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## Targeted Degradation of Trinitrotoluene Using Iron (II)- Cyclodextrin-Peroxide Systems

Bo Wei  
*University of New Orleans*

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TARGETED DEGRADATION OF TRINITROTOLUENE  
USING IRON (II)-CYCLODEXTRIN-PEROXIDE SYSTEMS

A Thesis

Submitted to the Graduate Faculty of the  
University of New Orleans  
in partial fulfillment of the  
requirements for the degree of

Master of Science  
in  
The Department of Chemistry

by

Bo Wei

B.S., Sichuan University, 1997

December 2003

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## ABSTRACT

Residues of 2,4,6-trinitrotoluene (TNT) in soil and groundwater near former production and processing plants generate large environmental concerns. A cyclodextrin (CD) mediated Fenton remediation of TNT contaminated water and sand (soil analogy) is presented. Kinetic studies were performed to elucidate the role of cyclodextrin in Fenton remediation of TNT contaminated water. The rate and extent of TNT degraded by  $\text{Fe}^{2+}$ -CD- $\text{H}_2\text{O}_2$  systems were significantly enhanced as compared to the classic Fenton method. Further, in water system with interfering substance - humic acid, which tends to associate with TNT, the addition of cyclodextrin helped to improve the efficiency of Fenton degradation. This technique has also been successfully applied to remediate TNT contaminated soil systems (sand). Four systems were investigated: clean sand, sand and humic acid, sand and fulvic acid, sand and natural organic matter. This technique has shown superior performance than classic Fenton method in all of the four above systems.

## CHAPTER ONE INTRODUCTION

### 1.1 Trinitrotoluene (TNT): Use and Physical Properties

Trinitrotoluene (TNT) is a yellow, odorless, crystalline solid that was largely produced for conventional warfare in the early 20<sup>th</sup> century. TNT was a major explosive used in military for filling shells, bombs and grenades during the two World Wars, when millions of tons of TNT were manufactured. It can be used as a pure explosive, or mixed with other explosives such as 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazocyclooctane (HMX). Another application of TNT in industry was a chemical intermediate during the production of dyestuffs and photographic chemicals. The melting point of TNT is 82 ° C, and its boiling point is 240 ° C. The solubility of TNT in water is 130 mg/L at 20 °C and it has a vapor pressure of 0.0002 mm Hg at 20 ° C. [1]

### 1.2 Toxicity of TNT

Trinitrotoluene entered the environment through liquid and solid wastes discharged from former munitions production plants in manufacturing, packaging and demilitarizing processes. TNT and its degradation products have toxic and mutagenic effects on several organisms, including humans [2]. TNT is absorbed by the human body through the digestive tract, skin, and lungs; is distributed primarily to the liver, kidneys,

lungs, and fat; and is excreted mainly in the urine and bile. TNT is metabolized either by nitroreduction to form amino and hydroxylamino benzene or by oxidation to form benzyl alcohol and benzoic acid derivatives [3]. Chronic exposure to TNT may cause several harmful health effects in human, including anemia, abnormal liver function, skin irritation, and cataract development. Animals that ate or breathed TNT have been observed to developed similar blood and liver effects, as well as spleen enlargement and other harmful effects on the immune system. The effects of TNT on birth defects in humans are not clear. However, male animals treated with high doses of TNT have developed serious reproductive system effects. [4, 5]

TNT is classified as a class C carcinogen by U.S. Environmental Protection Agency (EPA) [6]. The wastewater discharged from former military production sites during purification process and leachates from waste disposal sites made thousands acres of soil and groundwater contaminated with munitions like TNT. Nowadays, high concentrations of TNT, its precursors (mono and dinitrotoluenes) and their abiotic and biotic transformation products are still found in soil and groundwater near the former production plants where munitions were manufactured, loaded, and demilitarized.[7,8] The presence of TNT in groundwater and soil poses a great threat to a wide variety of organism including humans due to its toxicity, potential mutagenicity and carciogenicity.[2,9,10] The hazardous characteristics of TNT make it necessary to develop a fast and cost-effective remediation approach to clean up contaminated sites.

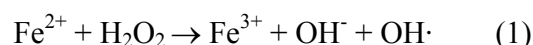
### 1.3 Remediation Processes

A variety of technologies have been utilized to remove TNT residues from the environment, including incineration, soil washing[12], bioremediation[13-15], ultrasonic irradiation[16], Fenton reaction[17-19] and other advanced oxidation processes such as TiO<sub>2</sub>/UV[20], O<sub>3</sub>/UV[21], and O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>[22], H<sub>2</sub>O<sub>2</sub> /UV[23]. Among these strategies incineration is the only technique accepted by U.S. authorities for remediating munitions contaminated soil. Although it is an effective method to destroy contaminants, the high cost and generation of undesirable air emission and by-products are of great concerns. As for soil washing, the major concern is that the produced aqueous effluent needs further treatment. Great efforts have been made to treat TNT contamination sites via biological degradation, but it does not apply well to highly contaminated sites, and requires long treatment time [22, 23]. Hence, a more rapid and robust method is in need to meet such criteria. A feasible alternative is the use of advance oxidation processes. Advanced oxidation processes (AOPs) consist of Fenton reaction, TiO<sub>2</sub>/UV, O<sub>3</sub>/UV, O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> /UV, which are based on the generation of the strong oxidant-hydroxyl radical (OH·) as reactive species. The AOPs have been shown sufficiently effective in remediating many refractory contaminants including nitroaromatics like TNT [24-27]. These technologies can be applied alone or used as a pretreatment followed by biodegradation methods. Dillert *et al* [28] have compared the effectiveness of titanium dioxide photocatalytic reaction and photo Fenton reaction to degrade TNT and 16 other nitroaromatic compounds, their results show both methods were suitable for transformation of nitroaromatic pollutants in aqueous solution and reaction rates were

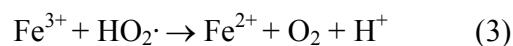
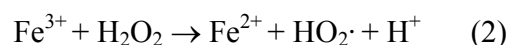
faster in the photo Fenton treatments as compared to TiO<sub>2</sub>-mediated photocatalytic reactions.

#### **1.4 Fenton Remediation: retrospect and future**

Recently significant efforts have been made to degrade explosives including TNT by Fenton reaction [29,30]. Fenton reaction [31] is one of the oldest and most powerful oxidizing techniques among the AOPs, it proceeds through the following pathway:



The highly reactive species, hydroxyl radical (OH·), is formed as an intermediate by Fe<sup>2+</sup> catalyzed hydrogen peroxide decomposition. The ferrous ion is regenerated by:



The optimum pH for Fenton reaction is around 2.5-3.0 because acidic conditions are necessary to prevent Fe<sup>2+</sup> from precipitating.

The use of Fenton reaction to treat organic contaminants like TNT is a feasible alternative to bioremediation processes. Hydroxyl radical is one of the strongest oxidant known, and is capable of degrading a wide range of pollutants. The second-order rate constant for reaction of hydroxyl radical with organic pollutants often approaches the diffusion controlled limit [32]. This reaction is suitable for removal of recalcitrant organic wastes, especially non-biodegradable compounds. Fenton oxidation is strong enough to achieve complete degradation and mineralization of TNT. Fe<sup>2+</sup> and hydrogen peroxide are non-hazardous and environmentally benign reagents and Fenton treatment

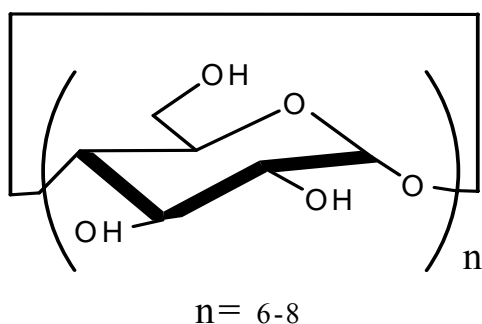
can be easily applied and controlled. The Fenton reagent has proven to be a simple, safe, fast and effective method to degrade toxic organic pollutants [33-35].

However, the development and application of Fenton reaction are inhibited by the complexity and difficulty of treating high concentrations mixtures of munitions in soils and groundwater. The Fenton remediation of recalcitrant organics is severely hindered when these pollutants are sorbed to natural organic matter (NOM), suspended particles, sand, or soil. It is due to the non-specific nature of the hydroxyl radical. This non-specificity will cause significant interferences from non-pollutant components, resulting in lower degradation efficiency and increased remediation costs.

## **1.5 Cyclodextrin: a brief introduction**

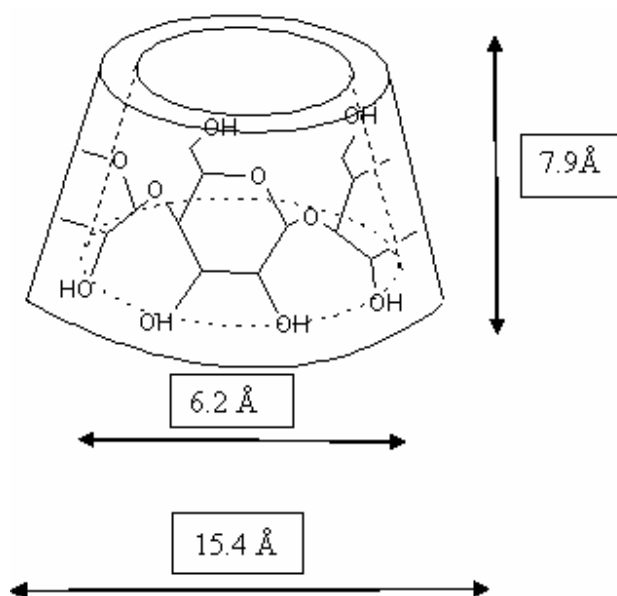
Cyclodextrins (CDs) are a series of enzymatically-modified starches formed by the action of the enzyme on starch and related compounds. Three naturally occurring  $\alpha$ -,  $\beta$ -, and  $\gamma$ - cyclodextrins have six, seven and eight  $\alpha$ -(1,4)-linked glucopyranose rings respectively (Fig. 1.1). They are torus shaped oligosaccharides with hydrophobic central cavities and hydrophilic rims (Fig.2.1). Their cylindrical structures with cavities of about 0.7 nm deep and 0.6-1 nm inside diameter yield various unique properties [36]. The hydrophilic exterior (primary and secondary hydroxyl groups) makes cyclodextrin molecules soluble in water, and the hydrophobic interior (alkyl group and ether-like oxygens) makes a good microenvironment for appropriately sized nonpolar compounds. Cyclodextrins and their derivatives are well-known as molecular hosts capable of including a range of guest molecules (organic and inorganic substrates) via noncovalent interactions [37-40]. The physicochemical properties of the guest molecules can be

changed significantly upon complex formation, and this is the basis of the wide usage of cyclodextrins. Cyclodextrins have been applied in various fields, such as chromatographic separation systems [41], drug stabilizing and solubilizing systems [42] and enzyme models [43].



**Figure 1.1** Structures of three natural occurring Cyclodextrins (CDs).

$n=6$ ,  $\alpha$ -CD;  $n=7$ ,  $\beta$ -CD;  $n=8$ ,  $\gamma$ -CD.

