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Biological and Chemical Treatments of High Explosive Contaminated Waters:
Application of a Packed-Bed Reactor, Membrane Bioreactor, and Fenton Oxidation

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Civil Engineering

by

Kyung-Duk Zoh

1998
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1998
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LIST OF SYMBOLS

Symbols

\( J \) the permeation flux

\( \Delta P \) the transmembrane pressure

\( \eta \) the dynamic viscosity of the permeate

\( R_t \) the total resistance

\( R_m \) the intrinsic membrane resistance

\( R_p \) the polarization layer resistance caused by the concentration resistance gradient

\( R_{ef} \) the external fouling resistance formed by a strongly deposited cake layer from physico-chemical interaction of solids with the membrane surface

\( R_{if} \) the internal fouling resistance due to some irreversible adsorption

\( R_t \) the portion of the total resistance dislodged only by water flushing

\( R_{ef} \) the resistance to be removed by manual cleaning of the membrane surface.

\( S \) the surface of the inorganic membrane

\( L^- \) the foulant ligand

\( Y \) the true yields coefficient, kg COD / kg COD removed

\( B_x \) the COD mass loading rate, kg COD removed/kg sludge expressed in COD/ d

\( b \) the decay rate coefficient, d\(^{-1}\).

\( Y_{obs} \) the observed yield coefficient

\( C_G \) the bulk concentration of bacteria

\( C_B \) the “gel” concentration at the membrane surface

\( D \) the diffusion coefficient
$k$ the mass transfer coefficient

$T$ the absolute temperature

$C_{HE}$ the concentration of high explosive (HE) compound

$C_{OH}^-$ the hydroxyl radical concentration

$k_{HE}$ the second order rate constant.

$k_{HE}'$ the pseudo first-order rate constant.

**Abbreviations**

- **RDX** Hexahydro-1,3,5,-trinitro-1,3,5,-triazine
- **HMX** Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
- **TNT** 2,4,6,-trinitrotoluene
- **HE** high explosive
- **PBR** packed-bed reactor
- **MBR** membrane bioreactor
- **SRT** sludge age
- **HRT** hydraulic retention time
- **F/M** food to microorganism ratio
- **MF** microfiltration
- **UF** ultrafiltration
- **RO** reverse osmosis
- **SPE** solid phase extraction
- **LLE** liquid-liquid extraction
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PUBLICATION AND PRESENTATIONS


ABSTRACT OF THE DISSERTATION

Biological and Chemical Treatments of High Explosive Contaminated Waters:
Application of a Packed-Bed reactor, Membrane Bioreactor, and Fenton Oxidation

by

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Doctor of Philosophy in Civil Engineering
University of California, Los Angeles, 1998
Professor Michael K. Stenstrom, Chair

In the first part, the application of biological denitrification for treating hydrolysis byproducts of high explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), consisting of acetate, formate, formaldehyde and nitrite were treated in a denitrifying packed-bed upflow reactor. Over 90% removal of the organic compounds and nitrite were observed in a reactor with a three-hour retention time. The stoichiometry of the experimental results closely matched the predicted stoichiometry. The volumetric removal rate was as high as 170 mg/L of NO$_2$-N per day with existing carbon sources. This culture was also capable of biodegrading RDX and HMX when using nitrate as an electron acceptor.
In the second part, a membrane bioreactor (MBR) system, consisting of a bioreactor coupled to a ceramic crossflow ultrafiltration (UF) module, was evaluated. This system was used to treat a synthetic wastewater containing same hydrolysates of high explosive RDX. The bench-scale anoxic MBR system effectively treated these wastewaters. The permeation flux was between 0.15 and 2.0 m$^3$/m$^2$/day and was restored to original flux after backwashing. Heterotrophic bacteria counts method showed that the membrane was very efficient in retaining biomass, which had resulted in the production of a clear final effluent. The reactor was operated over a range of transmembrane pressure, temperature, suspended solids concentration, and organic loading to evaluate the influence on the permeation flux and optimize its treatment.

In the third part, the feasibility of the Fenton oxidation of RDX and HMX was investigated as another option to treat RDX and HMX in acidic environment. It was found that the oxidation of RDX and HMX by Fenton’s reagent is rapid at between 20 and 50 °C at pH 3. All experimental data could be fit to a pseudo first-order rate equation. The temperature dependence follows the Arrhenius correlation. The activation energy using Arrhenius equation was determined to be 51.3 (RDX) and 48.6 (HMX) kJmol$^{-1}$, respectively. Experimental results show that there exists an optimal pH at 3 for the Fenton treatment process. The reaction rate coefficient was also strongly dependent on both H$_2$O$_2$ and Fe$^{2+}$ concentrations. Finally, the byproducts of the Fenton oxidation of RDX and HMX were discussed.
Munitions and military wastes have been a problem due to their threat to humans and the environment. Since the end of the World War II, removal of such hazardous wastes has been a more important issue due to various demilitarizing efforts. Hexahydro-1,3,5-Trinito-1,3,5-trazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are two common high explosive chemicals. Large amounts of RDX and HMX need to be disposed every year in the United States. RDX has toxic effects on humans, especially on the central nervous system. It is also a possible carcinogen. Therefore it is essential to find a safe and efficient way to dispose RDX.

Heilmann et al. (1996) combined the techniques of activated carbon adsorption and alkaline hydrolysis. The RDX contaminated wastewater is first adsorbed onto
granular activated carbon to concentrate RDX waste on carbon and to reduce the
treatment volume. Next, the laden carbon is treated with alkaline hydrolysis and the
regenerated carbon is then able to treat another charge of RDX contaminated water. He
also found that the alkaline hydrolysis of RDX produces 1.6 M NO$_2^-$, 1.5 M HCOO$^-$, 0.1
M CH$_3$COO$^-$, 1.1M HCHO, 0.9 M NH$_3$, 1.1 M N$_2$O, and 0.34 M N$_2$ per mole of RDX
hydrolyzed. HMX tends to be more resistant to alkaline hydrolysis than RDX, but the
byproducts are similar to that of RDX.

Activated carbon adsorption followed by alkaline hydrolysis appears to be the
efficient and safe way to decompose RDX/HMX containing wastewaters; however, the
hydrolysates can contain high concentrations of acetate, formaldehyde, formate,
ammonia, and nitrite. The hydrolysates (nitrite and organic byproducts) can not be
directly released to the environment, furthermore, some of the hydrolysates may be
hazardous to the environment.

Since these hydrolysates contain high concentrations of organic carbon and
oxidized nitrogen (NO$_2$), biological denitrification is a logical choice for the treatment
of these byproducts before release in the environment. Therefore, the first part of this
study is devoted to elucidation of biological denitrification of high explosives
hydrolysates using a packed-bed reactor. This work describes the results of a two-year
investigation to demonstrate effective hydrolysate treatment. The process was
developed in a step-wise fashion, by gradually increasing the number of organic
compounds and the mass of electron acceptor. Formate and acetate were first studied,
and formaldehyde was added after obtaining stable conditions.
The second part of the study involves membrane bioreactor (MBR) application. Nitrous oxides (NO$_3^-$ and NO$_2^-$) removal via biological packed- or fluidized-bed reactors may require post-treatment processes, such as filtration, aeration, and disinfection, to remove microorganism contaminants because the reactor effluent contains the excess biomass in the form of suspended solids. Membrane bioreactor (MBR) technology offers several advantages over conventional processes, mainly because a membrane takes place of conventional separation devices (Manem and Sanderson, 1996).

Conventional denitrification processes are usually addressed by a three-step procedure using sand filtration, followed by activated carbon filtration and, finally, by chlorination. As an alternative to these procedures, membrane processes are becoming increasingly popular for removal of turbidity and microbial matter. One of the principal advantages of the MBR is its ability to retain micron size particles. This allows the process to function as a biological process as well as a filtration process. Since this system is capable of simultaneously biologically treating and disinfecting the effluent. Another element to MBR technology is its ability to absorb variations and fluctuations in the applied and organic load to the system.

In this study, the operational performance of a bench-scale MBR system, consisting of a biological denitrification reactor coupled to a ceramic ultrafiltration membrane module, was investigated for treating hydrolysates of RDX. The results are compared with packed-bed denitrification results. In addition, the role of chemical and physical cleaning with backwashing to remove fouling of the membrane was studied.
The third part of this study presents advanced oxidation of RDX and HMX as an alternative for treating RDX and HMX in an acidic environment. Advanced oxidation processes are commonly used for remediating water contaminated with organic compounds (Sedlack and Andren, 1991; Venkatadri and Peters, 1993). The Fenton reaction is the one of the oldest and most powerful oxidative treatment available. This reaction has been used to treat wastewater containing recalcitrant organic pollutants. Fenton’s reagent is an also inexpensive and powerful oxidation for oxidizing a wide variety of organics (Sedlak and Andren, 1991; Watts et al., 1990). In this study, the chemical kinetics of Fenton oxidation of RDX and HMX under acidic aqueous conditions was investigated. Various factors that are important to optimize the oxidation were studied, and the byproducts and mineralization of RDX and HMX also are discussed.

