 columns for the detection of concentration of TNT and its metabolites in water and soil. The precision of this technique was >95% (SD < 2%). The TNT, 2-ADNT, and 4-ADNT standards (purity of 99.90%) were used to prepare stock solutions in pure acetonitrile. The calibration curves consisted of five standard solutions (ranging from 0-20 mg/L) provided linearity with correlation coefficients (R^2) greater than 0.99. According to the method of sample extraction, a 10 g subsample of each soil sample was placed in a 2 oz wide mouth bottle. Then, adding 20.0 mL of acetonitrile and vortex swirling for a minute. The sample was placed either on a platform shaker or in a cooled (<30 °C) ultrasonic bath for 18 hours. After extraction, centrifuge at 13000 rpm (\approx 12470 g-force) for 5 minutes. The supernatant of 8.0 mL was removed and filtered through a 0.45 μm PTFE filter before GC-ECD analysis was carried out. The detecting capability of this method is 0.003 $\mu\text{g/L}$.

VI. RESULTS AND DISCUSSION

A. Effects of Nanoscale Zero Valent Iron on Remediation of Trinitrotoluene Contaminated Soil in the Slurry Soil Reactor (Soil Washing)

This soil washing reactor was a tool assembled and used in the current study to investigate TNT remediation in slurry soil with nZVI. This reactor was basically designed to study reaction between TNT-contaminated slurry soil (20 mg/kg TNT in dried soil) and added nZVI particles. Slurry soil was the mixture of soil and water in 1:2 w/v ratio used in this batch reactor experiments. The optimal dosage of 5000 mg/kg nZVI was added in the batch reactor which contained 10 liters of 20 mg/kg TNT-contaminated slurry soil (5 kg of TNT- contaminated dried soil). So, this batch reactor of slurry soil treatments was the experiment to study TNT degradation and removal by using the combination of soil washing and nZVI particle addition.

The effects of nZVI particles on TNT remediation (with an initial concentration of 20 mg/kg of TNT) in soil by the slurry soil reactor or soil washing system are shown in Fig. 2 and Fig. 3. In the experiments without added nZVI particles, it was found that TNT removal efficiency was slightly increased with a maximal value of 11.89% (17.62 mg/kg TNT) at the time point of 100 minutes. In comparison, the TNT concentrations in washed soil with added nZVI were rapidly decreased in the first 50 minutes. In terms of removal efficiency, it was considerably increased up to 78.86% in the experiments with added nZVI particles at the time point of 50 minutes before it was relatively constant afterward.

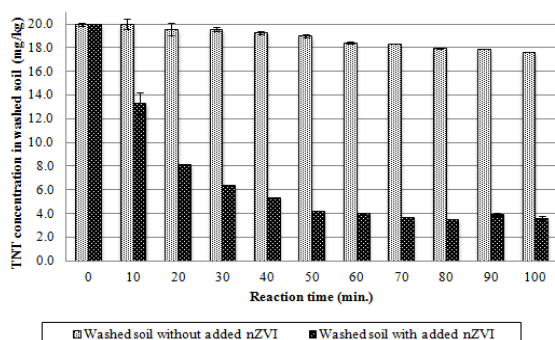


Fig. 2. Trinitrotoluene concentrations in washed soil in comparison between treatments with and without added nanoscale zero valent iron.

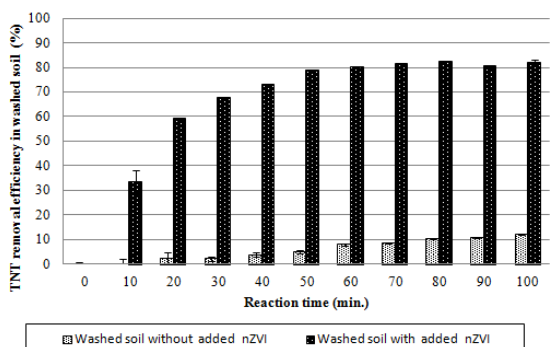


Fig. 3. Trinitrotoluene removal efficiency in washed soil in comparison between treatments with and without added nanoscale zero valent iron.

The TNT concentrations in wash water both with and without added nZVI particles were also determined (as presented in Fig. 4). According to these present experiments both with and without added nZVI particles, it found that

TNT concentrations in wash water and TNT washout efficiency were not significantly different. Amounts of the washout TNT concentrations were less than 1.6 mg/L (< 8.00 TNT washout efficiency) both with and without nZVI at all time points. The probably reason is due to the low solubility of TNT in water whereas TNT is high solubility in ether, acetone, benzene and pyridine.