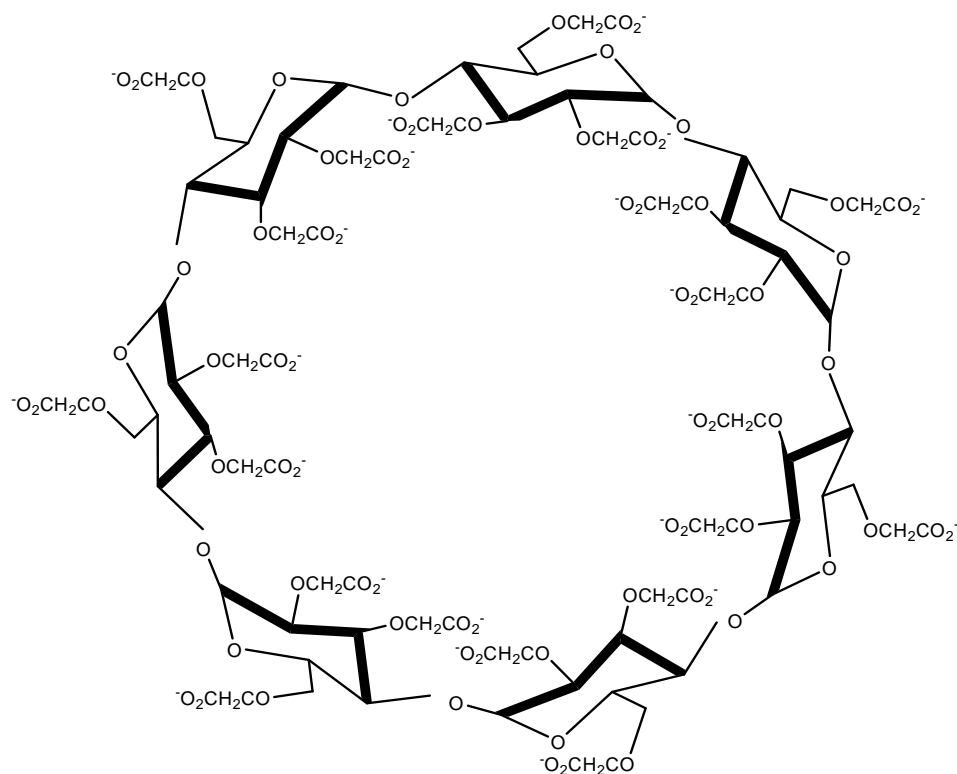


**Figure 1.2** Dimension of  $\beta$ -cyclodextrin ( $\beta$ -CD).



The idea of incorporating cyclodextrin with Fenton reagent was based on the unique capability of cyclodextrin to bind both metal ions and hydrophobic organic contaminants. Organic contaminants in water or sorbed to soil can partition into the internal region of CD, which helps to increase their apparent aqueous solubilities. In addition, the hydroxyl groups on the rims of CD have the ability to coordinate with  $\text{Fe}^{2+}$ , which reacts with peroxide to generate hydroxyl radical. In this manner, CD has brought hydroxyl radical in close proximity with organic contaminants, resulting in higher degradation efficiency and elimination of interfering matrix effects.

Carboxymethyl- $\beta$ -cyclodextrin (CM- $\beta$ -CD) is a mixture of derivatized  $\beta$ -CD by substituting of hydroxyl groups on both ends of toroid with carboxymethyl groups. The structure of CM- $\beta$ -CD is illustrated in Fig. 1.3. In fact, it only represents one out of thousands of isomers of CM- $\beta$ -CD with a degree of substitution equal 21. Not only does CM- $\beta$ -CD have improved water solubility than  $\beta$ -CD, but carboxymethyl groups have better metal binding ability as compared to hydroxyl groups. Wang and Brusseau have reported that CM- $\beta$ -CD could simultaneously bind phenanthrene and  $\text{Cd}^{2+}$  in their work [44-46].



**Figure 1.3** Structure of carboxymethyl- $\beta$ -cyclodextrin (CM- $\beta$ -CD).

In order to form a host-guest complex, the volume of the guest molecule should be comparable to the volume of the CD cavity. Tamaraw and Jalal [47] have presented data of calculated molecular volumes of TNT and two derivatized  $\beta$ -CD (hydroxypropyl- $\beta$ -cyclodextrin and Heptakis-2,6-di-O-methyl- $\beta$ -cyclodextrin). According to their data, the volume of TNT molecule is  $0.258 \text{ nm}^3$  (0.71 nm in width, 0.69 nm in length); hydroxypropyl- $\beta$ -cyclodextrin (HP- $\beta$ -CD) and Heptakis-2,6-di-O-methyl- $\beta$ -cyclodextrin (DM- $\beta$ -CD) have the same volume of  $0.346 \text{ nm}^3$  (0.75 nm in width, 0.78 nm in length). The data indicated that the interior volume of a  $\beta$ -CD cavity is larger than the volume of TNT; therefore, the formation of an inclusion complex between TNT and  $\beta$ -CD is theoretically possible.

A chemically modified  $\beta$ -cyclodextrin, carboxymethyl- $\beta$ -cyclodextrin (CM- $\beta$ -CD) is used in this study because it has the proper size to encapsulate TNT, better water solubility than underivatized  $\beta$ -CD, and is more likely to strongly coordinate with  $\text{Fe}^{2+}$ . The ability of CM- $\beta$ -CD to simultaneously bind with TNT and  $\text{Fe}^{2+}$  in solution will increase the availability of TNT to be attacked by hydroxyl radical, and result in improvements in the efficiency of Fenton degradation.

The objectives of this study were to determine the effectiveness of  $\text{Fe}^{2+}$ / CM- $\beta$ -CD / $\text{H}_2\text{O}_2$  to remediate TNT contamination in water and sand (soil analogy); investigate the effect of concentration of CM- $\beta$ -CD on the kinetics of Fenton degradation of TNT in water; explore the potential of application of  $\text{Fe}^{2+}$ / CM- $\beta$ -CD / $\text{H}_2\text{O}_2$  systems in natural water and soil system, and identify TNT degradation byproducts by Fenton reagent.

## CHAPTER TWO CYCLODEXTRIN-Fe(II)-HYDROGEN PEROXIDE DEGRADATION OF TNT IN AQUEOUS SOLUTION

### 2.1 Experiments

#### 2.1.1 Chemicals

2, 4, 6-trinitrotoluene (98%) was obtained from Chem Service. Prior to use, it was dried in the oven at 65°C for 45 min. Ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) was purchased from J. T. Baker. Sulfuric acid  $\text{H}_2\text{SO}_4$  (98%) was purchased from EM Science. Carboxymethyl- $\beta$ -cyclodextrin (CM- $\beta$ -CD) was supplied by Cerestar. 1-propanol was purchased from EM Science. Hydrogen peroxide (30%, aqueous) was obtained from Aldrich, and standardized by iodometric titration. Methanol and acetonitrile (HPLC grade) were purchased from Fisher Scientific. Suwannee river humic acid was obtained from the International Humic Substance Society (<http://www.ihss.gatech.edu/>). Distilled and deionized water was produced by a Nanopure UV (Barnstead) water treatment system using a distilled water feed.

#### 2.1.2 Degradation Procedures

##### (1) *General Procedures*

Aqueous stock TNT solutions were made by dissolving an appropriate amount of solid TNT in distilled and deionized water and magnetically stirring overnight. For pH

adjustment,  $\text{H}_2\text{SO}_4$  was added to bring to the pH of the TNT solution to 3.0.  $\text{FeSO}_4$  solutions were prepared fresh daily. Most of the degradation experiments were carried out in a 50 mL reaction vessel. Appropriate amounts of TNT and catalyst  $\text{FeSO}_4$  were added to a 10.00 mL volumetric flask which was then filled to the mark with water. The 10.00 mL sample was transferred into the reaction vessel. The reaction was initiated by continuously adding a diluted aqueous solution of hydrogen peroxide into the reaction vessel with a syringe pump (Kd Scientific) at a rate of 2.00 mL/h. This process generated a steady state of hydroxyl radical concentration. All reactions were performed at room temperature with constant stirring. At predetermined time intervals, a 300  $\mu\text{L}$  aliquot was taken from the reaction vessel. The sample was quenched by 300  $\mu\text{L}$  1% (v/v) 1-propanol to stop further reaction, and then analyzed by HPLC. Each experiment was performed in duplicate.

(2) *Cyclodextrin mediated Fenton degradation of TNT*

Carboxymethyl- $\beta$ -cyclodextrin (CM- $\beta$ -CD) was chosen to be included in the Fenton system because of its excellent aqueous solubility, appropriate cavity size to form inclusion complexes with TNT, and ability to coordinate ferrous ions. Carboxymethyl- $\beta$ -cyclodextrin was added into the aqueous system containing TNT and  $\text{Fe}^{2+}$  prior to adding the  $\text{H}_2\text{O}_2$ . The reaction solution was sonicated (Branson 1210, 60 Watts) for 30 min to expedite the formation of cyclodextrin inclusion complexes. The reaction solution was treated with continuous addition of hydrogen peroxide, and the rate and extent of destruction were compared to the systems treated without cyclodextrin.

(3) *Degradation in presence of free radical scavenger*

The effects of free radical scavenger were investigated using 1-propanol (50 mM), which is a major sink of hydroxyl radical in aqueous solution. The conditions investigated were as follows:  $C_{\text{TNT}} = 0.1 \text{ mM}$ ;  $C_{1\text{-propanol}} = 50 \text{ mM}$ ;  $C_{\text{Fe}^{2+}} = (1) 5 \text{ mM}, (2) 15 \text{ mM}$ ;  $C_{\text{CM-}\beta\text{-CD}} = (1) 0.5 \text{ mM}, (2) 1 \text{ mM}, (3) 2 \text{ mM}, (4) 3 \text{ mM}, (5) 4 \text{ mM}$ . Aqueous hydrogen peroxide solution was added continuously with a syringe pump at a rate of 2.00 mL/h. Total reaction time varied from 6-15 min, during which the volume changes of the solution by adding hydrogen peroxide were negligible. All experiments were performed under acidified conditions (pH =3.0) at ambient temperature.

(4) *Degradation in presence of natural organic matter*

Humic acid (HA) was chosen as natural organic matter investigated in this study. An aliquot of solid humic acid was dissolved in each aqueous TNT solution to yield a concentration of 30 mg/L. Then the solutions were treated with Fenton reagent ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) with or without CM- $\beta$ -CD as described above.

### 2.1.3 Analysis

The TNT and degradation byproducts withdrawn from every degradation experiment were analyzed by reverse phase HPLC (Agilent 1100 series, G1322A Degasser, G1311A QuatPump, G1315 DAD) equipped with Agilent A.08.03 ChemStation data system. All samples were separated on an Allsphere ODS-2 column (Alltech, Length 250 mm, ID 4.6 mm). The packing material was spherical silica with a pore size of 80 Å and a particle size of 5  $\mu\text{m}$ . The column was fitted with a guard

column (Alltech, OPTI-GUARD column, C18, 15mm×1mm) with the same packing material. UV absorbance was measured simultaneously at wavelengths from 200-400 nm using the diode array detector. The samples were centrifuged at 13,000 rpm for 2 min to remove particulates before injection using a 100 µl loop. The following elution gradient was employed: the ratio of Nanopure H<sub>2</sub>O/acetonitrile was 70/30 (v/v) at time zero and changed linearly to 50/50 in 15 min and was maintained at this ratio for 3 min. The gradient helped to resolve the intermediate product peaks in a reasonable time. The flow rate was set at 1 mL/min for all measurements. The total analysis of each run was 18 min and TNT eluted at around 16 min.