1.2 Dissertation Organization

This dissertation is divided into five chapters. Chapter 1 mainly describes an introduction and literature review. Chapter 2 presents biological denitrification of RDX hydrolysates using a packed-bed reactor. The alkaline hydrolysis byproducts of RDX containing high concentrations of acetate, formate, formaldehyde, nitrite, were treated. Portions of Chapter 2 have been accepted for publication in Water Science and Technology, and are also accepted for publication in Water Environment Research. Chapter 3 presents the membrane bioreactor application for treating hydrolysates of RDX and the microorganisms. Various conditions were investigated to optimize the
MBR. Comparisons of MBR with packed-bed reactor results are also made. This part will be submitted for review and publication in the *Water Environment Federation*.

Fenton oxidation of RDX and HMX is discussed in Chapter 4. Reaction kinetics and byproducts are presented in this chapter. Part of the materials will be submitted for review and possible publication in the *Environmental Science and Technology*. Lastly, Chapter 5 presents the conclusions and the highlights the important results found from RDX and HMX treatments.

### 1.3 Background and Related Research

#### 1.3.1 High Explosives RDX and HMX

Explosives have been manufactured in the United States and other countries for many decades. Among the high explosives that are manufactured, RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (Octahydro-1,3,5,7-Tetranitro-1,3,5,7-tetrazocine) and TNT(2,4,6-trinitrotoluene) are the most common. During World War II, RDX production in the United States and Germany averaged from 15,200,000 to 7,100,000 kg per month, respectively (Urbanski, 1964).

The US EPA (McLellan *et al.*, 1988) classifies RDX as a Possible Human Carcinogen (Class C), and act a lifetime health advisory for exposure in drinking water to 0.002 mg/L by EPA. HMX is found together with RDX because it is an unwanted byproduct in contaminant. HMX is a Class D carcinogen, and its primary toxic effect is cardiovascular depression, and it has adverse effects on mammals’ central nervous system.
system (McLellan et al., 1988). RDX and HMX are more energetic than TNT, and they are used in both conventional and nuclear weapons. The molecular structure formula of RDX and HMX are shown in Figure 1-1.

The recent dismantling activity is producing large amounts of explosives that require disposal. Currently the U.S. Department of Energy (DOE) reports that 45,000 kg of high explosives waste is disposed every year at Pantex Plant, Texas (Heilmann et al., 1996). Because of the Intermediate Range Nuclear Forces need to be treated every year. In addition, the contaminated wastewater produced by the production, packing and washing of conventional explosives need to be treated as well.

Recent increases in waste production due to the end of the cold war have increased disposal and treatment problems. In the past, RDX containing wastewater was disposed in lagoons. This practice often resulted in the contamination of groundwater via the contamination of explosives through the soil. Open burring and open detonation (OBOD) are time-honored methods for disposal of explosives. However, the combustion of RDX leads to various unwanted toxic products such as cyanic acid (HCN), and OBOD has been or is being phased-out at most location. Therefore, environmental transformation of RDX and methods of remediation have been extensively explored.

1.3.2 Treatment of High Explosives Compounds

1.3.2.1 Biological Methods
Figure 1-1. The Formula of RDX and HMX
There are three possible methods for treating high explosives: aerobic, anaerobic, and anoxic. Aerobic treatment does not degrade RDX (McCormick et al., 1981; Ro and Stenstrom, 1991). The degradation function of microorganisms is probably inhibited when oxygen is present.

However, RDX can be degraded under anoxic and anaerobic conditions. McCormick et al. (1981) reported that RDX could be degraded or transformed under anaerobic conditions. Anaerobic RDX transformation process is generally considered as a co-metabolic process, and require an organic carbon source. The fact that no RDX was transformed anaerobically in Holston River water in the absence of a yeast extracts suggests that the transformation of RDX by microorganism is a cometabolic process (Spanggord et al., 1980). McCormick et al. (1984) also stated that the transformation efficiency increases when the culture is supplied with a nutrient broth high in organic substrate. They concluded that the activity of biotransformation is directly proportional to the concentration of the available carbon sources in the medium.

Hesselmann (1992) found that anoxic transformation of RDX was fortuitous cometabolism. He applied an “indirect-off line bioregeneration” system to treat the water contaminated with low concentration of RDX. The contaminated water is first concentrated by running through series of activated carbon. The RDX adsorbed on the activated carbon is then desorbed by one of the polar organic solvents. He used several different organic substrates under fermentative (anaerobic), sulfate (anoxic), and nitrate (anoxic) reducing conditions to find the best solvent for desorption, and co-substrate. He
found that denitrifying cultures using nitrate as electron acceptor and ethanol or acetic acid as a co-substrate was best for RDX biotransformation.

Wilkie (1996) compared the degradation efficiencies of several different organic co-substrates that include ethanol, acetic acid, propionic acid, formic acid, ethyl acetate, acetone and methanol in anoxic system. She found that ethanol and acetic acid give the highest degradation efficiency and the co-substrates also support the greater cell growth. In addition, ethanol is an effective desorption solvent; that is, ethanol can be bifunctionally in the "indirect-off-line bioregeneration".

1.3.2.2 Physico-Chemical Methods

Activated carbon is often used to treat process waters at munitions plants as well as to remediate explosives contaminated groundwaters (Wujick et al., 1992; Sisk, 1993). However the disposal of the RDX-laden carbon creates another problem. Regenerating the column is difficult and poses safety problem (Wujick et al., 1992). Hydrolysis at high temperature and pH can destroy explosives, and has been known for many years (Jones, 1953; Hoffsommer et al., 1977). More recently alkaline hydrolysis has been shown to convert RDX to smaller, less harmful compounds such as acetate, formate, and nitrate (Spontarelli et al., 1993). However, cost of increasing the pH and thus neutralizing large quantities of wastewater is problematic. Therefore, Heilmann et al. (1996) suggested a combination of activated carbon adsorption followed by alkaline hydrolysis for treating the explosives and regenerating the column.
1.3.2.3 Alkaline Hydrolysis of RDX/HMX

The RDX contaminated wastewater is first adsorbed onto granular activated carbon to concentrate the RDX and reduce the volume of water to be treated. Next, the laden carbon is treated with alkaline hydrolysis and the regenerated carbon is then able to treat another charge of RDX contaminated water. Figure 2-1 shows the scheme for the treatment of high explosives contaminated water using activated carbon adsorption and regeneration of laden activated carbon by alkaline hydrolysis. He also found that the alkaline hydrolysis of RDX produces 1.6 M NO$_2^-$, 1.5 M HCOO$^-$, 0.1 M CH$_3$COO$^-$, 1.1M HCHO, 0.9 M NH$_3$, 1.1 M N$_2$O, and 0.34 M N$_2$ per mole of RDX hydrolyzed. HMX tends to be more resistant to alkaline hydrolysis than RDX, but the byproducts are similar to that of RDX (Heilmann et al., 1996).

1.3.2.4 Hydrolysis Byproducts (Hydrolysates) of RDX

Activated carbon adsorption followed by alkaline hydrolysis appears to be an efficient and safe way to decompose RDX/HMX containing wastewaters; however, the hydrolysates can contain high concentrations of acetate, formaldehyde, formate, ammonia, and nitrite. The hydrolysates can not be directly released to the environment, and require further treatment.

Exposure to hydrolysate products can lead health effects. Chronic inhalation of formaldehyde induces irritation and nasal cancers. It is carcinogenic in rats when inhaled continuously at high doses (> 2 ppm) for a lifetime (Albert et al., 1982; Turoski, 1984). Formate is also reported to cause albuminuria, and hematuria, and acetic acid
ingestion may cause severe corrosion of mouth with vomiting, hematemesis, diarrhea, circulatory collapse, uremia (Argeda and Zoeller, 1993). When diluted and released to natural waters or wastewaters, the compounds degrade and exert as an oxygen demand.

Nitrite is a nitrogenous contaminant along with ammonia, nitrates, and pesticides. The presence of nitrogen compounds, as inorganic nutrients, in the aquatic environment accelerates eutrophication and leads to severe water-quality problems due to the resulting increase of algae concentration and concomitant oxygen depletion in natural water bodies.

For these reasons, hydrolysates require further treatment before being released to the environment. Since the hydrolysates are composed of nitrite, and low molecular weight organic compounds, they can be degraded with denitrifying bacteria. The biological denitrification can convert the hydrolysates of RDX/HMX to harmless endproducts, such as nitrogen and carbon dioxide. The biodegradation process can be accomplished in a mixed culture of denitrifying bacteria with nitrite as the electron acceptor and formaldehyde, formate, acetate as substrates.

1.3.3 Biological Denitrification

1.3.3.1 Nitrogen Oxides (NO$_3^-$, NO$_2^-$) Contamination

Nitrogenous and organic contaminants such as ammonia, nitrates, nitrite, and pesticides from human activities are often found in water sources. The widespread agricultural use of nitrates in fertilizers and pesticides in crops leads to high concentrations of these substances in waters (Spalding and Exner, 1993).
A recent study of nitrate (NO$_3^-$) risk assessment concluded that the maximum contaminant level (MCL) in groundwater supplies should be lower than 10 mg/L NO$_3^-N$ (Lee et al., 1995). Nitrogen oxide contamination, especially nitrate (NO$_3^-$) contamination, in water and groundwater resources is becoming a problem in the United States and in Europe and also in Asia. In many areas the nitrate (NO$_3^-$) concentration in groundwater exceeds the limit of 10.0 mg/L as NO$_3^-N$ (nitrate nitrogen) set by the U.S. Environmental Protection Agency (EPA) (Sayre, 1988), or 50 mg/L as NO$_3^-$ (nitrate), which is equal to 11.3 mg/L NO$_3^-N$, set by the World Health Organization (World Health Organization, 1984) and the European Economic Community.

