

Enhanced Phytoremediation Efficiency of TNT-Contaminated Soil by Nanoscale Zero Valent Iron

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Abstract. Nano-phytoremediation is a combined technology between nanotechnology and phytotechnology for remediation of contaminated environments. This research aimed to investigate the capability of combination between phytoremediation and nanoscale zero valent iron (nZVI) for removal of Trinitrotoluene (TNT) from contaminated soil. The nZVI particles were synthesized by the reductive precipitation process between sodium borohydride (NaBH₄) and iron (III) chloride (FeCl₃). Purple guinea grass (*Panicum maximum*) was used as a hyperaccumulated plant for this study. The plants at the age of 2 weeks were transplanted to the pots containing soil with various concentrations of TNT and nZVI. The residue TNT concentrations in soil with and without plants were measured by GC-ECD analysis during an experimental period of 120 days. The results indicated that nano-phytoremediation demonstrated more effective than either nano-remediation or phytoremediation as a method for degradation and removal of TNT-contaminated soil. Overall, the highest removal efficiency of nano-phytoremediation was found in soil with the TNT/nZVI ratio of 1/10 (100 mg/kg initial TNT concentration) with the complete TNT remediation by day 60.

Keywords: *Panicum maximum*, Trinitrotoluene (TNT), Nanoscale zero valent iron particles (nZVI), phytoremediation, Nano-phytoremediation

1. Introduction

Phytoremediation, so called phytotechnology, is a relatively new technology involved the plants which play a role in remediation of contaminated environment. It is a green technology and environmental friendly. There are several types of plants to remedy and take up contaminants from soil, surface water, ground water, and sediment. Phytoremediation has been used to take up heavy metals, organic compounds and toxic chemicals such as 2,4,6-trinitrotoluene (TNT), trichloroethylene, benzene, toluene, ethylbenzene, xylene, lead, mercury, arsenic and radionuclides from contaminated environment. Although, phytotechnology is a long time treatment technology, it is a technology with low cost and no impact on the environment in comparison with other technologies. Thus, this technology is more cost effective than other chemical methods for the toxic and hazardous remediation.

One of the important factors for the phytoremediation technology is the species of hyperaccumulated plants (hyperaccumulators). In recent years, there have been many kinds of plants that researchers used for experiments in terms of contaminant uptake. Purple guinea grass (*Panicum maximum*) has been recognised as one of hyperaccumulators.^{[1][2]}

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Panicum maximum is found in the tropical region. *Panicum maximum* is 0.5-3.5 (1.5 m on average) meters in height and it can tolerate several conditions including low fertility, low pH, and limited water. Phytoremediation by *Panicum maximum* has been reported by several researchers. Paquin *et al.* (2004)^[1] reviewed over 100 species of plants that were used for phytoremediation in Hawaii, it was stated that *Panicum maximum* can reduce RDX (a kind of explosives) more effectively than the other species (12 species were used in the test).

The aim of this study was to investigate the capability of nano-phytoremediation involving *Panicum maximum* and nanoscale zero valent iron (nZVI) for TNT removal in contaminated soil. The percentages of removal efficiency were calculated in relation to various concentrations of TNT and nZVI in soil with and without *Panicum maximum* during a period of 120 days.

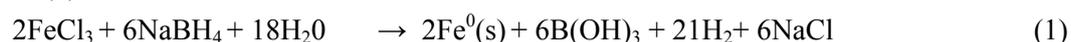
2. Materials and Methods

2.1. Materials

Seeds of *Panicum maximum* (*P. maximum* TD58) were obtained from Pakchong district, Nakhon Rachasima province. The commercial potting soil (Lumdol soil) was obtained from Taladthai market, Phatumtanee Province. Background soil was obtained from Chulachomklao Royal Military Academy, Prommanee sub-district, Muang district, Nakhon Nayok province. The major chemical stock (2,4,6-trinitrotoluene) was purchased from SUPELCO Co., USA.

2.2. Nanoscale zero Valent Iron Synthesis

The nZVI particles were synthesized by the reductive precipitation process using two chemicals, namely, sodium borohydride (NaBH₄) and iron (III) chloride (FeCl₃). The procedure for nZVI synthesis followed the method of Wang and Zhang (1997)^[3], Choe *et al.* (2001)^[4], Sun *et al.* (2007)^[5] and Jiamjitpanich *et al.* (2010)^[6] in which NaBH₄ (0.25 M) aqueous solution was added drop wise to FeCl₃·6H₂O (0.045 M) aqueous solution at 1:1 volume ratio. The solution was homogenized for 20 min in a nitrogen gas purged reactor allowing the reaction to come to completion. The synthesized nZVI particles were separated from supernatant using magnet. The supernatant was later decanted and discarded, while the synthesized nZVI particles were rinsed with de-oxygenated milli-Q water for three times, and methanol for three times, before drying with nitrogen gas and stored in methanol at 4°C. The nZVI particles were immediately formed according to Equation (1) as follows^[7]:



2.3. Nano-phytoremediation Potting Experiment for TNT with nZVI and Plants

The potting experiment of nano-phytoremediation is the novelty combination technology between nanotechnology and phytotechnology. Nano-phytotechnology is an advantage technology which decreases a retention time of phytotechnology and decreases cost of nanotechnology.