#### **2.1.4 Analysis of TNT transformation products**

In order to identify the transformation products of TNT treated by Fenton reagents, a large amount of TNT in the reaction matrix and a preconcentration step were necessary. Two procedures have been used: 100.0 mL aqueous solution (pH 3.0) containing 0.2 mM TNT and 5 mM FeSO<sub>4</sub> was degraded with addition of 1.2 M H<sub>2</sub>O<sub>2</sub> solution at a fixed rate of 2.00 mL/h. The reaction was carried out for 10 minutes, and then the whole reaction solution was extracted with either (1) liquid-liquid extraction using 20 mL of ethyl acetate and nitrogen dry to near dryness, then redissolved in 1 mL acetonitrile; or (2) solid phase extraction using maxi-clean C18 cartridge (Alltech, 900 mg). The cartridge was conditioned with 5 mL methanol and then 5 mL deionized water. The solution was applied to the cartridge and then eluted with 5 mL acetonitrile. The eluent was evaporated with nitrogen to near dryness and redissolved in 1 mL acetonitrile. The concentrated samples were then analyzed by HPLC. Most samples were separated on an Allsphere ODS-2 column (Alltech, Length 250 mm, ID 4.6 mm, and 5 µ). The

gradient elution program was: deionized water (A) and acetonitrile (B). 0 min 30% B, 0-16 min linear to 50 % B, 16-19 min maintained at 50% B, 19-30 min linear to 90% B. Some samples were also analyzed on an Adsorbosphere XL C8 column (Alltech, 150 mm × 4.6 mm, 5 μ). The gradient elution program was: deionized water (A) and acetonitrile (B). 0 min 10% B, 0-16 min linear to 40 % B, 16-19 min maintained at 50% B, 19-30 min linear to 90% B. The flow rate was 1 mL/min. Each run was 30 min.

## **2.2 Results and Discussion**

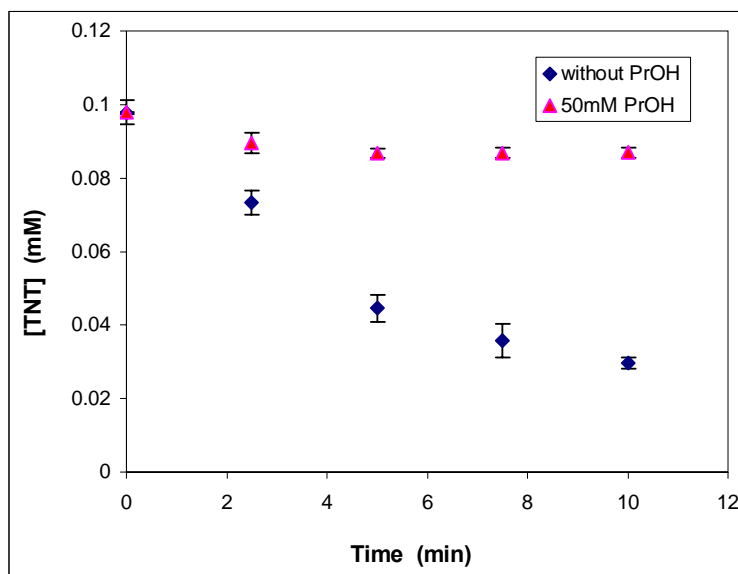
Initially, pure water was spiked with TNT and then treated with Fenton reagents ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) for a certain amount of time (around 10 to 20 min). The reactions were monitored by taking samples from the reactor at pre-determined time intervals. The data of HPLC analysis shows that TNT can be easily degraded by Fenton oxidation with complete degradation achieved within 20 min. The result proved that Fenton oxidation works well for a simple matrix with little or no interferences.

### **2.2.1 Scavenging effect of 1-propanol**

1-propanol (PrOH) was added to the TNT aqueous solution as a scavenger of hydroxyl radical. Taking into account all sorts of natural scavengers existing in real TNT polluted systems, it is plausible to include PrOH in reaction solutions to be treated with Fenton reagents. In addition, one objective of this study was to investigate the effect of CM-β-CD on the kinetics of Fenton reagents reacting with TNT. Unfortunately, CM-β-CD can act as a scavenger of hydroxyl radical as well. Therefore, it is necessary to make



PrOH in large amount of excess to minimize the scavenging influence caused by CM- $\beta$ -CD.

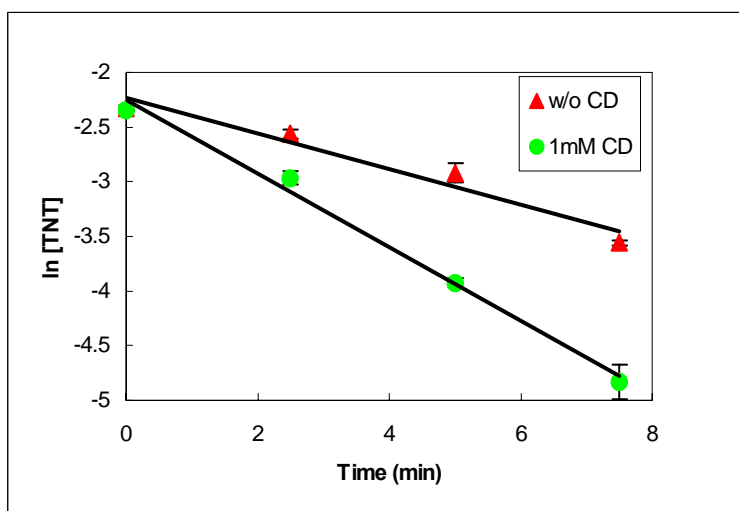


**Figure 2.1** Time dependent concentration of TNT during degradation by Fenton treatment ( $\blacklozenge$ ) in pure water; ( $\blacktriangle$ ) with 50 mM 1-propanol. Initial [TNT] = 0.1 mM,  $[\text{Fe}^{2+}] = 5$  mM, 110 mM  $\text{H}_2\text{O}_2$  added at 2.00 mL/h. pH = 3.0, initial solution volume = 10.00 mL.

Figure 2.1 shows the results of TNT degraded by Fenton reagents in the presence and absence of radical scavenger: 1-propanol. In the system with no scavenger, the reaction between TNT and hydroxyl radical followed pseudo first order kinetics ( $k = 0.12 \pm 0.01 \text{ min}^{-1}$ ). If PrOH was present, most of the  $\text{OH}\cdot$  generated in solution was consumed by 1-propanol, resulting in a small portion of TNT (around 10%) degraded. The rate of the reaction was much slower in comparison to the experiment without PrOH. This suggested that the scavenging effect of PrOH was large enough that little TNT degradation could proceed.

### 2.2.2 Degradation of TNT in pure water

Degradation of TNT in pure water was performed using both Fenton reagents ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) and CD mediated Fenton reagents ( $\text{Fe}^{2+}$ -CD-  $\text{H}_2\text{O}_2$ ). The kinetic studies show that degradation of TNT by hydroxyl radical followed apparent pseudo first order kinetics. When CM- $\beta$ -CD was introduced into the system, it is obvious that the rate of the degradation reaction was enhanced. This is illustrated in the following plot (Fig. 2.2). Two samples of aqueous TNT solution (10.00 mL) were degraded by Fenton reagents under the same conditions except that only one solution contained 1 mM CM- $\beta$ -CD. The initial concentration of TNT in both cases was about 0.1 mM. The initial concentration of  $\text{Fe}^{2+}$  was 15 mM.  $\text{H}_2\text{O}_2$  (152 mM, aqueous) was added into each solution at a rate of 2.00 mL/h. TNT decayed by pseudo first order kinetics in both cases, and the rate constants were  $0.16 \pm 0.01 \text{ min}^{-1}$  ( $\blacktriangle$  without CD) and  $0.34 \pm 0.02 \text{ min}^{-1}$  ( $\bullet$  with 1 mM CM- $\beta$ -CD) respectively. The rate of degradation was enhanced by 2-fold with addition of 1 mM CM- $\beta$ -CD. After 7.5 min, 91% of the TNT was degraded in the solution with 1 mM CM- $\beta$ -CD compared to 70% loss of TNT in the solution without CM- $\beta$ -CD. At each time interval, a substantial difference was observed between the two experiments: more TNT was degraded by hydroxyl radical in presence of CD than in absence of CD. This indicated that adding CM- $\beta$ -CD did improve the efficiency of Fenton degradation.



**Figure 2.2** The relationship between  $\ln[\text{TNT}]$  and time. Initial  $[\text{TNT}] = 0.1 \text{ mM}$ , initial  $[\text{Fe}^{2+}] = 15 \text{ mM}$ , initial  $[\text{PrOH}] = 50 \text{ mM}$ ,  $152 \text{ mM H}_2\text{O}_2$  added at  $2.00 \text{ mL/h}$ .  $\text{pH}=3.0$ , initial solution volume= $10.00 \text{ mL}$ .  $\blacktriangle$ : without  $\text{CM-}\beta\text{-CD}^*$ ;  $\bullet$ : with  $1 \text{ mM CM-}\beta\text{-CD}$ .

Lines are liner regression of the data.

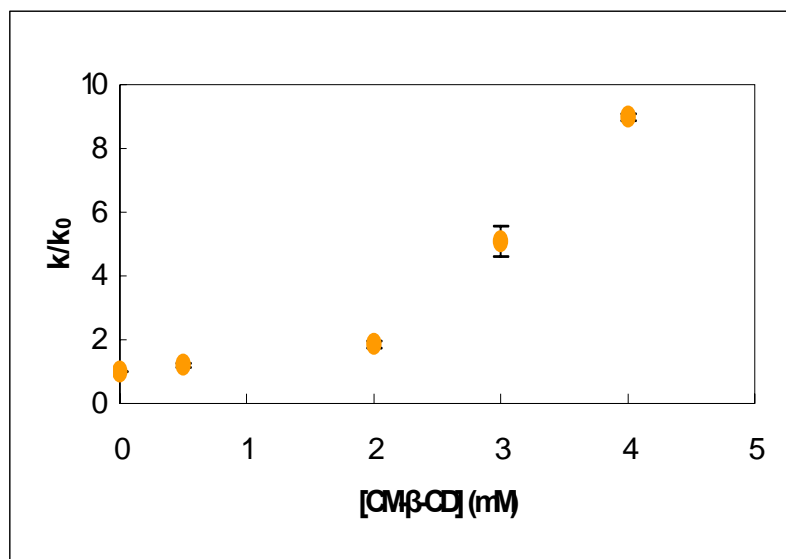
\* :  $\text{CM-}\beta\text{-CD}$  is a mixture of compounds with an average degree of substitution equal to 3. The molarity of  $\text{CM-}\beta\text{-CD}$  is an approximate number based on the median molecular weight of the mixture.

To verify if this enhancement effect exists at other concentrations of  $\text{CM-}\beta\text{-CD}$ , a set of experiments was carried out at various concentrations of  $\text{CM-}\beta\text{-CD}$  ( $0.5, 1, 2, 3, 4 \text{ mM}$ ). Results of these experiments are presented in Table 2.1.

Concentration of CM- $\beta$ -CD (mM)	Pseudo first order rate constants k (min <sup>-1</sup> )
0	0.16 $\pm$ 0.01
0.5	0.18 $\pm$ 0.01
1	0.34 $\pm$ 0.02
2	0.37 $\pm$ 0.09
3	0.41 $\pm$ 0.04
4	0.28 $\pm$ 0.01

**Table 2.1** Pseudo first order rate constants for TNT degraded by Fe<sup>2+</sup>/CD/ H<sub>2</sub>O<sub>2</sub> systems at different concentration of CM- $\beta$ -CD. Initial [TNT] = 0.1 mM, initial [Fe<sup>2+</sup>] = 15 mM, initial [PrOH] = 50 mM, 152 mM H<sub>2</sub>O<sub>2</sub> added at 2.00 mL/h. pH=3.0, initial solution volume=10.00 mL.

Aqueous TNT solutions with radical scavenger PrOH were treated by Fe<sup>2+</sup>/CD/ H<sub>2</sub>O<sub>2</sub> systems with CM- $\beta$ -CD concentration ranging from 0 to 4 mM. The decay of TNT concentration followed a pseudo first order kinetics in all experiments. The results show that for all the concentrations investigated, CM- $\beta$ -CD did play a role in the more rapid removal of TNT in water. The extent of rate improvement varied with different levels of CM- $\beta$ -CD. At 3 mM CM- $\beta$ -CD, the maximum improvement was observed.