Nitrite (NO$_2^-$) formed under favorable conditions (low redox potential), either in the environment, or in the gastrointestinal tract, is also the toxic compound. Nitrite (NO$_2^-$) can cause a disease called methemoglobinemia that affects infants. At a pH lower than 6.5, nitrite can also react with secondary amines to form N-nitroso compounds, which are highly carcinogenic (Hiscock et al., 1991; Kamath et al., 1991; Schuval and Gruner, 1996). Consequently, the guidelines for nitrite (NO$_2^-$) are much more severe than for nitrates (NO$_3^-$). The nitrite maximum contaminated levels (MCLs) in drinking water are 0.03 mg/L NO$_2^-N$ in the European Union (EU) and 1 mg/L NO$_2^-N$ in the United States (Schuval and Gruner, 1996).

Furthermore, the presence of nitrogen and phosphorus compounds, as inorganic nutrients, in the aquatic environment accelerates eutrophication and leads to severe water-quality problems due to the resulting increase of algae concentration and the concomitant oxygen depletion in natural water bodies.
1.3.3.2 Technologies for Removing Nitrous Oxides

There are a number of biological and physico-chemical processes for removing nitrogenous compounds, especially nitrate, from water and wastewaters. Conventional physico-chemical technologies for removing nitrogenous oxides from contaminated waters include electrodialysis, distillation, reverse osmosis (RO), and ion exchange.

Distillation, electrodialysis, and RO processes uniformly remove dissolved solids but do not selectively target nitrate. The cost of indiscriminate dissolved solids removal, added to the associated energy and brine disposal costs, makes these treatments uneconomic for many nitrate-contaminated waters. Ion exchange technology, although more nitrate-selective than distillation, electrodialysis, or RO, extracts constituents other than nitrate from the water. For example, ion exchange typically removes sulfate ions, which are often present in groundwater at higher concentrations than nitrate. However, ion exchange may be associated with public health implications because of the increased concentration of the exchanged ion in the treated water, e.g. chloride. Furthermore, a significant portion of the overall treatment costs for ion exchange processes is associated with disposal of the spent regenerate brines.

To contrast with physico-chemical processes, which concentrate nitrates from the contaminated water supply to a concentrated brine solution, biological process can destroy nitrate and nitrite and produce nitrogen gas. Biological denitrification process represents a promising alternative to physico-chemical techniques. This process has been used for years in wastewater treatment. This process is highly selective for nitrate
removal. The efficiency of the process is very high and can reach nearly 100 %, which is not matched by any other methods available for nitrate reduction.

1.3.3.3 Microbiology for Biological Denitrification

All microorganisms require nitrogen for protein synthesis and growth. Many may use either ammonium-N or nitrate-N, although ammonium is preferred since it is in the form most easily used for protein synthesis. The reduction of nitrate to ammonium to synthesize protein is called *assimilatory nitrate reduction*. The microbial reduction of nitrate to gaseous nitrogen products is termed *dissimilatory denitrification* or *nitrate respiration*. Throughout this thesis, the term denitrification refers to *dissimilatory denitrification*, unless stated differently.

Many bacteria are capable of growing anaerobically by reducing ionic nitrogenous oxides to gaseous products (Payne, 1973; Gayle *et al.*, 1989; and Knowles, 1982). Reduction of nitrate to nitrogen gas proceeds in four steps according to Equation 1. The last three compounds are gaseous products that can be released to the atmosphere. Each step is catalyzed by a different enzyme system. Nitrates serve as terminal electron acceptors in the absence of oxygen, results in generation of ATP (Koike and Hattori, 1975).

\[
\begin{align*}
\text{NO}_3^- & \rightarrow \text{NO}_2^- \rightarrow (\text{NO}) \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2
\end{align*}
\]  

(1)

Denitrification is considered to be an anoxic process, occurring when nitrate or nitrite is used instead of oxygen as the terminal electron acceptor, and requires an organic or inorganic substrate for energy (electron donor) and cell synthesis. A wide variety of solid, liquid and gaseous substrates have been reported to be used by denitrifying organisms. The substrates include pure compounds (methanol, ethanol, and acetic acid), raw domestic water, waters from food industries (brewery waters, molasses), and sludge. Other less-studied organic substrates, preferably used in laboratory denitrification systems, include glucose, methane, and amino acids.

When electrons are transferred from the donor to the acceptor, the organism gains energy which can be applied for the synthesis of a new cell mass and the maintenance of the existing cell mass. This denitrification can only occur under anaerobic or anoxic conditions. Autotrophic bacteria oxidize inorganic compounds and heterotrophic species oxidize organic material in denitrification. Generally, autotrophic bacteria grow slowly and denitrification rates are lower (Rogalla et al., 1993)

1.3.3.4 **Stoichiometry for Denitrification**

During denitrification, nitrate (an electron acceptor) is reduced to gaseous nitrogen in accordance with the following general equation:
Reduced organic carbon or reduced sulfur compounds are oxidized, which can be generally represented as

\[ 0.2 \text{NO}_3^- + 1.2 \text{H}^+ + \text{e}^- \rightarrow 0.1 \text{N}_2 + 0.6 \text{H}_2\text{O} \]  \hspace{1cm} (2)

These equations do not include consumption of substrates for cell mass synthesis and maintenance.

Denitrification is classically considered to be a heterotrophic process by microorganisms that require a reduced organic substrate for respiration and cell synthesis, while autotrophic process require molecular hydrogen or reduced sulfur compounds as an electron donor. Heterotrophic denitrifying bacteria can use a wide variety of organic compounds, such as methanol, ethanol, glucose, and acetate. However, most of the published studies use methanol, ethanol, and acetic acid because they are relatively inexpensive and have low solids yields (McCarty et al., 1969). If methanol is used as a carbon source and nitrate is an electron acceptor, the stoichiometric relationships describing bacterial energy equations are written as follows

\[ 0.25 \text{CH}_2\text{O} + 0.25 \text{H}_2\text{O} \rightarrow 0.25 \text{CO}_2 + \text{H}^+ + \text{e}^- \]  \hspace{1cm} (3)

\[ \text{Fe}_2\text{S} + 4 \text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 0.5\text{Fe}^{2+} + 8 \text{H}^+ + \text{e}^- \]  \hspace{1cm} (4)
Overall energy reaction is:

\[
6 \text{NO}_2^- + 2 \text{CH}_3\text{OH} \rightarrow 6 \text{NO}_2^- + 2 \text{CO}_2 + 4 \text{H}_2\text{O} \quad (5)
\]

\[
6 \text{NO}_2^- + 6 \text{CH}_3\text{OH} \rightarrow 3 \text{N}_2 + 3 \text{CO}_2 + 3 \text{H}_2\text{O} + \text{OH}^- \quad (6)
\]

These equations show that the stoichiometric relationship between carbon sources required for nitrite reduction, but additional carbon is required for deoxygenation and cell synthesis. If methanol is used as the carbon source, an additional 25 to 30% is needed for deoxygenation and cell synthesis according to following equation (Metcalf and Eddy, 1992):

\[
\text{O}_2 + 0.93 \text{CH}_3\text{OH} + 0.056 \text{NO}_3^- + 0.056 \text{H}^+ \rightarrow
\]

\[
0.056 \text{C}_5\text{H}_7\text{NO}_2 + 0.65 \text{CO}_2 + 1.69 \text{H}_2\text{O} \quad (8)
\]

\[
14 \text{NO}_3^- + 3 \text{CH}_3\text{OH} + 4 \text{H}_2\text{CO}_3 \rightarrow 3 \text{C}_5\text{H}_7\text{NO}_2 + 20 \text{H}_2\text{O} + 3 \text{HCO}_3^- \quad (9)
\]

In practice, 25 to 30% of the methanol required is used for bacterial cell synthesis. If residual dissolved oxygen is present, the methanol requirement is correspondingly higher.
Denitrification can also be accomplished by autotrophic bacteria, which can use hydrogen or various reduced-sulfur compounds as energy sources. Under autotrophic growth conditions no organic carbon source is required. Carbon dioxide or bicarbonate is used as a carbon source for cell synthesis. *Paracoccus denitrificans* and *Thiobacillus denitrificans* can denitrify using hydrogen and reduced-sulfur compounds, respectively. Both can also grow heterotrophically if an organic carbon source is present (Knowles, 1982). The following stoichiometric relationships for hydrogen and sulfur have been reported:

**Hydrogen (Kurt et al., 1987)**

\[
2 \text{NO}_3^- + 5 \text{H}_2 \rightarrow \text{N}_2 + 4 \text{H}_2\text{O} + 2 \text{OH}^- \quad (10)
\]

**Thiosulfate (Claus and Kutzner, 1985)**

\[
5 \text{S}_2\text{O}_3^{2-} + 8 \text{NO}_3^- + \text{H}_2\text{O} \rightarrow 4 \text{N}_2 + 10 \text{SO}_4^{2-} + 2 \text{H}^+ \quad (11)
\]

**Sulfide (Barrenstein et al., 1986)**

\[
5 \text{S}^{2-} + 8 \text{NO}_3^- + 8 \text{H}^+ \rightarrow 5 \text{SO}_4^{2-} + 4 \text{N}_2 + 4 \text{H}_2\text{O} \quad (12)
\]

**1.3.3.5 Denitrifying Bacteria**
Most denitrifying bacteria are able to use nitrogen oxides as electron acceptors in place of oxygen, with the evolution of major gaseous products. Denitrifying bacteria are biochemically and taxonomically very diverse. Most are heterotrophs and are able to utilize a wide range of carbon compounds (sugars, organic acids, and amino acids) as sources of electrons.