The 0-15 cm surface layer of background soil was collected and used for this investigation. Soil sample was placed in clean polyethylene bags and brought to the laboratory where it was air-dried for a week until totally dry and ground to pass through a 2-mm mesh stainless steel sieve. The soil was then homogenized and stored at room temperature. The soil was later spiked with TNT and served as TNT-contaminated soil where the soil without spiking TNT was used as control soil. The concentrations of TNT selected for this experiment were 100 and 500 mg/kg.

The transplantation method was selected and used in this study as a suitable method for nano-phytoremediation.^[2] Initially, the seeds were soaked in water in a container for 24 hr and germinated in commercial soil for 2 weeks. The seedlings were watered daily. After 2 weeks, healthy plants with similar height and biomass were selected. Plants were later transplanted and grown in the TNT-contaminated potting soil with or without added nZVI for a period of 120 days (4 months). The experiments were carried out in a greenhouse illuminated with natural light. Greenhouse temperature was 30 °C on average in the daytime and 27 °C on average at night. Doses of nZVI were varied in concentrations at 100, 500, and 1000 mg/kg. Thus, the categories of soil treatments were divided into two sets. The first set was the treatment with *Panicum*

maximum. The other one was the treatment without *Panicum maximum*. Each set was subdivided into 9 soil treatments as follows: control soil, 100 mg/kg TNT soil, 100 mg/kg TNT +100 mg/kg nZVI soil, 100 mg/kg TNT+500 mg/kg nZVI soil, 100 mg/kg TNT+1000 mg/kg nZVI soil, 500 mg/kg TNT soil, 500 mg/kg TNT+100 mg/kg nZVI soil, 500 mg/kg TNT+500 mg/kg nZVI soil, and 500 mg/kg TNT+1000 mg/kg nZVI soil. The TNT residue concentrations in potting soil were determined (both treated and untreated with *Panicum maximum*) and the percentage removal efficiency were calculated. The determination of TNT residue concentration was carried out during a period of 120 days (D0, D2, D3, D4, D5, D10, D20, D30, D40, D50, D60, D70, D80, D90, D100, D110, and D120).

TNT was analyzed by GC-ECD (Hewlett Packard 5890 series II, USA.) following U.S.EPA method 8095 (U.S.EPA, 2000).^[8] Regarding the procedure of sample extraction, the 10 g subsample of each soil sample was placed in a 2 oz wide mouth bottle. The 20 ml of acetonitrile was added, capped with a PTFE-lined cap, vortex swirl for one min, and either were placed on a platform shaker or in a cooled (<30 °C) ultrasonic bath for 18 hours. After extraction, the sample was allowed to settle for 30 min. By using a 10-ml disposable syringe, 8 ml of supernatant was removed and filtered through a 0.45 µm PTFE filter, discarding the first ml and later transferring 2 ml to vial for GC-ECD analysis.

2.4. Analytical Method of TNT

For analyzing TNT, the supernatant and nZVI particles were separated by transferring 1 ml of the mixed liquid to a 2 ml polypropylene microcentrifuge tube containing 1 ml of 35% methanol. After centrifugation at 13000 rpm (\approx 12470 g-force) for 5 min, the supernatant was filtered through a 0.45 µm PTFE filter prior to analysis of TNT concentrations using gas chromatography with an electron capture detector (GC-ECD: Hewlett Packard 5890 series II, USA.) based on U.S.EPA method 8095.^[8]

3. Results and Discussion

Due to the differences in initial concentrations of TNT in potting soil (100 mg/kg and 500 mg/kg), the percentages of removal efficiency was performed to compare the efficiency among the different initial concentrations of TNT in both untreated and treated potting soil by *Panicum maximum*.

The results shown in figures 1 and 2 demonstrated that overall the removal efficiency (%) of all treatments in treated potting soil by *Panicum maximum* was higher than that of untreated potting soil. Profiles of removal efficiency in each treatment of both untreated and treated potting soil were relatively similar. The highest removal efficiency was found in the treatment of 100 mg/kg TNT+1000 mg/kg nZVI at all time points, and followed by 100 mg/kg TNT+500 mg/kg nZVI. Notably, 100 mg/kg TNT and 500 mg/kg TNT without nZVI were found that the percentages of removal efficiency treated potting soil by *Panicum maximum* were higher than those of untreated potting soil at most of time points. With regard to untreated potting soil by *Panicum maximum*, the removal efficiency between 100 mg/kg TNT and 500 mg/kg TNT without nZVI were not significantly different but, in treated potting soil, the results showed significant differences after day 10. There was the removal efficiency of 100 mg/kg TNT (100%) substantially higher than 500 mg/kg TNT (86.07%) at day 120.