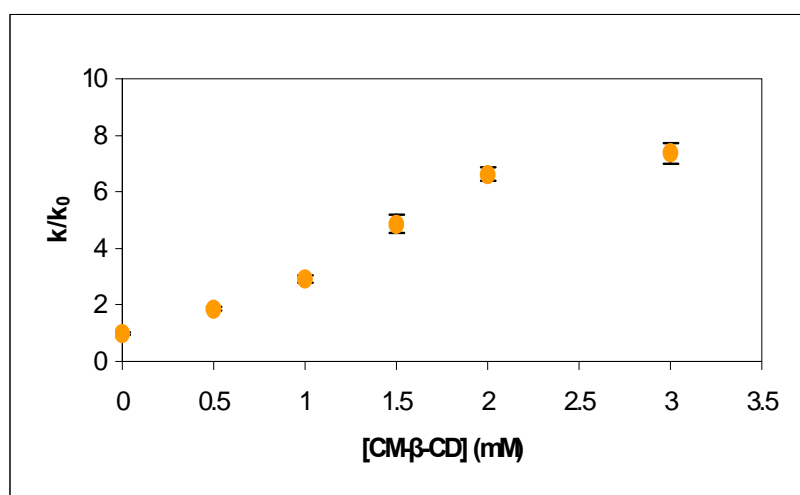


**Figure 2.3** The relationship between the concentration of CM-β-CD and the normalized rate constant ( $k/k_0$ ) for TNT reaction with hydroxyl radical.  $k_0$ : the first order rate constant in the absence of CM-β-CD. Initial [TNT] = 0.1 mM, initial  $[\text{Fe}^{2+}] = 5$  mM, 164 mM  $\text{H}_2\text{O}_2$  added at 2.00 mL/h. pH=3.0, initial solution volume=10.00 mL.

The effect of CM-β-CD on Fenton remediation of TNT was also investigated in the absence of the scavenger 1-propanol (Fig. 2.3). The degradation rate constant of TNT increased with concentration of CM-β-CD, and the most efficient condition was observed at  $[\text{Fe}^{2+}] = 5$  mM and  $[\text{CM-}\beta\text{-CD}] = 4$  mM. Under these conditions, a nearly nine-fold increase in TNT degradation rate constant was observed. The destruction rate enhancement was even greater as compared to experiments with scavenger, indicating there may be some interference from the interactions between 1-propanol and CM-β-CD.

### 2.2.3 The effect of dissolved organic matter

The fact that organic matter is ubiquitous in natural water must be taken into account when evaluating Fenton remediation for field application. Humic acid was used as a model substance to bind TNT in this study. Adding humic acid (30 mg/L) to the TNT reaction solution did marginally decrease the TNT transformation rate. The transformation rate of TNT changed from  $0.11 \text{ min}^{-1}$  (without HA) to  $0.10 \text{ min}^{-1}$  (with HA 30 mg/L). The other reaction conditions were kept constant: initial  $[\text{TNT}] = 0.1 \text{ mM}$ , initial  $[\text{Fe}^{2+}] = 5 \text{ mM}$ ,  $164 \text{ mM H}_2\text{O}_2$  added at  $2.00 \text{ mL/h}$ ; pH adjusted to 3.0 with  $\text{H}_2\text{SO}_4$ . However, adding CM- $\beta$ -CD can dramatically improve the efficiency of TNT transformation rate even though the detrimental impact of humic acid exists. The TNT transformation rate enhancement reached almost 8 fold when 3 mM CM- $\beta$ -CD was introduced into the system.



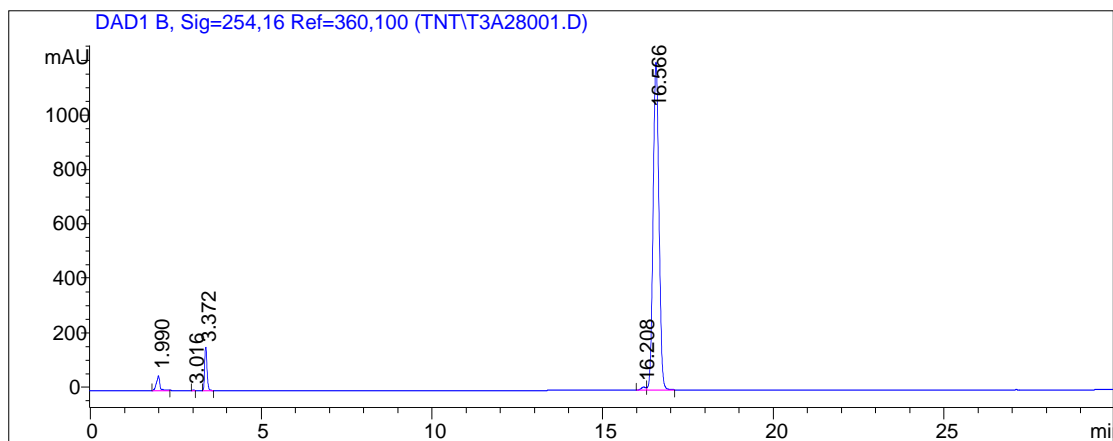
**Figure 2.4** The relationship between the concentration of CM- $\beta$ -CD and the normalized rate constant ( $k/k_0$ ) for TNT transformation by  $\text{Fe}^{2+}/\text{CD}/\text{H}_2\text{O}_2$  systems in the presence of Suwannee River humic acid. Initial  $[\text{TNT}] = 0.1 \text{ mM}$ , initial  $[\text{Fe}^{2+}] = 5 \text{ mM}$ , initial  $[\text{HA}]$

= 30 mg/L, 164 mM H<sub>2</sub>O<sub>2</sub> added at 2.00 mL/h. pH=3.0, initial solution volume=10.00 mL.

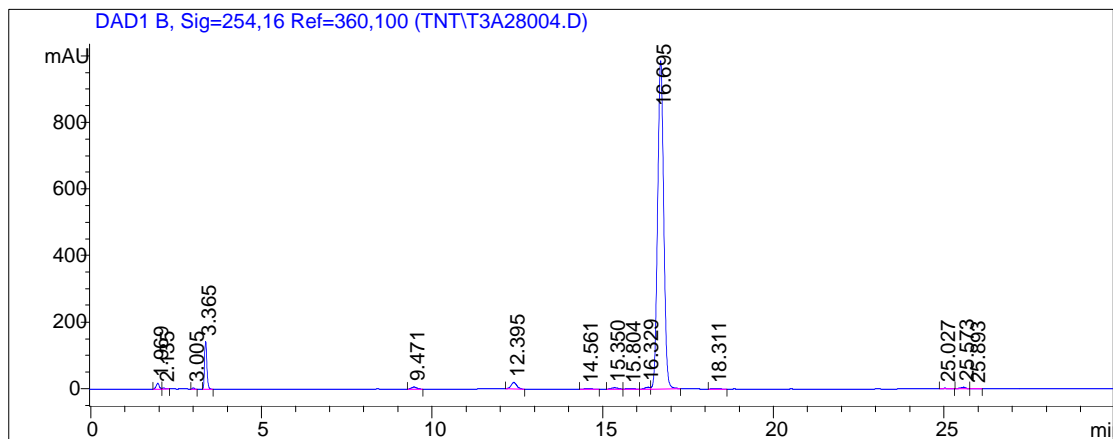
#### 2.2.4 Identification of degradation byproducts

The intermediate byproducts from TNT degradation are of great interest because it is important to determine their toxicity and persistence in the environment. In addition, studies on degradation products will help to gain an understanding of the reaction mechanism. Fig. 2.5 shows transformation products of TNT formed in Fenton reaction at different reaction times. The total volume of the reaction solution was 100.0 mL. At each time interval (t = 0, 3, 7, 10 min), an aliquot of 300 µl was taken from the solution and injected into the HPLC. The peak of TNT was eluted around 16.5-16.9 min (Fig. 2.5 **a**). As reaction began, several product peaks were observed at retention times of 9.5, 12.4, 15.4 and 18.3 min. These four peaks were tiny compared to the large peak of TNT at 16.5 min, but they were consistent during the whole reaction process (shown in Fig. 2.5. **b**. **c**. **d**). Fig. 2.5 **e** is an enlargement view of Fig. 2.5 **d**, which gives a clear evidence of transformation products eluted before and after TNT peak.