The most common denitrifying bacteria genus is *Pseudomonas*, which is frequently isolated from soil and aquatic sediments (Gamble et al., 1977; Heitzer and Ottow, 1976). It may be the most active denitrifying genes in the natural environment. Other important groups are the *Alcaligenes* and *Flavobacterium*. A typical autotrophic denitrifying bacterium is *Thiobacillus denitrificans*.

Other bacterial genera that are known to contain denitrifying species include (Yull-Rhee and Fuhs 1978; Payne 1976) *Achromobacter*, *Aerobacter*, *Alicaligenes*, *Bacillus*, *Brevibacterium*, *Chromobacter*, *Corynebacterium*, *Halobacterium*, *Lactobaciilus*, *Methanomonas*, *Micrococcus*, *Moraxella*, *Paracoccus*, *Propionibacterium*, *Proteus*, *Pseudomonas*, *Spirillum*, *Thiobacillus*, and *Xanthomonas*.

1.3.3.6 Factor Controlling denitrification

The factors affecting induction and repression of denitrifying enzymes are not universal because denitrifying bacteria as a group are genetically diverse and metabolically versatile. The influence of oxygen concentration, pH, temperature, electron donor, and nitrate and intermediate concentrations on denitrification performance of some bacterial species has been investigated.
Oxygen, which competes with nitrates as an electron acceptor in the energy metabolism of cells, is an important inhibitor (Hiscock et al., 1991). It is reported that nitrate reduction is not observed at oxygen concentration above 0.2 mg O₂/L (Hiscock et al., 1991), and it is generally assumed that the nitrogen oxide reductases are repressed by oxygen. Thus, the gradual depletion of oxygen or provision of microaerophilic (semi-anaerobic) conditions appears to favor denitrification.

Second, the availability of electrons in organic carbon compounds is one of the most important factors controlling the activity of the heterotrophs (Knowles, 1982). The availability of nutrients is also an important requirement in sustaining biological growth.

Denitrification is also positively related to pH with an optimum in the range of 7.0 - 8.0. Denitrification may occur in wastes up to pH 11. At low pH values, nitrogen oxide reductase, especially that which reduces N₂O, are progressively inhibited so that the overall rate of denitrification decreases (Knowles, 1982).

Temperature is another important controlling factor influencing the usefulness of denitrification for nitrate removal. At a low temperature, denitrification decreases markedly, but is measurable between 0 and 5 °C. Generally, doubling denitrification rate is possible with every 10 °C increase in temperature (Gauntlett and Craft, 1979). The kinetic response of biological denitrification to temperature can be expressed by a modified Arrhenius formula for substrate utilization rate constants (Oleszkiewicz and Berquist, 1988).

\[ SA = SA_{20} \times 10^{k(T-293)} \]  \hspace{1cm} (13)

20
where $SA \ (kg \ N-NO_3^-/kg \ MLSS / \ day)$ is the specific denitrification activity at the temperature $T \ (K)$, and $k \ (K^{-1})$ may be regarded as a temperature constant for temperature ranges used for bacterial growth. The $k$ value can be determined through a logarithmic regression after measuring specific activity at various temperatures. Lewandoski (1982) measured $k$ value as $0.029 \ K^{-1}$ using various carbon sources. Delanghe et al. (1994) measured $k$ equal to $0.028 \ K^{-1}$ in a membrane bioreactor system.

1.3.3.7 Advantages and Disadvantages of Biological Denitrification

The advantage of biological denitrification processes is that nitrates are selectively and completely removed in the form of nitrogen gas, and the only waste involved in the process consists of biological sludge. Energy costs are also lower than for processes such as reverse osmosis (RO), which requires high operating pressures and additional treatment for brine disposal.

However, a major difficulty in the biological wastewater treatment process is the retention of a sufficient quantity of active biomass in the reactor. The bacteria in anaerobic systems have a slower net growth rate than those in aerobic systems, thus making anaerobic systems requiring longer minimum solids retention time (SRT). Operating at less than the minimum SRT results in microorganism being washed out of the system faster than they can grow. The loading rates in an anaerobic wastewater treatment system are mostly dictated by biomass retention in the reactor. High biomass retention generally improves reactor performance leading to better gas yields and better
quality effluent, and vice versa. Poor biomass retention must be compensated by large hydraulic retention time (HRT), which increases cost. These problems can be overcome if the biomass in the reactor is retained longer than the wastewater undergoing digestion, thus increasing bacterial populations in the reactor. Great retention efficiency creates high bacteria populations and high rates of digestion in spite of very low growth rates (Fakhru’l-Razi, 1994).

The nitrate removal via biological packed- or fluidized-bed reactors is also uneconomic especially for drinking water treatment as a result of the costly post-treatment processes, such as filtration, aeration, and disinfection, that are required to remove process contaminants. Because, with packed- or fluidized-bed reactors, the water to be treated passes directly over the denitrifying bacteria. Bacterial cells, soluble microbial products such as endotoxins, and reactor-bed materials can contaminate the treated water and must be removed in the downstream.

Another important disadvantage of biological denitrification is the requirement of a carbon (C) source. In many cases the carbon source is not naturally present, and must be added. The carbon dose must be carefully controlled to avoid any release of nitrogenous compounds (too little carbon) or an increase in oxygen demand (too much carbon). Any remaining carbon must be removed by a downstream treatment process (Bouwer and Crowe, 1988; Dahab and Lee, 1988). Instead of heterotrophic bacteria, autotrophic bacteria can be used to avoid organic carbon energy source addition; however lower rates of denitrification result (Rogalla et al., 1993).
1.3.4 Membrane Bioreactor (MBR)

In drinking water applications, removal of microorganisms is important because treated water must be disinfected before distribution. A membrane bioreactor (MBR) may be a promising alternative to conventional practices. MBR technology offers several advantages over conventional processes, mainly because a membrane takes place of conventional separation devices. Conventional denitrification processes are usually addressed by a three-step procedure involving sand filtration, followed by activated carbon filtration and disinfection. The main advantage of the MBR is its ability to retain cells, resulting in improved effluent. In effect, the reactor can simultaneously denitrify and disinfect. Another element to MBR technology is its ability to absorb variations and fluctuations in the applied and organic load to the system. The UF and MF membranes used in the MBR allows greater biomass concentrations and, therefore, greater loads than traditional clarified activated sludge process based on gravity separation. Consequently, the systems can be very compact. The membrane can also retain soluble material with a high molecular weight, increasing its retention time and, therefore, increasing the opportunity for its biodegradation in the bioreactor.

The efficiency of biological processed depends on two main factors: the biomass concentration in the reactor and the specific conversion rate of the microorganisms. Efforts to improve biological processes over past hundred years have generally increased the concentration of microorganisms in the bioreactor, either by separating the solids and liquids and then recirculating the biomass (activated sludge) or by developing fixed
culture reactors in which the microorganisms are fixed on a support. This support may be static (packed- or fixed-bed) or mobile (fluidized-bed).

Smith et al. (1969) reports the first combination of membranes with biological wastewater treatment. An ultrafiltration membrane was used for the separation of activated sludge from the final effluent with recycle of biomass to the aeration tank. This application is an attractive technique in biological treatment and created a new concept: the membrane bioreactor (MBR). The concept is popularized because of the recent development of a new generation of more productive and less expensive ultra-(UF) and microfiltration (MF) membranes. These new technologies offer several advantages over conventional processes used to date; these include reliability, compactness and, excellent treated water quality. The resulting high-quality and well disinfected effluent means that MBR processes can be used for many purposes—e.g. drinking water, industrial and municipal wastewater treatment and reuse, recycling in buildings, and landfill leachate treatment.

Membrane bioreactor processes are well suited to applications that require small land area footprint. Application of membrane bioreactor technology makes it possible to recuperate valuable components from effluent streams, reuse contaminated process water, and provide the means for the application of pollutant specific microbial populations. Though commercial membrane separation bioreactors exist, the durability and long-term integrity of the process needs to be improved. Research is needed to understand the energy requirements to sustain biological activity and ensure effective and continued membrane performance. Methods to increase and sustain high permeate
Figure 1-2. The general operation of MBR.
fluxes, maintain biomass viability, and reduce membrane fouling and salt accumulation in the bioreactor are needed. Additionally, minimizing process shutdown for membrane cleaning and replacement, and the cost of membrane material, are necessary to make this technology more attractive to industry.

1.3.4.1 MBR Description

A Membrane bioreactor can be defined as the combination of two basic processes—biological degradation and membrane separation—into a single process where suspended solids and microorganisms responsible for biodegradation are separated from the treated water by a membrane filtration unit (Lazarova and Manem, 1994). The entire biomass is confined within the system, providing absolute control of the cell residence time (SRT), and the disinfection of the effluent.

The general operation of the MBR is illustrated in Figure 1-2. The influent enters the bioreactor where it is brought into contact with the biomass. The mixture is pumped from the bioreactor through the membrane. The permeate is discharged from the system and the biomass is returned to the bioreactor. Excess biomass is pumped from the reactor to maintain the desired solid retention time (SRT). Membrane backwashing, chemical washing, or both are routinely used to maintain membrane flux.