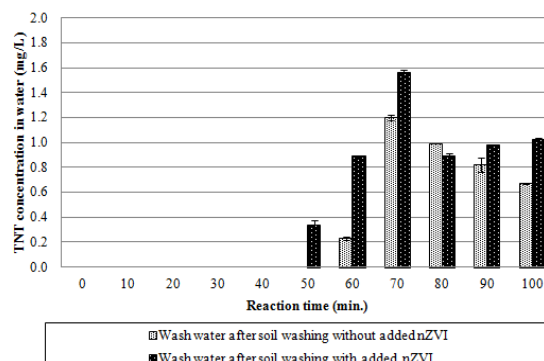


Fig. 4. Trinitrotoluene concentrations in wash water in comparison between treatments with and without added nanoscale zero valent iron.

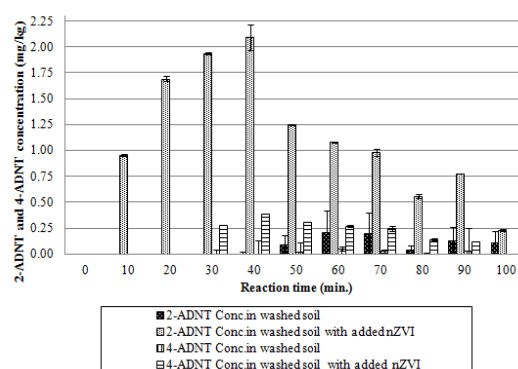


Fig. 5. 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitro toluene concentrations in washed soil in comparison between treatments with and without added nanoscale zero valent iron.

In addition, it is known that the washout efficiency of TNT contaminated soil by water partly depends on a soil type and other factors such as pH, temperature etc. Basically, water is able to wash out TNT from sandy soil with better efficiency.

Regarding this current study, the soil was the clay loamy sand. It has higher absorbability than sandy soil. Also, the nZVI particles used in this study could possibly lead to the elevation of the TNT transformation to its metabolites (2-ADNT and 4-ADNT) which may be partly held in soil. As a result of this, there was a low concentration of TNT in wash water as found in this soil washing system in this study.

The 2-ADNT and 4-ADNT concentrations in washed soil are shown in Fig. 5. The results showed that the concentration of 2-ADNT was found in washed soil higher than that of 4-ADNT both with and without nZVI. The concentrations of 2-ADNT and 4-ADNT were found in washed soil in the system with nZVI higher than those without nZVI. It was known that 2-ADNT and 4-ADNT were from transformation of TNT degradation to its metabolites. However, the amounts of 2-ADNT and 4-ADNT concentrations were much less in comparison with the TNT removal as reported earlier in this study. The highest concentration was 2.09 mg/kg of 2-ADNT formation in soil of washing system with nZVI at 40 minutes. Generally, the TNT metabolite formation showed quite fluctuation with a

rapid increase in the first 40 minutes after that it was dropped. Meanwhile, there was no detection of 2-ADNT and 4-ADNT concentrations in wash water in both with and without added nZVI particles. There may be no clear explanations. It was possibly due to varying rates of TNT transformation to 2-ADNT and 4-ADNT according to different reaction time points.

Finally, the results from this study showed that no 2-ADNT and 4-ADNT were found in wash water both with and without added nZVI. This may be due to TNT transformation to the metabolites and they subsequently combined with H^+ of H_2O molecules such as 2,4-DNT, 2,6-DNT, and TAT. These similar results were recently reported that no 2-ADNT and 4-ADNT was found in reacted water with nZVI particles [9].

VII. CONCLUSION

The results of these experiments without added nZVI particles demonstrated that TNT removal efficiency was slightly increased with a maximal value of 11.89 % at the time point of 100 minutes. In comparison, it was considerably increased up to 78.86 % TNT removal efficiency of slurry soil in the experiments with added nZVI particles at the time point of 50 minutes before it was relatively constant afterward. The efficiency of TNT removal by washing system alone was lower than that of the washing system combined with nZVI.

The 2-ADNT concentrations in remediation of TNT-contaminated soil was higher than that of 4-ADNT in washed soil from the slurry soil reactor. The highest concentration was 2.09 mg/kg of 2-ADNT formation in washed soil with added nZVI at 40 minutes. There were no 2-ADNT and 4-ADNT in wash water of soil washing system with added nZVI. It may be due to TNT transformation to other metabolites such as 2,4-DNT, 2,6-DNT and TAT which are later combined with H^+ of H_2O molecule.

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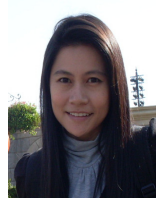
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