(a) T=0 min

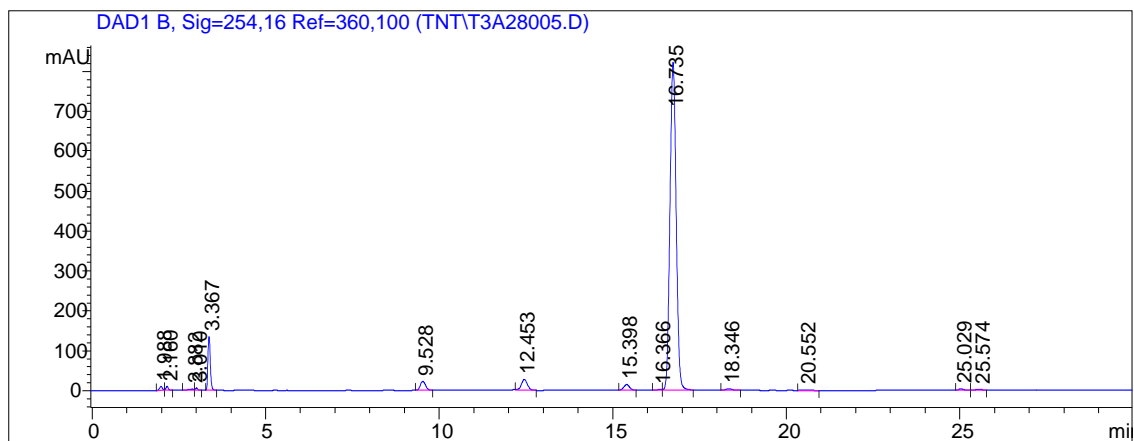


(b) T=3 min

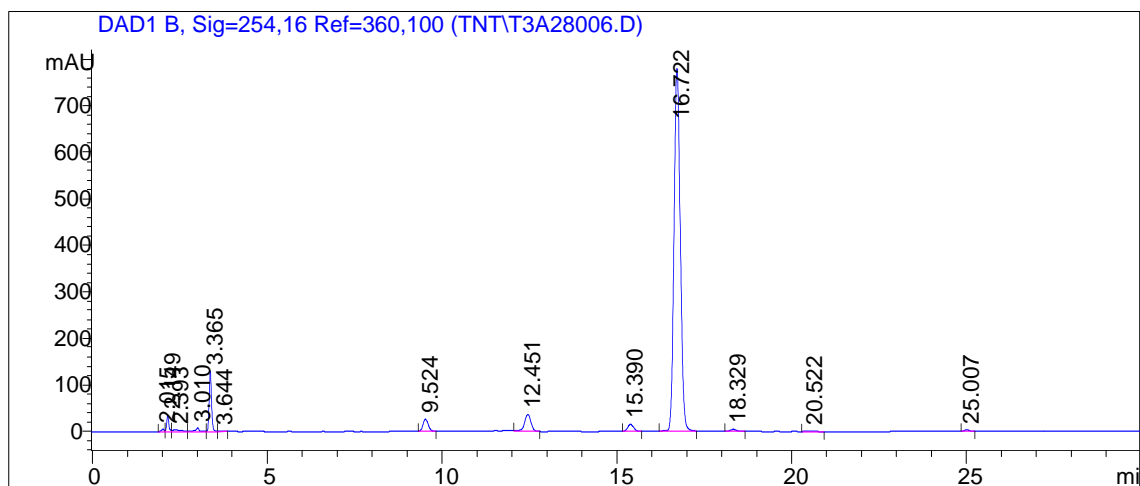




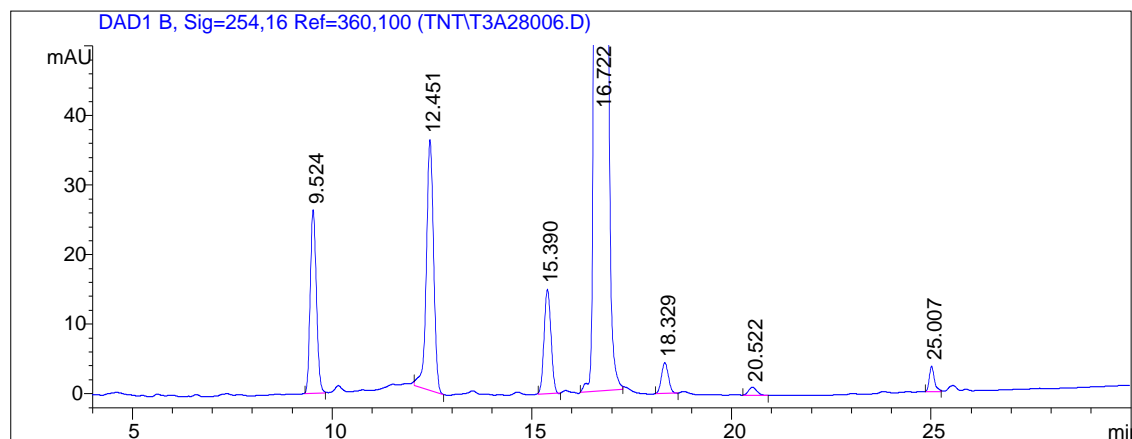
(c) T=7 min



(d) T=10 min



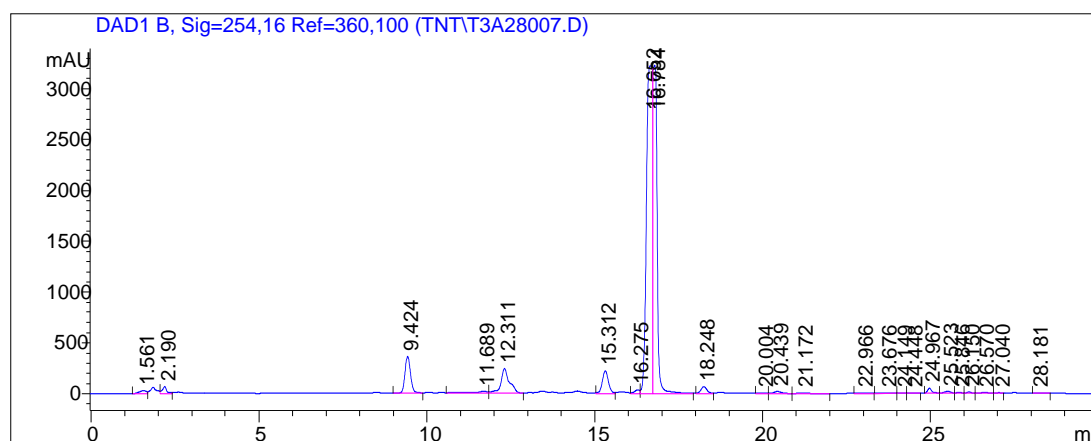
(e) T=10 min, enlargement of chromatogram d from retention time 4 to 30 min.



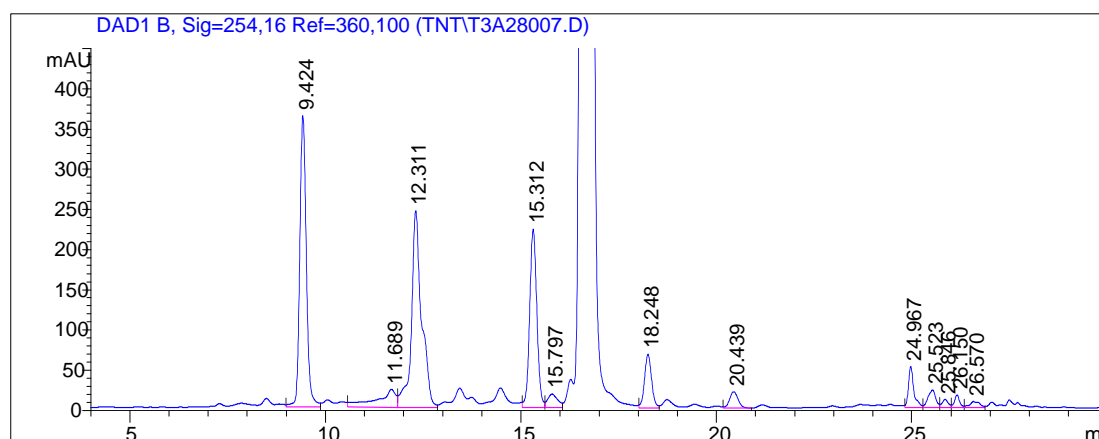
**Figure 2.5** Products formation in Fenton degradation of TNT in aqueous solution at different reaction times. Reaction conditions: Initial [TNT] = 0.2 mM, initial  $[\text{Fe}^{2+}] = 5$  mM, 1.18 M  $\text{H}_2\text{O}_2$  added at 2.00 mL/h, pH=3, initial solution volume = 10.00 ml. The reaction was stopped at 10 min. (a)  $t = 0$  min; (b)  $t = 3$  min; (c)  $t = 7$  min; (d)  $t = 10$  min; (e) enlargement of chromatogram d from retention time 4 to 30 min.

The presence of transformation peaks was further confirmed by the chromatogram (Fig.2.6 a) obtained following a preconcentration step performed after the whole reaction stopped at 10 min. All of the peaks were 10 times higher than the peaks in Fig. 2.5 d.

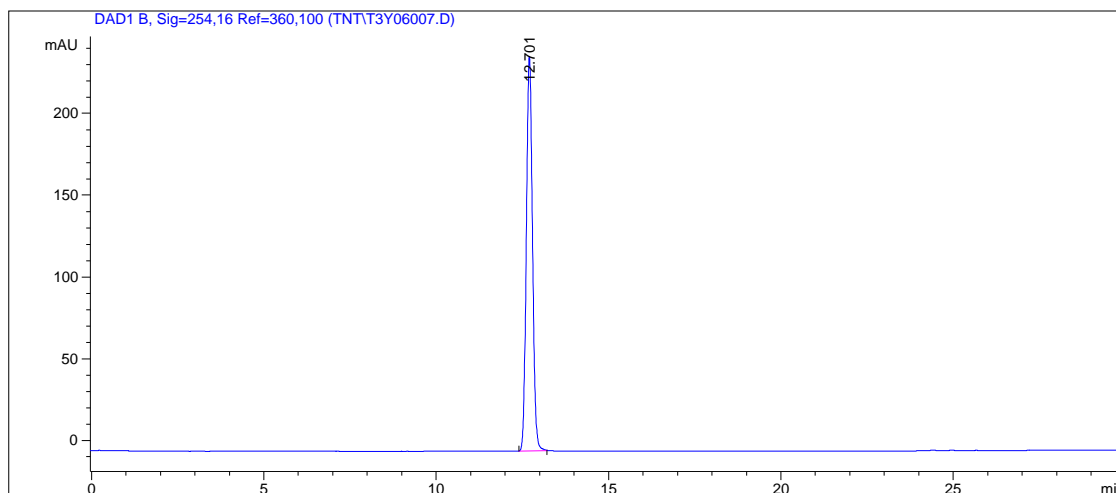
(a)



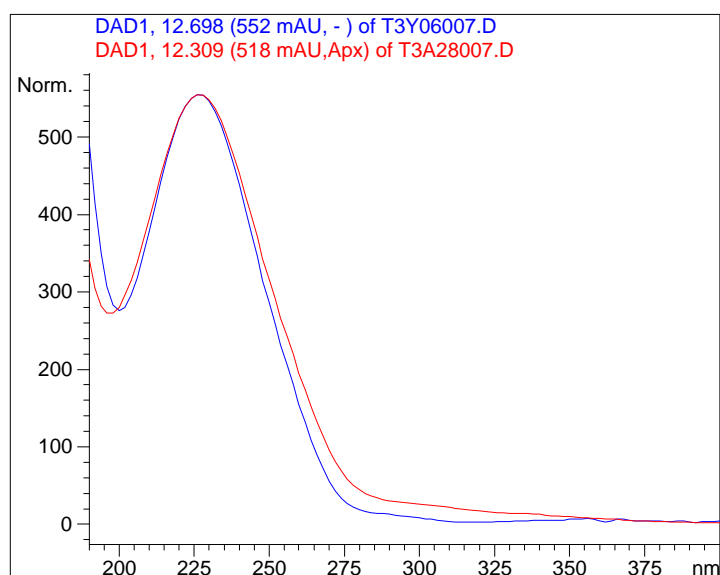
(b)



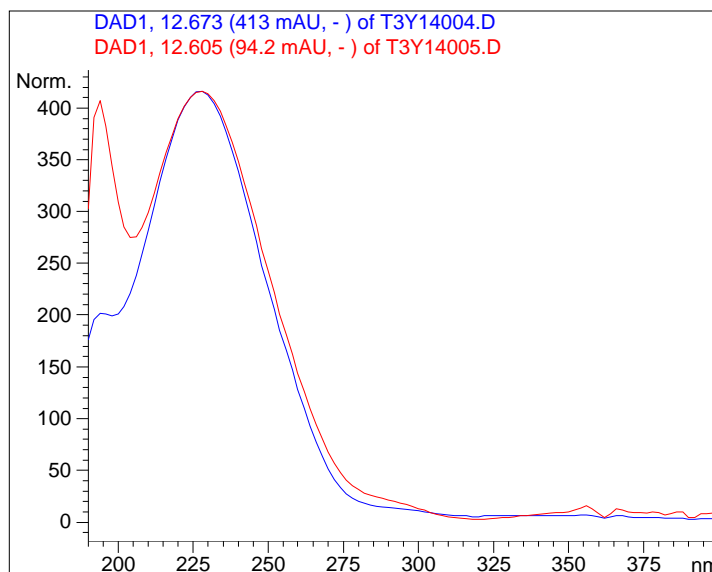
**Figure 2.6** Products formation in Fenton degradation of TNT in aqueous solution. (a)  $t = 10$  min; (b) enlargement of chromatogram a from retention time 4 to 30 min. Conditions: Initial  $[\text{TNT}] = 0.2$  mM, initial  $[\text{Fe}^{2+}] = 5$  mM,  $1.18$  M  $\text{H}_2\text{O}_2$  added at  $2.00$  mL/h,  $\text{pH} = 3.0$ , initial solution volume =  $100.00$  mL. The reaction was stopped at 10 min. The aqueous solution was extracted with  $20$  mL of ethyl acetate and then evaporated with nitrogen to near dryness, then redissolved in  $1$  mL acetonitrile.



**Figure 2.7** Chromatogram of 1,3,5-trinitrobenzene (0.21 mg/mL 30:70 CH<sub>3</sub>CN:H<sub>2</sub>O). C18 column. The gradient elution program was: deionized water (A) and acetonitrile (B): 0-16 min linear from 30 to 50 % B, 16-19 min maintained at 50% B, 19-30 min linear to 90% B. The flow rate was 1.00 mL/min.