The bioreactor and membrane units of the MBR can be combined externally (Manem and Sanderson, 1996). In this case, the biomass must circulate between the membrane and bioreactor. The second configuration is the combination of integrating membranes inside the bioreactor. This configuration, defined as integrated MBR,
requires outer skin membranes. The configuration is currently the most common MBR, is called recirculated MBR, and can be operated with either inner or outer skinned membranes. These two configuration can be distinguished by the technology used to created the pressure gradient between the two sides of the membrane (driving force). The pressure across the membrane in the integrated MBR can be applied only by the suction through the membrane (Kayawake et al., 1991; Chiemchairaisri et al., 1993) or by pressurizing the bioreactor. In the recirculated MBR, recirculating flow through the membrane can also create pressure across the membrane.

The current limited number of MBR applications around the world is primarily due to the high cost of the filtration units. However, the recent development of a more productive and less expensive ultra- (UF) and microfiltration (MF) is making the MBR application feasible. Using this technology, MBR processes are competitive with conventional treatment when at least one of the following conditions exists: (1) high-strength effluent (some industrial wastewaters, sludge, etc.) in which the MBR system can take advantage of high biomass concentration and smaller biological basic counterbalances the cost of the filtration: (2) stringent disinfection requirements for treated water; or (3) biomass composed of very slow growing microorganisms (xenobiotic degradation, soil or groundwater remediation). Most of the applications described in the following satisfies at least one of the these conditions.

### 1.3.4.2 Three types of MBR
The combination of bioreactor and membrane unit has led to the development of three generic membrane processes in biological treatment (Brindle and Stephenson, 1996). *Solid-liquid membrane separation bioreactors* employ ultra- or microfiltration modules for the retention of biomass for recycle to the bioreactor. *Gas-permeable membranes* are used to provide bubbleless oxygen mass transfer to degradative bacteria present in the bioreactor. Additionally, the membrane can act as support for biofilm development, with direct oxygen transfer through the membrane wall in one direction and nutrient diffusion from the bulk liquid phase into the biofilm in the other direction. *An extractive membrane* process has been devised for the transfer of degradable organic pollutants from hostile industrial wastewaters, via a nonporous silicone membrane, to a nutrient medium for subsequent biodegradation. These three membrane processes are not mutually exclusive and, if necessary, could be coupled together into one bioreactor. The details of each type of MBR are explained in following section.

The first type of MBR is *solid-liquid separation membrane bioreactor*. Microfiltration (MF) and ultrafiltration (UF) are attractive techniques in practical industrial processes for solid/liquid separation or fractionation of macromolecule and colloidal species in solution. Membranes in the ultra- or microfiltration range can prevent the loss of biological solids and high molecular-weight solutes from a bioreactor. Complete mineralization of influent organic matter and maintaining a high biomass concentration and the retention of high-molecular-weight compounds facilitates denitrification of nitrogenous compound by such membranes. As a result of membrane separation, solid retention time (SRT) is independent of hydraulic retention time (HRT).
Using the solid/liquid separation concept, Ueda et al. (1996) treated the domestic sewage from rural settlements. The operation was continued for 250 days without membrane cleaning, and more than 90% of organic matter, suspended solids, and coliforms were successfully removed. As another example, the treatment of municipal wastewater on a semi-industrial aerobic pilot-scale MBR which has 24 hrs of HRT and 25 days of SRT was accomplished (Trouve et al., 1994). This experiment resulted in complete nitrification from 93 to 99.9% removal of COD, N-NH₃, and suspended solids.

The second type of MBR is an oxygen mass transfer bioreactor using a synthetic membrane. This type of MBR can provide bubbleless aeration for the biological treatment of wastewaters. Since no oxygen bubbles are formed, gas stripping of volatile organic compounds and foaming due to the presence of surfactants can be prevented. Bubbleless oxygen mass transfer can be accomplished using gas-permeable, dense membranes or hydrophobic microporous membranes.

Oxygen diffusion through dense membrane material can be achieved at high gas pressures without bubble formation. In hydrophobic microporous membranes the pores remain gases filled; oxygen is transported to the shell side of the membrane through the pores by gaseous diffusion or Knudsen flow transport mechanisms. The partial pressure of the gas is kept below the bubble point to ensure the bubbleless supply of oxygen.

Bubbleless oxygenation can also be achieved using independently sealed hollow fibers of gas-permeable polypropylene to transfer oxygen to wastewater moving across the outside wall of the fibers (Ahmed and Semmens, 1992). These fibers are arranged in a bundle in a tubular reactor within the ends of the sealed fibers free to move with the
wastewater flow. In addition to bubbleless oxygen diffusion, the fibers also provide a site for biofilm attachment, with highly efficient transfer and uptake of oxygen to the bacteria. Good fluidization of the fibers ensures they are distributed uniformly in the wastewater, providing excellent contact between the attached biofilm and the water. Close to 100% oxygen mass transfer efficiency is theoretically achievable. Until recently dead-end operation of hydrophobic fibers has been avoided, due to condensate formation in the fiber lumen resulting in reduction in the length of fiber available for oxygen mass transfer. The pores of hydrophobic membranes tend to remain gas filled and oxygen transfer proceeds by direct gaseous diffusion into the wastewater (Ahmed and Semmens, 1992)

The third type is an Extractive Membrane Bioreactor. Biological oxidation treatment is a viable approach for treating VOC-contaminated waters. For example, aerobic biological degradation of DCE has been performed previously by several authors (Freitas dos Santos and Livingston, 1993; Stucki et al., 1992). However, air stripping is a major problem when conventional bioreactor configurations are used to treat VOC-contaminated wastewater aerobically. The oxygen supplied through aeration with air causes air-stripping and consequent loss of DCE to the gas exit. This result in the toxic compound being transferred from the wastewater into an alternative effluent stream rather than being biodegraded. Several bioreactor configurations are advocated to overcome the air-stripping problem. Stucki et al. (1992) investigated the mineralization of low concentrations of DCE in two different fixed bed reactors, adding oxygen as a
solution of H₂O₂. This was feasible only because the low concentrations of DCE required small quantities of oxygen for their degradation.

An alternative to these systems is an *extractive membrane bioreactor* process for detoxifying industrial wastewaters. Membranes used for the extraction of pollutants into a bioreactor have been developed from pervaporation by exchanging the vacuum with a nutrient biomedium phase where biodegradation mechanisms maintain the concentration gradient needed to transfer organic pollutants present in industrial wastewater (Nguyen and Nobe, 1987; Yun et al., 1992).

This process employs a silicone rubber membrane to extract organic pollutants from a wastewater and transfer them to a biologically active zone where they are biodegraded by specifically acclimatized microorganisms. Undesirable direct contact between the volatile organic compounds and the aerating gas can be avoided in the EMB since the biofilm separates the VOC diffusing across the membrane from the aerated biomedium. The driving force for extraction across the membrane is maintained by the biological degradation of pollutants as they diffuse through the membrane into the biofilm. The process is concentration driven and no pressure gradients exist.

1.3.4.3 Membrane selection

The optimum design of an MBR process is very complex since many dependent factors have to be considered, including membrane performance and cost, energy consumption, and sludge treatment and disposal. Furthermore, the majority of these is interrelated and can influence capital and operation costs in adverse ways. Technical
and economical analyses of the first industrial-scale MBR projects showed that the filter installation (membrane block) and the energy necessary for operating, are the major investment and operating costs.

Filtration of biological solutions has been the object of numerous experiments. Many types of membranes have been tested. These include ultra- (UF) and microfiltration (MF), inner and outer skin, hollow fiber, tubular and flat, organic metallic, and ceramic. Depending on the membranes used, filtration performances vary from 0.05 to 10 m³/m²·h, and the typical fluxes for internal skin membranes are between 0.5 and 2 m³/m²·h, whereas outer membrane fluxes are often between 0.2 and 0.6 m³/m²·h⁻¹ (Manem and Sanderson, 1996).

Besides membrane flux, the main factors affecting filtration costs are the price of the membrane itself and its installation, including all required appurtenance, operating costs (energy, membrane replacement, and regeneration costs), and the desired effluent quality. A technical development of membranes and economic analysis tends to level the actual cost of filtration when considered over a period of several years for the different membranes.

At the present time, the use of a MBR is reserved for specific situations that require excellent effluent quality such as low COD, or disinfection. Applications exist mainly for high-strength industrial effluents. Large-scale use of MBR in urban wastewater treatment will require new technological developments or a significant decrease in the price of membranes. The application of MBRs for municipal wastewater treatments will probably occur first in areas where land is scarce.
Whatever system is adopted, the membrane must satisfy a certain number of basic criteria. To limit fouling, the size distribution of membrane pores should have as little interference as possible with the size distribution of the particles or molecules to be filtered. High porous membranes with evenly distributed pores enhance filtration efficiency (Fane et al., 1989). The membrane should preferably be hydrophilic (Fane et al., 1989) and be either negatively charged or neutral in order to limit biomass adsorption (Shimizu et al., 1989). The membrane should be nonbiodegradable by the microorganisms present in the solution and easy to clean and regenerate when it is fouled. This criterion is important because biological failure or sudden effluent modification (as in industrial wastewaters) could lead to severe membrane fouling. The membranes must also be resistant to chemical attack.