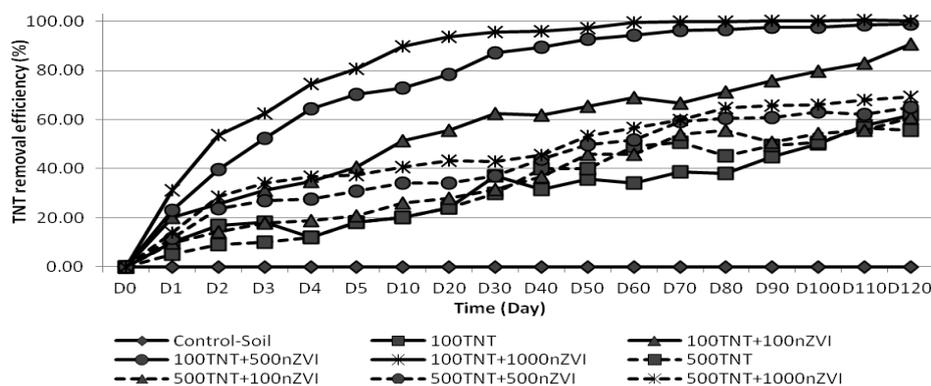


Fig. 1: Percentages of Trinitrotoluene removal efficiency in untreated potting soil (without *Panicum maximum*)

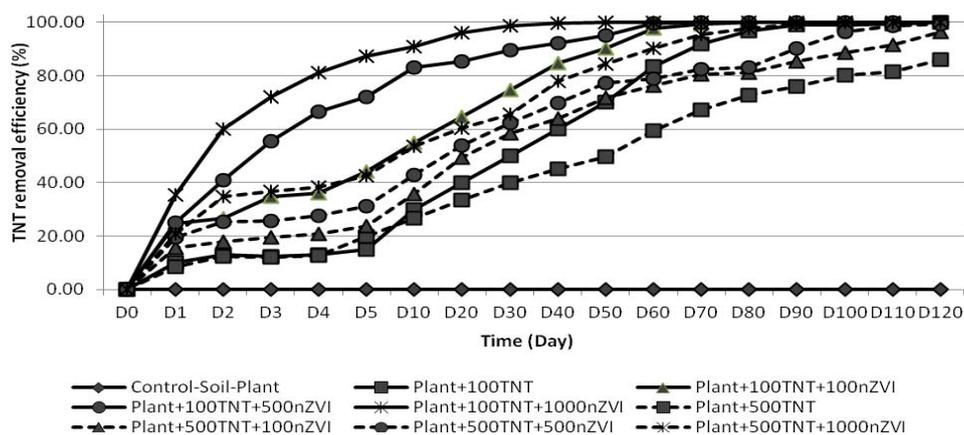


Fig. 2: Percentages of Trinitrotoluene removal efficiency in treated potting soil (with *Panicum maximum*)

The overall results showed that the removal efficiency of 100 mg/kg initial TNT concentration soil higher than that of 500 mg/kg. Regarding the results of untreated potting soil with the treatment of 100 mg/kg TNT+1000 mg/kg nZVI, and 100 mg/kg TNT+500 mg/kg nZVI, it showed a dramatic increase of the removal efficiency during the first ten days and a moderate increase during day 10 and 60. It was slow down after day 60. In treated potting soil with the same experiment groups, it was found a dramatically continuous increase in the removal efficiency during day 0 and 50. It went up toward complete TNT remediation by day 60.

According to the experiment of untreated potting soil by *Panicum maximum*, the complete TNT remediation (not detectable) were found only in soil with 100TNT+1000nZVI at day 80. In comparison with untreated potting soil by *Panicum maximum*, the complete TNT remediation (not detectable) were found in 100TNT+1000nZVI, 100TNT+500nZVI, 100TNT+100nZVI, and 500TNT+1000nZVI at days 60, 70, 80 and 100, respectively in treated potting soil by *Panicum maximum*. Moreover, this study showed the half life of TNT, there were 100 days in background soil, 30 days in background soil with *Panicum maximum*. The shortest half life was found in soil with the TNT/nZVI ratio of 1/10 (2 days in untreated potting soil and 1.5 day in treated potting soil by *Panicum maximum*).

This nano-phytoremediation method for TNT removal in contaminated soil was found to be a very promising method in the future. In terms of half life, it showed to be more effective than other methods such as biodegradation that was previously reported by some researchers.^[9-10] It was reported that the thermophilic and mesophilic half-lives were 11.9 and 21.9 days for TNT remediation by biodegradation method.^[9]

4. Conclusions

According to the experimental results obtained from this study, it indicated that nano-phytoremediation for degradation and removal of TNT-contaminated soil has obviously more effective than either nano-remediation or phytoremediation. Regarding the time points of the complete TNT remediation and half life of TNT, the highest removal efficiency of nano-phytoremediation was found in soil with the TNT/nZVI ratio of 1/10 (100 mg/kg initial TNT concentration) in treated potting soil by *Panicum maximum*.

5. Acknowledgments

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