**Figure 2.8** Comparison of two spectra. The spectrum in red is the product peak eluted at 12.3 min. The spectrum in blue is the peak of 1,3,5-trinitrobenzene eluted at 12.7 min. Both peaks were separated on C18 column with the same elution gradient.



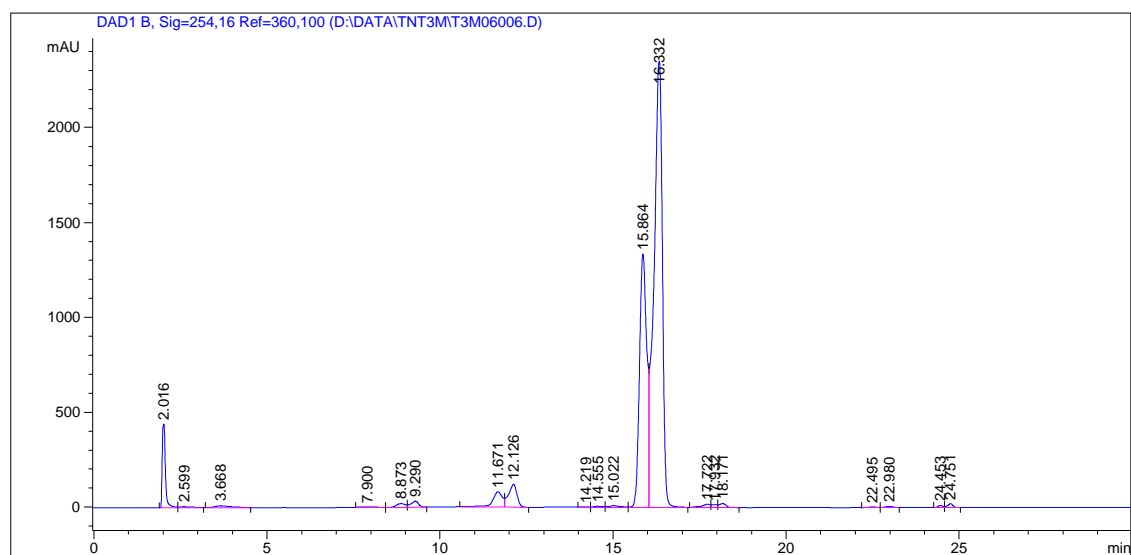
**Figure 2.9** Comparison of two spectra. The spectrum in red is the product peak eluted at 12.6 min. The spectrum in blue is the peak of 1, 3, 5-trinitrobenzene eluted at 12.6 min. Both peaks were separated on C8 column with the same elution gradient.

Two of the product peaks (1,3,5- trinitrobenzene and 2,4,6-trinitrobenzoic acid) were identified by comparing the retention time and UV spectra from DAD detector with the peaks of pure standards.

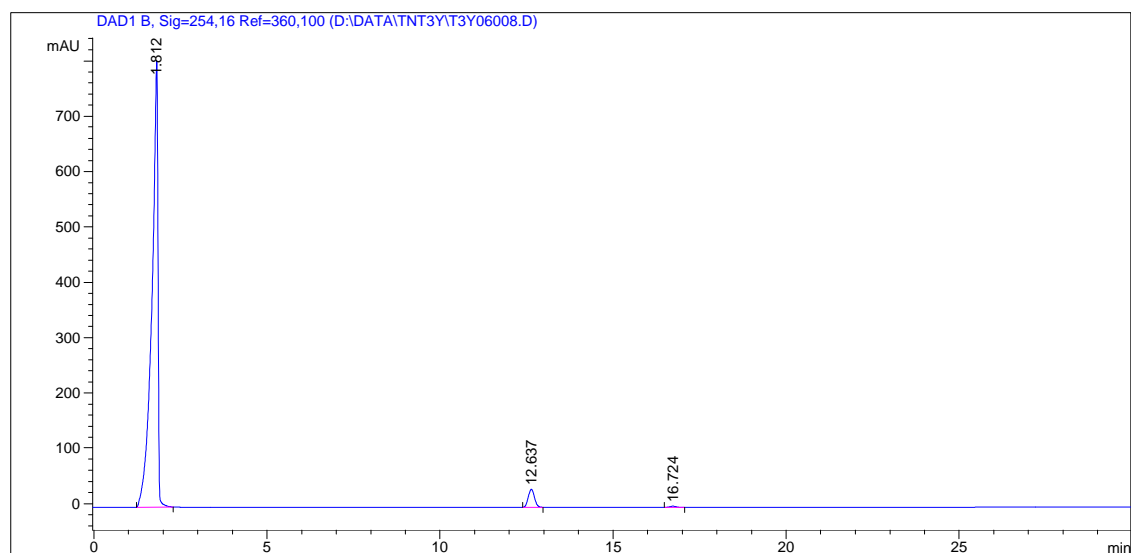
Figure 2.7 is the chromatogram of standard 1, 3, 5-trinitrobenzene (TNB). TNB was eluted about 12.7 min. Analysis of 1, 3, 5-trinitrobenzene and TNT transformation products were performed using the same chromatographic conditions. By comparing the UV spectrum of TNB and the spectrum of unknown peak eluted at 12.3 min in Figure 2.6 b, it is confirmed that unknown peak eluted at 12.3 min is 1, 3, 5-trinitrobenzene (Figure 2.8).

The identity of 1, 3, 5-trinitrobenzene in TNT degradation products was further confirmed by analysis the 1, 3, 5-trinitrobenzene and TNT degradation sample on C8 column using same chromatographic conditions (chromatograms not shown). By comparison of retention time and UV spectrum (Fig. 2.9), it is certain that 1, 3, 5-trinitrobenzene is one of the degradation product of TNT in Fenton reaction.

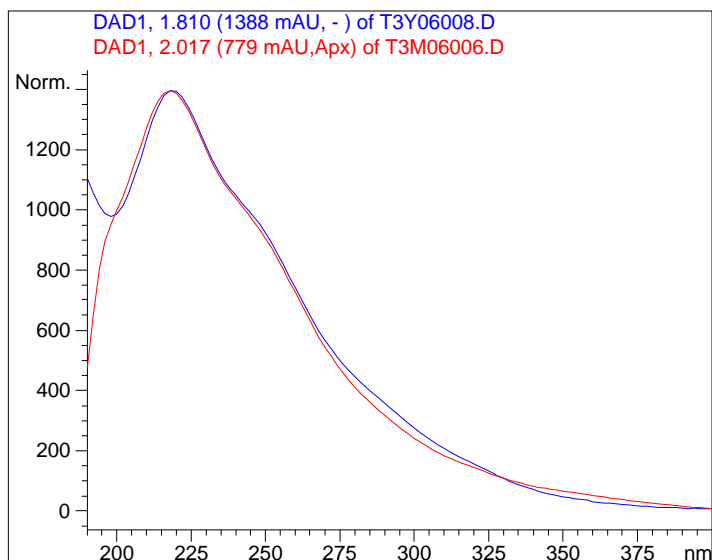
(a)



(b)



**Figure 2.10** Comparison of two chromatograms. a. collected during Fenton degradation: Initial [TNT] = 0.1 mM, initial [Fe<sup>2+</sup>] = 5 mM, 253.6 mM H<sub>2</sub>O<sub>2</sub> added at 2.0 mL/h, reaction time = 10 min. preconcentrated using C18 SPE cartridge. b. 2,4,6-trinitrobenzoic acid.



**Figure 2.11** Product identification (comparison of two spectra). The spectrum in red is product peak eluted at 2.01 min. The spectrum in blue is the peak of 2, 4, 6-trinitrobenzoic acid eluted at 1.81 min. Both peaks were separated on C18 column with the same elution gradient.

The identification of 2, 4, 6-trinitrobenzoic acid (TNBA) in TNT degradation products is shown in Figure 2.10. Chromatogram **a** is TNT degradation sample. Chromatogram **b** is standard 2, 4, 6-trinitrobenzoic acid. Analysis of 2, 4, 6-trinitrobenzoic acid and TNT degradation sample were performed using the same chromatographic conditions. By comparing the UV spectrum of TNBA and the spectrum of unknown peak eluted at 2.01 min in Figure 2.10a, it is confirmed that unknown peak eluted at 2.01 min is 1, 3, 5-trinitrobenzene (Figure 2.11).

## **CHAPTER THREE REMEDIATION OF TNT SORBED TO SOLIDS USING Fe(II) - CYCLODEXTRIN -HYDROGEN PEROXIDE SYSTEMS**

The previous chapter has discussed the effectiveness of remediation of TNT contaminated water using  $\text{Fe}^{2+}$  - CM- $\beta$ -CD -  $\text{H}_2\text{O}_2$  systems. In this chapter, the potential of this technique to remediate TNT contaminated soil is addressed. Decontamination of TNT adsorbed soil is more challenging than contaminated water because of the complexity of soil matrix and the lower accessibility of TNT to hydroxyl radical. To simplify the treatment, sand was used as analogy of soil in this study. This study has been divided into two sections: (1) remediation of clean sand spiked with TNT and (2) remediation of TNT from sand with interfering additives (Suwannee River humic acid, fulvic acid, and natural organic matter).

### **3.1 Experiments**

#### **3.1.1 Chemicals**

$\text{SiO}_2$  (sand) was purchased from Aldrich. 2, 4, 6-trinitrotoluene (98% purity) was obtained from Chem Service. Prior to use, it was dried in the oven at  $65^\circ\text{C}$  for 45 min. The sand/TNT mixture was made by mixing desirable amount of TNT (in acetone) with sand and stirring for one to two days to ensure homogeneity. Ferrous sulfate  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was purchased from J. T. Baker. Sulfuric acid  $\text{H}_2\text{SO}_4$  (98%) was purchased from EM



Science. Carboxymethyl- $\beta$ -cyclodextrin (CM- $\beta$ -CD) was supplied by Cerestar. Hydrogen peroxide (30%, aqueous) was obtained from Aldrich, and standardized by iodometric titration. Methanol and acetonitrile (HPLC grade) were purchased from Fisher Scientific. Suwannee river humic acid, fulvic acid and natural organic matter (NOM) were obtained from International Humic Substance Society (<http://www.ihss.gatech.edu/>). Distilled and deionized water was produced by a Nanopure UV (Barnstead) water treatment system.

### 3.1.2 Degradation Procedures

#### (1) *General Procedures*

Aliquots of sand (0.30 g or 1.00 g) were weighed out and put in 20 mL scintillation vials. Then water (pH = 3.0 with H<sub>2</sub>SO<sub>4</sub>) was added, and the vials were put on the vortexer for a few seconds. CM- $\beta$ -CD was added to some samples, and all samples were sonicated (Branson 1210, 60 Watts) for 30 min. Then an aliquot of FeSO<sub>4</sub> solution was added into water to yield a concentration of 2.5 or 5 mM. FeSO<sub>4</sub> solutions were prepared fresh daily. The reaction was initiated by single addition of an aliquot of hydrogen peroxide solution. The total reaction time was 10 min. The sample was then quenched by adding an equal amount of methanol to stop further reaction. Methanol also served to extract unreacted TNT. All reactions were performed at ambient temperature (about 25°C). Each experiment was performed in triplet.

#### (2) *Degradation of TNT adsorbed on sand in presence of Suwannee River humic acid, fulvic acid, and natural organic matter.*

An appropriate amount of Suwannee river (SR) humic acid (HA) was mixed with sand to make 0.1% HA/sand mixture (w/w). Similarly, Suwannee river fulvic acid (FA)

and Suwannee river natural organic matter (NOM) were mixed with sand to make 0.1% FA/sand (w/w), 0.1% NOM/sand (w/w), and 1% NOM/sand (w/w) mixtures. The sand mixtures were spiked with TNT (in acetone), acetone was evaporated, and the sand mixtures were stirred continuously for one to two days to ensure homogeneity. Degradation of TNT on sand/HA, sand/ FA and sand/NOM mixtures followed the procedure described above for clean sand.