1.3.4.3.1 Filtration type - Crossflow filtration

Crossflow filtration membranes have been used for solids/liquid separation in water treatment applications since the 1950s when reverse osmosis (RO) became an option for the desalination of sea and brackish water (Cheryan, 1996). Cross-flow filtration is a continuous process in which the feed stream moves parallel to the membrane filtration surface and purified liquid passes through the membrane. The separation is driven by the pressure difference across the membrane that is parallel to the surface of the membrane (transmembrane). The feed stream flow, combined with the boundary layer turbulence created by the cross-flow velocity, continuously sweeps away particles and other substances that would build up on the membrane surface. As a result,
cross-flow filters inherently maintain higher permeate than conventional dead-end filters (Baily et al., 1994).

Inoue et al. (1981) concluded that acceptable operating costs for using UF modules for the filtration of various wastewater treatment streams could only be obtained from processes that operate at low pressures. Crossflow microfiltration processes studied by Lee et al. (1980) used 40 W m\(^{-2}\) of energy. This was 25 times less than the energy requirement of 1000 W m\(^{-2}\) necessary for UF processes, making cross-flow filtration more feasible for use in wastewater treatment.

In crossflow filtration, the filter cake that would build up on the membrane surface during conventional “dead-end” filtration is usually removed by the scouring action of the suspension flowing across the membrane surface. With a low-cost product such as water, UF system have proved to be too expensive for reactor-coupled processes. Crossflow filtration has become a viable alternative due to the increased permeate fluxes and the much lower operating pressure of the process, which reduces the energy requirements (Tran, 1985; Inoue et al., 1981)

1.3.4.3.2 Membrane Type - Inorganic Membranes

Inorganic membranes for separation in liquid media appeared on the market in the beginning of the 1980s. These were porous, permeable, ceramic membranes with a composite structure. They were called 3rd generation membranes to distinguish them from the purely organic membranes. In the field of food and dairy industries, inorganic membranes are now used in a wide range of processes, especially in microfiltration and
ultrafiltration. Ceramic membranes are more durable than polymeric membranes especially at high temperatures.

The properties of a ceramic microfiltration membrane unit as another application of inorganic membrane to MBR have been investigated as a component of a cell recycle bioreactor for the production of ethanol/sorbitol (Chun and Rogers, 1988). In this research, both the retentate and permeate were recycled to the feed tank to maintain a constant cell concentration (8.5 g/L). From the results, it is evident that the ceramic membrane module showed less fouling with cells and gave rise to a more stable flux. The other recent studies on ceramic materials have also increased the potency of bioindustrial applications (Suzuki et al., 1990; Suzuki et al., 1991).

Based on discussion of membrane selection in the previous section, cross-flow ceramic membranes, especially the zirconia ceramic membrane, is attractive for use in bioprocess applications because they are usually resistant to damage from sterilization, high pressure, and organic solvents (Suzuki et al, 1991; Nishizawa et al. 1993). They are also durable in both acid and alkaline solutions, and have high mechanical strength.

1.3.4.4 Membrane Fouling

1.3.4.4.1 Background

Even though a membrane bioreactor has a lot of advantages, the major obstacle to their use is the continuous reduction of permeable flux caused by concentration polarization and membrane fouling. In the MBR, membrane fouling could be attributed to the adsorption of organic species, the less soluble inorganic species, and adhesion of
microbial cells at the membrane surface. Since the permeation flux is the main factor in determining the economic feasibility of MBR systems, careful attention to membrane fouling is required. In particular, membrane fouling is associated with the physico-chemical and biological properties of solutes and the membrane. For instance, the increase of biomass concentration (Li et al., 1984), the size reduction of mixed liquor biosolids (Baile et al., 1994b), or the size distribution of particles being filtered (Chang et al., 1994) all reduced membrane permeability. Several remedial actions have been tried to prevent this phenomenon, such as increasing fluid velocity (Choo et al., 1996), backwashing (Kim and Vigneswaran, 1991), multiphase flow (Imasaka et al., 1989), and controlling the membrane surface charge.

Membrane flux also depends on factors such as suspended solids, cross-flow velocity, temperature, transmembrane pressure, surface fouling due to submicrometer particle deposition, and the extent of concentration polarization. Concentration polarization arises from the accumulation of solutes on the membrane surface, some of which will form a viscous layer. This gel acts as a secondary membrane, reducing the flux and often reducing the passage of low-molecular-weight solutes.

An increase in temperature can also lead to a decrease in mixed-liquor viscosity and a consequential increase in membrane flux. Ross et al. (1992) found that the permeate flux was 42.7 L m\(^{-2}\) h\(^{-1}\) at 47 °C compared to 32.1 L m\(^{-2}\) h\(^{-1}\) at 40 °C during treatment of brewery effluent by anaerobic digestion ultrafiltration (ADUF\(^{®}\)). However, others have shown the permeate flux decline due to a short-term temperature drop is not
linear to the reciprocal of the viscosity, suggesting that flux decline is not solely affected by increased liquor viscosity (Chiemchaisri and Yamamoto, 1994).

The need for comprehensive study of membrane fouling in the MBR system still exists. There are many unknown factors regarding the fouling mechanisms, which are further complicated by chemical and biochemical reactions as well as interactions between various solutions and the membrane surface. In addition, an understanding of the fouling phenomena is essential for achieving optimum MBR design and efficient operation.

1.3.4.4.2 Estimation of Membrane Fouling

One of the most frequently used models is the resistance-in-series model, which is a simple means of describing permeate flux-transmembrane pressure relationship. According to Choo and Lee (1996), the permeation flux \( J \) takes the following form:

\[
J = \frac{\Delta P}{\eta R_t}
\]  
(14)

\[
R_t = R_m + R_p + R_{ef} + R_{if}
\]  
(15)

where \( \Delta P \) is the transmembrane pressure; \( \eta \) is the dynamic viscosity of the permeate; \( R_t \) is the total resistance; \( R_m \) is the intrinsic membrane resistance; \( R_p \) is the polarization layer resistance caused by the concentration resistance gradient (concentration polarization);
Ref is the external fouling resistance formed by a strongly deposited cake layer from physico-chemical interaction of solids with the membrane surface; and \( R_f \) is the internal fouling resistance due to some irreversible adsorption. For a solution of constant composition and temperature, the reduction of flux at a constant applied pressure is due to \( R_f \). Here, the \( R_p \) term is experimentally defined as the portion of the total resistance dislodged only by water flushing, while the \( R_g \) term is the resistance to be removed by manual cleaning of the membrane surface.

1.3.4.5 Cleaning technique to increase membrane flux

Various cleaning techniques can be used to increase the membrane flux. First, the application of jet aeration can be used to prolong the operational life of the membrane in the bioreactor. Jet aeration, using a series of air nozzles improved the performance and operation of the membrane bioreactor (Chiemchaisri et al., 1993). HRT (Hydraulic Retention Time) of bioreactor was reduced and permeate flux increased due to the injection of air. Jet aeration removed the attached solids on the membrane surface and caused higher permeate flux.

Membrane regeneration with an alkaline detergent solution (containing NaOH) followed by a sanitizing acid solution (1-2% HNO₃) is also very efficient cleaning technique. Using this method, the original permeate flux can be restored after cleaning. However, polymeric membranes are relatively difficult to clean due to their limited chemical resistance. The use of chlorine and chemical complexation can improve cleaning efficiency.
Nitric acid is another commonly used cleaning agent which effectively removing fouling due to mineral scaling. Here, it was hypothesized by a ligand exchange model, where anionic ligands replace the surface hydroxyl groups of alumina or zirconia, surface as the following reaction:

$$S-OH + L^- \leftrightarrow S-L + OH^-$$

(16)

where $S$ is the surface of the inorganic membrane, and $L^-$ is the foulant. At lower pH, the reaction proceeds which promote the adsorption of the foulants remaining in the cleaning solution. This might be a possible reason for flux decline.

The high strength sintered ceramic bond between the membrane filtration layers and the support structure allows cleaning by high pressure/short duration backflushing. Backflushing causes a reverse flow of filtrate through the membrane, lifting the fouling layer so that it is carried away by the crossflow. Short and frequent backpressure pulses can remove the fouling layer, maintaining a higher filtrate flux.

Steam sterilization can be carried out by steadily increasing the temperature of the crossflow to 100 °C. Steam is added to displace the water and then raise the temperature steadily until the required sterilization temperature is achieved. The water used for steam should be deionized, and 0.2 μm prefiltered.

1.3.4.6 Membrane Kinetics
Since the usual MBR is as an ideally mixed suspended growth bioreactor, the following equation (Li et al., 1984) can be applied to calculate biological kinetic coefficient

$$\frac{1}{SRT} = Y \times B_x - b$$  \hspace{1cm} (17)

where $Y$ is the true yield coefficient, kg COD / kg COD removed, $B_x$ is the COD mass loading rate, kg COD removed/kg sludge expressed in COD/ d, and $b$ is the decay rate coefficient, d$^{-1}$.

Again strictly for active biomass, the observed yield coefficient ($Y_{obs}$) can be calculated by the following equation (Li et al., 1984):

$$Y_{obs} = \frac{Y}{1 + b \times SRT}$$  \hspace{1cm} (18)

This equation predicts observed cell yield, approaching zero, or the sludge age (SRT) is in increase. The cell yield never can be zero, but can be very small. Accumulation of inorganic solids will also build up in the system. Nevertheless, very long SRT are possible with MBRs under reasonable volumetric loading rate. Long SRT are more difficult to achieve in conventional suspended growth system because of the loss of solids in the effluent, and the poor settling properties of activated sludge at high concentration (Fan et al., 1996).
In a MBR, a design procedure can be used that is similar to the conventional activated sludge process design procedure. The procedure will be more feasible, because the limiting flux for secondary clarifier does not exist. Membrane area will need to be determined by anticipating the membrane flux, which will be a function of process variables and cleaning frequency.

1.3.5 Fenton Oxidation

1.3.5.1 High Explosives Contaminated Soils

Wastewaters generated at former munitions production facilities often contain nitrated organics, particularly, 2,4,6-trinitrotoluen (TNT), RDX and HMX (Ubanski, 1964). Past disposal of these wastewaters to the surrounding environment has resulted in numerous instances of contaminated soils and groundwater (Comfort et al., 1995; Spalding and Fulton, 1988).

Biodegradation, although possible, may require longer time to oxidize RDX and HMX in aqueous solutions. Therefore, a strong oxidant may be useful for the treatment of RDX and HMX in specific situations. Products resulting from chemical oxidation might be more amenable to biological treatment than the parent compound. Munitions compounds and some of their degradation products may be mutagenic (Kaplan and Kaplan, 1982; McCormick et al., 1981), carcinogenic (Stayner et al., 1993), or otherwise toxic to aquatic and terrestrial life (Klausmeier et al., 1973; Liu et al., 1976; Smock et al., 1976). Soils high contaminated with RDX need to remediated to prevent ground and surface water contamination and ensure public safety.
1.3.5.2 Advanced Oxidation

Advanced oxidation processes (AOPs), based on generation of reactive radicals to destroy organic pollutants, are commonly used for remediating wastewaters contaminated with synthetic organic compounds (Sato and Leung, 1991; Sedlak and Anderson, 1991; Venkatadri and Peters, 1993; Watts et al., 1990). The Fenton reaction (Fenton, 1894) is one of the oldest, most powerful oxidation treatments available. The Fenton reagent is a mixture of ferrous iron and hydrogen peroxide that generates reactive radicals, primarily the hydroxyl radical (·OH). Hydroxyl radicals react non-specifically with organic compounds at a rate of 10^7 to 10^9 L/mol·sec (Buxton et al., 1988).

The following equation shows the general Fenton reaction (Walling, 1975).

\[
H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + HO^-
\]  

The hydroxyl radical is a highly reactive species, with oxidation potential second only to atomic fluorine; it is capable of reacting with most organic substances at near diffusion-controlled rates (Hoigne et al., 1989). There may be numerous competing reactions involved with Fenton's reagent, depending on the nature of the reacting substrates. A reasonable pathway for the decomposition of a substrate with hydroxyl radical is classified as follows (Cooper et al., 1989; Kunai et al., 1986):

\[
HO^- + RH \rightarrow H_2O + R^-
\]
\[ R' + Fe^{3+} \rightarrow R^+ + Fe^{2+} \]  
(21)

\[ R' + O_2 \rightarrow ROO' + R' + \cdot OH_2 \]  
(22)

\[ R' + Fe^{3+} \rightarrow Fe^{2+} + R'' + \text{products} \]  
(23)

1.3.5.3 Application of Fenton Oxidation

The Fenton reagent has been receiving wide recognition recently because of its ability to decompose many organic compounds, including nitroaromatics and azo dyes (Fenerstein et al., 1981; Ho, 1986; Kitao et al., 1982; Mohanty and Wei, 1993; Pignatello and Day, 1996). For the application of advanced oxidation of high explosives, Li et al. (1997) previously showed that the Fenton reaction could effectively destroy TNX in water and soil. He found that adding the Fenton reagent to a 0.31-mM TNT (70 mg L^-1) solution resulted in complete destruction within 8 h, and 40% mineralization within 24 h. Oxalate, NO_3^-, H_2O, and CO_2 were the primary end products of TNT oxidation by Fenton reagent in the dark. No research has been reported on RDX and HMX using Fenton oxidation.

In Chapter 4, we investigate the chemical kinetics of Fenton oxidation of RDX and HMX under acidic aqueous conditions. Various factors that are important to optimize the oxidation of organics were studied, and the byproducts and mineralization of RDX and HMX also are discussed. Understanding the reaction mechanism for the oxidation of RDX and HMX under conditions relevant to waste treatment is an essential step in design of efficient, cost-effective Fenton reagent treatment systems.
Furthermore, identification and quantification of intermediate products is important because intermediates may be recalcitrant or toxic.
1.4 References


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CHAPTER 2
Biological Denitrification of Hydrolysates of RDX and HMX Using a Packed-Bed Reactor

2.1 Introduction

Explosives have been manufactured in the United States and other countries for many decades. Among all the high explosives (HEs) that are manufactured, RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and TNT (2,4,6-trinitrotoluene) are the most common. RDX is classified as a possible human carcinogen (Class C) by the U.S.-Environmental Protection Agency (EPA), and has various effects on mammals, fish, protozoa (McLellan et al., 1988a). HMX is produced with RDX and is usually found together with RDX as an environmental contaminant. HMX has adverse effects on the central nervous system in mammals, but at higher concentrations than RDX, and has been classified as class D.
carcinogen by the EPA (McLellan et al., 1988b). RDX and HMX are more energetic than TNT, and have been used in both conventional and nuclear weapons.

The end of the cold war created a worldwide surplus of both conventional and nuclear weapons. The United States and other countries are destroying large quantities of weapons (demilitarization), which creates the need for safe and reliable disposal technologies for energetic materials and wastewaters associated with their processing. Bulk high explosives were previously destroyed using open burning or detonation that can produce various unwanted toxic products, such as cyanic acid. Open detonation is not 100% efficient and explosives may be released to the environment along with explosion byproducts.

In the past, wastewaters containing RDX and HMX were often disposed in lagoons. This practice has sometimes resulted in soil and groundwater contamination. Therefore, environmental transformations of RDX and HMX, and remediation methods have been extensively researched. Biodegradation of RDX and HMX to partially known byproducts under anaerobic or anoxic conditions have been investigated by McCormick et al. (1981) and in our laboratory (Hesselmann et al., 1992; Wilkie and Stenstrom, 1996; Alatriste-Mondragon, 1996; Chiou et al., 1997, 1998). In spite of previous research, biological treatment of HE containing wastewaters is seldom practiced, and activated carbon is often used at munitions plants as well as groundwater remediation (Wujcik et al., 1992). Granular activated carbon (GAC) adsorption is effective in removing HE from contaminated waters, but produces HE-laden carbon. The spent carbon is a hazardous waste, and if allowed to dry may become explosive.
Alkaline hydrolysis is a simple and effective process to convert RDX to smaller, less harmful compounds such as acetate, formate, and nitrite (Spontarelli et al., 1993). The process is suitable for destroying bulk quantities; however, for dilute wastewaters with relatively low RDX concentrations (RDX solubility is approximately 40 mg/L at 25 °C), the process is costly and ineffective. The cost of raising the pH and later neutralizing large volumes of water is prohibitive.

To overcome these costs, Heilmann et al. (1994) proposed a combined process that uses activated carbon adsorption and alkaline hydrolysis regeneration of the spent carbon. Adsorption concentrates the HE that reduces the volume of material being treated to a manageable size. The combined process has all the advantages of carbon adsorption, and the waste carbon can be regenerated and reused. Furthermore, the regeneration process is relatively simple, and may be performed without removing the carbon from the contactor. Figure 2-1 shows the proposed process. The HE contaminated wastewater is first passed through granular activated carbon columns that dramatically reduces the volume of material to be treated. The laden carbon is treated with an alkaline solution that effectively regenerates it. Heilmann et al. (1996) found that alkaline hydrolysis of RDX yields 1.6 M NO₂⁻, 1.5 M HCOO⁻, 0.1 M CH₃COO⁻, 1.1M HCHO, 0.9 M NH₃, 1.1 M N₂O, and 0.34 M N₂ per 1 M of RDX hydrolyzed. Hydrolysis of adsorbed RDX proceeds at a slower rate than hydrolysis of dissolved RDX, but produces the same byproducts. HMX hydrolyzes at slower rates than RDX, but produces the same byproducts with slightly different stoichiometry.
Figure 2-1. Treatment scheme for waters and wastewaters contaminated with high explosives (Heilmann et al., 1994).
Activated carbon adsorption with carbon regeneration using alkaline hydrolysis appears to be an efficient and safe way to treat RDX/HMX-containing wastewaters; however, the hydrolysates can contain high concentrations of acetate, formaldehyde, formate, ammonia, and nitrite. These hydrolysates cannot be directly released to the environment, and require further treatment. The organic compounds will exert an oxygen demand on the receiving water and the byproducts can have negative health consequences. Furthermore, nitrite probably could not be released because of its potential to contaminate groundwaters. Nitrite can be oxidized to nitrate and both are important groundwater contaminants.

For these reasons it is necessary to develop a process to treat the hydrolysates. An ideal process would remove both nitrite and the organic compounds. The organic compounds are simple and quite amenable to biological degradation. The nitrite can be used as an electron acceptor. For these reasons it was decided to demonstrate the effectiveness of a denitrifying treatment process. A synthetic wastewater identical in composition to RDX hydrolysates was used; it was not possible to use actual hydrolysate because laboratory safety would have been compromised with the required mass of explosive (our laboratory is limited to several grams of explosives).