### 3.1.3 Analysis

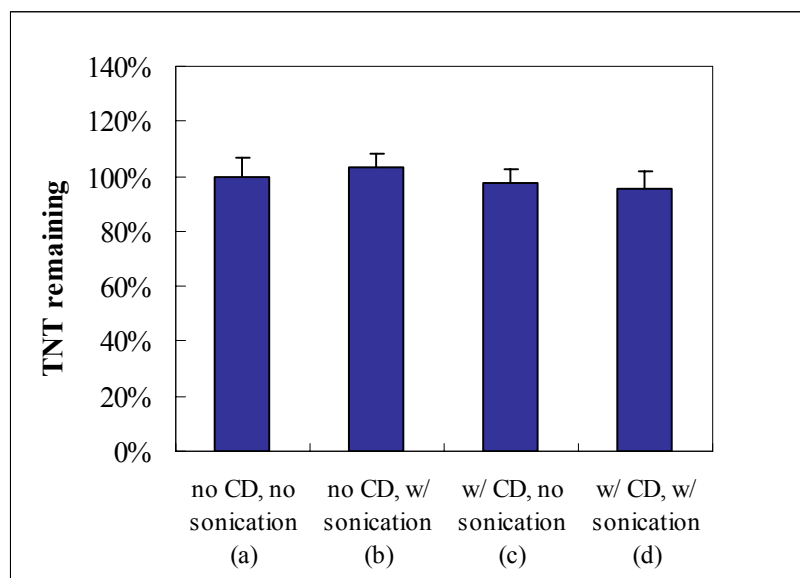
The concentration of TNT in each degradation experiment was quantitated by reverse phase HPLC (Agilent 1100 series, G1322A Degasser, G1311A QuatPump, G1315 DAD). TNT was separated on an Allsphere OSD-2 5 $\mu$  column (Alltech, Length 250 mm, ID 4.6 mm). UV absorbance was measured simultaneously at wavelengths from 200-400 nm using the diode array detector (DAD). The samples were centrifuged at 13,000 rpm for 2 min before injection using a 100  $\mu$ l loop. The following elution gradient was employed: the ratio of Nanopure H<sub>2</sub>O/acetonitrile was 70/30 (v/v) at time zero and changed linearly to 50/50 in 5 min and was maintained at this ratio for the remainder of the separation. The total analysis time was 13 min. The flow rate was set at 1 ml/min for all measurements. The peak of TNT was eluted at about 11 min.

## 3.2 Results and Discussion

Before Fenton degradation started, it was necessary to determine the recovery rate of TNT adsorbed to sand. The basic procedure consisted of adding water to the sand followed by adding an equal amount of methanol. The calculated results show that the

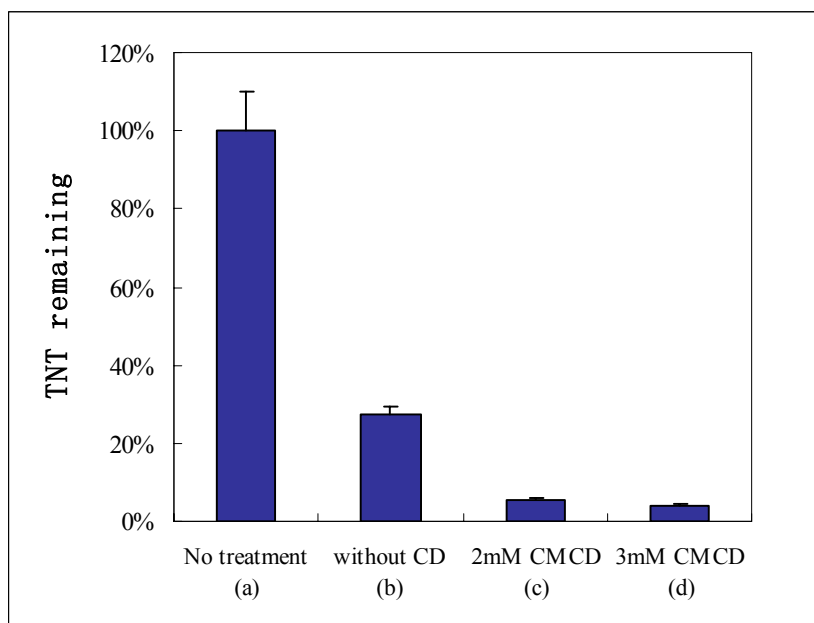
recovery rate was near 100%. CM- $\beta$ -CD was added in water in some experiments, and most experiments included the step of sonication for 30 min. The next step was to determine whether the addition of CM- $\beta$ -CD and sonication would interfere with the extraction process. The test results are shown in Fig. 3.1 **a** is the basic extraction process. TNT contaminated sand was mixed with water and then equal volume of methanol. The recovery rate of TNT was considered as 100%. **b** is almost the same procedure as **a** except that after adding water, the samples were sonicated for 30 min before addition of MeOH. Taking into account the experimental errors, **b** is considered to have the same recovery rate of TNT as **a**. That is to say, the sonication does not degrade TNT. In experiment **c**, water with 6 mM CM- $\beta$ -CD was mixed with sand before adding methanol. CM- $\beta$ -CD will help to increase the apparent water solubility of TNT, but the concern is: will the TNT partitioned into the inner cavity of CM- $\beta$ -CD be extractable after adding MeOH? The result indicated nearly 98% extraction rate in this experiment. The last experiment **d** tested if sonication and addition of 6 mM CM- $\beta$ -CD into the aqueous phase have dual effects on extraction. The average extraction rate was around 96%, which is acceptable.

This set of experiments covered most of situations that will be discussed below. First of all, it is certain that all TNT adsorbed on sand is extractable to liquid phase, in which the amount of undegraded TNT could be quantitated. Secondly, it has been proven that neither sonication nor the presence of CM- $\beta$ -CD has any influence on the extraction efficiency of TNT.



**Figure 3.1** Extraction rates of TNT from contaminated sand ( $450 \text{ mg TNT kg}^{-1}$ ) using equal volumes of water and methanol: (a) 1.00 g sand, 4.00 mL  $\text{H}_2\text{O}$ , 4.00 mL MeOH; (b) 1.00 g sand, 4.00 mL  $\text{H}_2\text{O}$ , 30 min sonication, 4.00 mL MeOH; (c) 1.00 g sand, 4.00 mL  $\text{H}_2\text{O}$ , 6 mM CM- $\beta$ -CD, 4.00 mL MeOH; (d) 1.00 g sand, 4.00 mL  $\text{H}_2\text{O}$ , 6 mM CM- $\beta$ -CD, 30 min sonication, 4.00 mL MeOH.

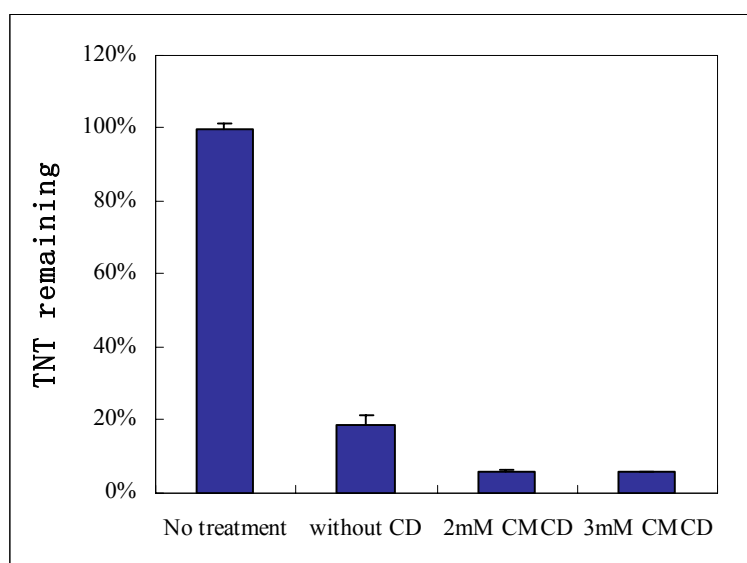
The first part experiment was to degrade TNT adsorbed on clean sand ( $445 \text{ mg TNT kg}^{-1}$ ). Figure 3.2 illustrates the degree of TNT adsorbed on sand degraded by Fenton reagent ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) and CM- $\beta$ -CD modified Fenton reagent. 0.30 g sand was mixed with 4.00 ml pH 3.0 water to make a 1:12 (w/v) sand slurry. The sand slurry was degraded by classic Fenton reaction and CM- $\beta$ -CD modified Fenton reaction.



**Figure 3.2** Degradation of TNT adsorbed on sand under conditions: sand = 0.30 g (445 mg TNT kg<sup>-1</sup>); V<sub>H<sub>2</sub>O</sub> (pH 3.0) = 4.00 mL; C<sub>Fe<sup>2+</sup></sub> = 2.5 mM; C<sub>H<sub>2</sub>O<sub>2</sub></sub> = 7.35 mM; C<sub>CM-β-CD</sub> = (1) 2 mM, (2) 3 mM; V<sub>MeOH</sub> = 4.00 mL. Total reaction time = 10 min. (a) Control. (b) Classic Fenton degradation. (c) CM-β-CD modified Fenton degradation (2 mM). (d) CM-β-CD modified Fenton degradation (3 mM).

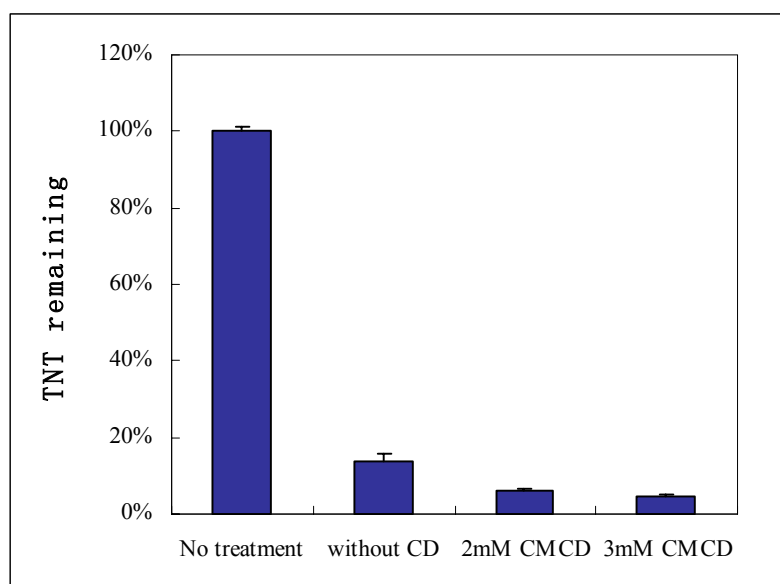
Experiment **a** was the extraction step to recover TNT from sand to organic/aqueous mixed phase. In experiment **b**, after adding H<sub>2</sub>O, the samples were treated with 2.5 mM Fe<sup>2+</sup>/7.35 mM H<sub>2</sub>O<sub>2</sub> for 10 min, then were quenched and extracted with 4.00 mL MeOH. Around 70 % of TNT in the samples was degraded by this method. In experiments **c** and **d**, 2 mM and 3 mM of CM-β-CD were added into the aqueous solutions before adding Fenton reagents. All other conditions in **c** and **d** were kept the same as **b**. Results show that around 90% TNT disappeared in **c** and more than 95 % TNT on average was transformed in **d**.

The  $\text{Fe}^{2+}$ -CM- $\beta$ -CD- $\text{H}_2\text{O}_2$  system works well for TNT in pure sand system. The next step is to find out if it can go further to work in more complex systems. The following solid systems were investigated: (1) sand + 0.1% SR HA; (2) sand + 0.1% SR FA; (3) sand + 0.1% SR NOM; (4) sand + 1% SR NOM. Humic acid (HA), fulvic acid (FA) and natural organic matter (NOM) are ubiquitous in environmental systems. They are prone to bind hydrophobic molecules and sequester them from being contacted with hydroxyl radical in aqueous phase. This will make degradation harder to proceed and waste reagents. The role of CD is to compete with NOMs to form complexes with TNT which can overcome the detrimental effects of HA, FA and other NOM on remediation of TNT.

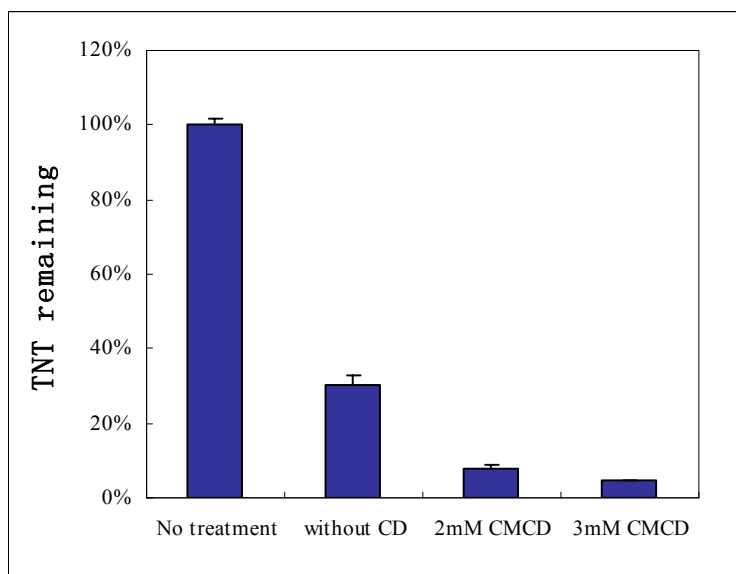


**Figure 3.3** Enhanced remediation of TNT from contaminated sand with 0.1% HA (w/w) additive mixture, condition used: sand = 0.30 g (445 mg TNT  $\text{kg}^{-1}$ );  $V_{\text{H}_2\text{O}}$  (pH 3.0) = 4.00 mL;  $C_{\text{Fe}^{2+}}$  = 5 mM;  $C_{\text{H}_2\text{O}_2}$  = 7.35 mM;  $C_{\text{CM-}\beta\text{-CD}}$  = (1) 2 mM, (2) 3 mM;  $V_{\text{MeOH}}$  = 4.00 mL. Total reaction time = 10 min.

The results show that the addition of CM- $\beta$ -CD has been successfully applied to improve the degradation efficiency of TNT sorbed on sand and HA (0.1 %, w/w) mixture. After 10 min reaction, around 84% of TNT sorbed on 0.1% HA/sand mixture was degraded by classic Fenton reagent, while 96% and 97% of TNT were degraded by CM- $\beta$ -CD (2 mM and 3 mM) modified Fenton reagent respectively. Similar experiments were performed to remediate TNT from 0.1% FA/sand (w/w) and 0.1% NOM /sand (w/w) mixtures. The results are shown in Fig. 3.4 and Fig. 3.5 respectively.



**Figure 3.4** Enhanced remediation of TNT from contaminated sand with 0.1% FA (w/w) additive mixture, condition used: sand = 0.30 g (445 mg TNT kg<sup>-1</sup>); V<sub>H<sub>2</sub>O</sub> (pH 3.0) = 4.00 mL; C<sub>Fe<sup>2+</sup></sub> = 2.5 mM; C<sub>H<sub>2</sub>O<sub>2</sub></sub> = 7.35 mM; C<sub>CM- $\beta$ -CD</sub> = (1) 2 mM, (2) 3 mM; V<sub>MeOH</sub> = 4.00 mL. Total reaction time = 10 min.

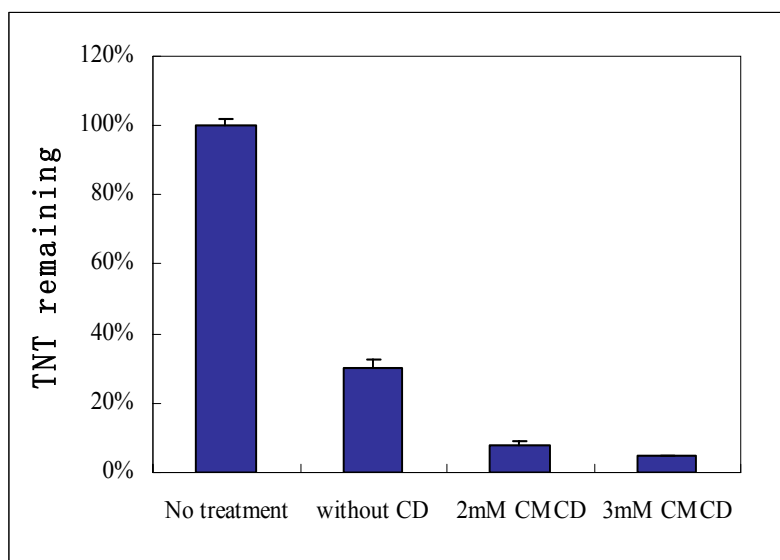


**Figure 3.5** Enhanced remediation of TNT from contaminated sand with 0.1% SR NOM (w/w) additive mixture, condition used: sand = 0.30 g (445 mg TNT kg<sup>-1</sup>): V<sub>H<sub>2</sub>O</sub> (pH 3.0) = 4.00 mL; C<sub>Fe<sup>2+</sup></sub> = 2.5 mM; C<sub>H<sub>2</sub>O<sub>2</sub></sub> = 7.35 mM; C<sub>CM-β-CD</sub> = (1) 2 mM, (2) 3 mM; V<sub>MeOH</sub> = 4.00 mL. Total reaction time = 10 min.

The enhancement of degradation efficiency by cyclodextrin-Fenton system was obvious in both cases. 82% of TNT was degraded by Fenton reagent after 10 min, as compared to around 94% of TNT degraded by both CD modified Fenton systems in the TNT/sand/0.1%FA experiment (Fig. 3.4). In TNT/sand/0.1% NOM (Fig. 3.5), 86% of TNT was degraded by Fenton reagent after 10 min, as compared to 94%-95% of TNT degraded by CD modified Fenton systems.

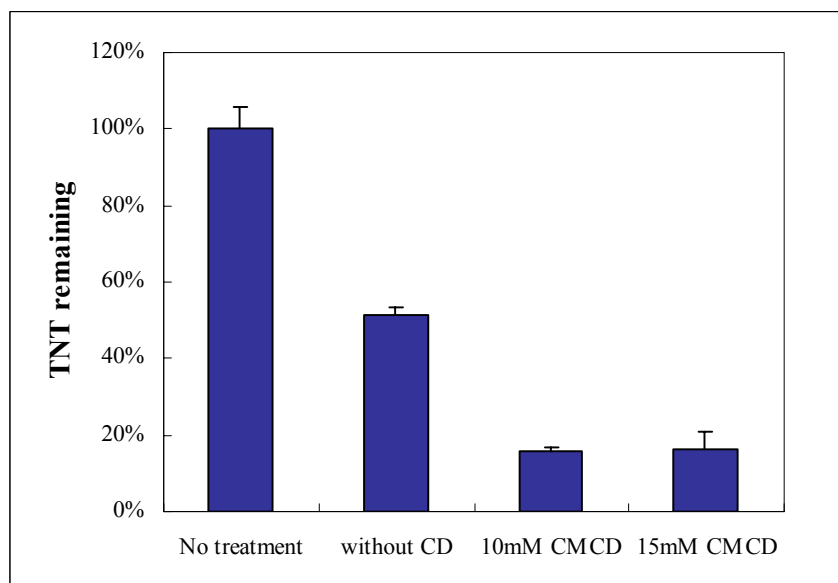
In pervious experiments, the sand mixtures have small portion of interfering additives (0.1% HA, FA and NOM). In experiment shown in Fig. 3.6, remediation TNT from 1% NOM/sand was performed. 70% of TNT was degraded by Fenton reagent after 10 min, as compared to 92%-95% of TNT degraded by CD modified Fenton system.





**Figure 3.6** Enhanced remediation of TNT from contaminated sand with 1% SR NOM additive mixture, condition used: sand = 0.30 g (445 mg TNT kg<sup>-1</sup>); V<sub>H<sub>2</sub>O</sub> (pH 3.0) = 4.00 mL; C<sub>Fe<sup>2+</sup></sub> = 2.5 mM; C<sub>H<sub>2</sub>O<sub>2</sub></sub> = 11.0 mM; C<sub>CM-β-CD</sub> = (1) 2 mM, (2) 3 mM; V<sub>MeOH</sub> = 4.00 mL. Total reaction time = 10 min.

The data presented so far were from remediation conditions with high water: solid ratio (12:1 v/w). For instance, 4.00 mL water: 0.30 g sand. An additional experiment was designed to explore the possibility of Fe<sup>2+</sup>-CD-H<sub>2</sub>O<sub>2</sub> system to degrade TNT with low water: solid ratio (2:1 v/w), 2.00 mL water:1.00 g sand.



**Figure 3.7** Degradation of TNT in sand slurry. Conditions: sand = 1.00 g (445 mg TNT  $\text{kg}^{-1}$ );  $V_{\text{H}_2\text{O}}$  (pH 3.0) = 2.00 mL;  $C_{\text{Fe}^{2+}}$  = 10 mM;  $C_{\text{H}_2\text{O}_2}$  = 117.4 mM;  $C_{\text{CM-}\beta\text{-CD}}$  = (1) 10 mM, (2) 15 mM;  $V_{\text{MeOH}}$  = 2.00 mL. Total reaction time = 10 min. (1) Control. (2) Classic Fenton degradation. (3) CM- $\beta$ -CD modified Fenton degradation (10 mM). (4) CM- $\beta$ -CD modified Fenton degradation (15 mM).

Figure 3.7 shows promising results in removing TNT from low water: solid ratio (2:1 v/w) of sand slurry. While only 49% of TNT degraded by classic Fenton treatment in 10 min reaction, 83%-84% degradation of TNT was achieved by CM- $\beta$ -CD Fenton systems, which was a significant improvement.

## CHAPTER FOUR SUMMARY AND CONCLUSIONS

The combination of cyclodextrin with Fenton reagent did improve the efficiency of Fenton reagent to degrade TNT. Fe(II)-cyclodextrin-hydrogen peroxide systems have been proven to be a fast, safe and cost-effective method to remediate TNT from contaminated water and sand (soil analogy). The advantage of Fe(II)-cyclodextrin-peroxide systems over traditional Fenton reagent is attributed to the ability of cyclodextrin to bind ferrous ion and TNT simultaneously. This explained the rapid removal of TNT by Fe(II)-cyclodextrin-peroxide systems. This method has been successfully applied to degrade TNT from aqueous and solid systems with interfering matrix including humic acid, fulvic acid and natural organic matter.

Fe(II)-cyclodextrin-hydrogen peroxide systems have shown great promise in decontaminating TNT from soil and groundwater.

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## VITA

Bo Wei was born in August 1975 in China. She went to Department of Chemistry, Sichuan University in 1993. After four years of study, she got her bachelor's degree in 1997. Later on, she pursued higher education in US and got admission to the Department of Chemistry, University of New Orleans. She joined Dr. Matthew Tarr's research group in May 2000. She earned her Master's degree in December 2003.