This paper describes the results of a two-year investigation to demonstrate effective hydrolysate treatment. The process was developed in a step-wise fashion, by gradually increasing the number of organic compounds and the mass of electron acceptor. Formate and acetate were first studied, and formaldehyde was added after obtaining stable conditions.
2.2 Experimental

2.2.1 Continuous Flow Experiment

Figure 2-2 shows the treatment scheme for waters contaminated with hydrolysates of RDX. A continuous flow reactor was used that was constructed from a 200-mm acrylic column with an internal diameter of 25 mm, resulting in an empty bed volume of 98.17 mL. The inlet and outlet to the reactor were equipped with stainless steel screens to retain the packing material. This column was packed with 42 grams of 2-mm diameter silicon tubing (size 13), cut to lengths of 1-2 mm. The column was sealed with Plexiglas end caps. The novel packing was used because it was difficult to find packing this small from materials other than glass.

This column was inoculated with the mixed denitrifying cultures described later by injecting 1 mL of mixed culture into the lower quarter of the reactor which had been prefilled with feed solution. Feed flow was initiated two weeks after inoculation to allow for microbial growth and attachment to packing material. The column was operated at room temperature (20-25 °C) in an upflow mode and fed by a cartridge pump. A single 2 L feed flask was used to supply the nutrients spiked with hydrolysates. Feed solution was mixed in this flask every other day. Influent was pumped to the reactor using a multi-cartridge peristaltic pump using tygon tubing. A rubber stopper was used to prevent the transfer of oxygen to the feed. Nitrogen gas was used to purge the feed flask to further reduce the entry of oxygen into the reactor. The flask tubing was flushed with a dilute acid solution every other day to prevent growth of bacteria.
Figure 2-2. Schematic diagram of experimental set-up.
outside the reactor. The feed rate was 0.3 ml/min, except during the kinetics experiment. The influent and effluent ions and RDX/HMX concentrations were measured weekly. The influent sample was taken directly from the feed and the effluent was collected as the solution exited the reactor, using a sampling tube located outside the reactor.

2.2.2 Denitrifying Cultures

The initial culture was started using anaerobic digester sludge from the Hyperion wastewater treatment plant in El Segundo, CA. All samples were diluted with oxygen free phosphate buffer, filtered, and incubated for three weeks in a minimal medium with ethanol, potassium nitrate, and phosphate buffer. This culture was originally grown on ethanol and nitrate and used to transform RDX and HMX to non-explosives byproducts (Wilkie, 1994). The inoculum from this culture was used to start degrading the hydrolysates of RDX. Ethanol and nitrate for degradation of RDX were gradually removed and replaced with nitrite (electron acceptor) and formate, acetate and formaldehyde (carbon sources). All constituents of the liquid growth medium except the carbon sources and electron acceptors are listed in Table 2-1. Phosphate buffer was provided to maintain pH between 7-7.5, and also as a nutrient.

2.2.3 Ion chromatography - Formate, Nitrite and Nitrate.

Formate (HCOO⁻), nitrite (NO₂⁻), and nitrate (NO₃⁻) were analyzed using a Dionex Ion Chromatograph (basic chromatography module CMB-2, gradient pump GPM-1; Dionex, Sunnyvale, CA) with suppressed conductivity detection (conductivity
**Table 2-1.** Composition of the culture medium used for continuous flow experiment.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$HPO$_4$</td>
<td>5000</td>
</tr>
<tr>
<td>NaH$_2$PO$_4$·H$_2$O</td>
<td>2875</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>200</td>
</tr>
<tr>
<td>MgCl$_2$·H$_2$O</td>
<td>100</td>
</tr>
<tr>
<td>CaCl$_2$·2H$_2$O</td>
<td>40</td>
</tr>
<tr>
<td>Na$_2$SO$_3$</td>
<td>19.7</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>3.9</td>
</tr>
<tr>
<td>MnCl$_2$</td>
<td>0.95</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>0.66</td>
</tr>
<tr>
<td>CoCl$_2$·6H$_2$O</td>
<td>0.58</td>
</tr>
<tr>
<td>CuCl$_2$·2H$_2$O</td>
<td>0.30</td>
</tr>
<tr>
<td>Na$_2$Mo$_4$·2H$_2$O</td>
<td>0.46</td>
</tr>
<tr>
<td>Na$_2$B$_4$O$_7$·10H$_2$O</td>
<td>0.2</td>
</tr>
</tbody>
</table>
detector CDM-1). An Ion Pac AS9-SC analytical column (4 mm I.D.) was used with a subsequent suppressor column. The mobile phase consisted of 0.75 mM NaHCO$_3$ and 2 mM Na$_2$CO$_3$ dissolved in deionized water from Milli-Q water system (Millipore Co., Bedford, MA). The eluent flow rate was set to 2 mL/min. Samples were manually injected into a 50-μl sample loop.

Peaks were detected at retention times between 1.4 and 1.5 minutes for HCOO$^-$, 2.0 and 2.1 minutes for NO$_2^-$, and 2.8 and 2.9 minutes for NO$_3^-$, respectively. The peak area was a linear function of the concentration between 0.66 and 6.13 mg HCOO$^-$/L, between 0.77 and 6.13 mg NO$_2^-$/L, and 0.5 to 10.0 mg NO$_3^-$/L, respectively. For the external calibration, at least three data points were gathered for each standard concentration. The mean was then used for the calibration curve. All samples were filtered through sterile Acrodisc-13 0.2-μm syringe-microfilters (Gelman Sciences, Ann Arbor, MI) before injection.

2.2.4 High Performance Liquid Chromatography (HPLC) – Formaldehyde Analysis

A modification of the technique reported by Kuwata et al. (1979) was used. The reaction solution for formaldehyde was prepared by dissolving 0.5 g of 2,4-dinitrophenylhydrazine (DNPH) in 500 mL of 2 N hydrochloric acid and purified by shaking with 5 mL of chloroform. Formaldehyde in the sample (0.4 mL) was first allowed to react with 2,4-dinitrophenylhydrazine in acidic solution (4 mL) in order to
form 2,4-dinitrophenylhydrazone. The solid phase extraction (SPE) method (Richard and Junc, 1986) was used and the eluent was analyzed by HPLC.

HPLC analysis was performed with a Hewlett Packard 1500 Series instrument (Avondale, PA) equipped with a variable wavelength detector and autosampler. An Adsorbosphere C-18 10-µm reversed-phase column (Alltech, Deerfield, IL) with prefilter element and guard column (C-18, 5-µm, Alltech) was used with a mobile phase consisting of 50 % acetonitrile and 50 % water (volume %) at a flow rate of 1.5 mL/min. A UV detector (254 nm) was used to detect the dinitrophenylhydrazone peak at a retention time of 5.9 min. The peak area was a linear function of the concentration between 0.5 - 20 mg/L of formaldehyde. Standards were prepared for 0.50, 1.00, 2.50, 5.00, 10.00 and 20.00 mg formaldehyde/L. For the external calibration, at least three data points were collected for each standard concentration. The mean was then used for calibration. All samples were also filtered through sterile Acrodisc-13 0.2-µm syringe-microfilters before injection.

2.2.5 Gas Chromatography (GC) - Acetate

Acetate ion (CH$_3$COO$^-$) analysis was performed on a Hewlett Packard model 5890 gas chromatograph. A glass column with 15% SP-1200/1% H$_3$PO$_4$ on 100/200 mesh Chromosorb (Supelco, Bellefonte, PA) and a guard column (Supelco, Bellefonte, PA) were used to resolve the compounds. Oven temperature and injection temperature was 115 °C; detector temperature was 200 °C. The retention time for acetate with this
method was approximately 1.65 min. Standard curves were obtained from 2.93 to 29.25 mg C/L of acetate. The detection limit was approximately 3 mg C/L of acetate.

2.2.5 Solid Phase Extraction (SPE) for RDX and HMX

Richard and Junc's (1986) SPE method was used to concentrate liquid samples containing explosives for analysis. Varian Bond Elut (Harbor City, CA) C-8 SPE cartridges were used and recoveries were generally greater than 90% when analyzing 5 to 10 mL samples. First, 10 mL of HPLC grade methanol was passed through a 5 cc-SPE cartridge under vacuum that provided a flow rate of approximately 5 mL/min. This was equivalent to about 25-mm Hg vacuum pressure. The sorbent bed was then washed with 5 mL of HPLC grade water. Before the sorbent bed dried, liquid sample that contained explosives was passed through the cartridge while the vacuum was still drawing liquid. When all the sample had passed through the cartridge, 4 mL of HPLC grade water was used to rinse the cartridge and to remove interference. The SPE cartridge was then dried under full vacuum (~600 mm Hg) for 20 minutes (a maximum of 0.4 mg of explosive was retained on the column using this procedure). 1 mL of HPLC grade acetonitrile was used for elution. The eluent was then collected in a vial and analyzed using HPLC. Even though HE can be concentrated up to 10 times in the SPE column, the maximum concentration of HE is at most 50 mg/L, therefore, there is no explosive hazard associated with drying of the SPE tubes containing the explosives.

2.2.7 RDX and HMX Analysis
RDX and HMX were measured with SPE method followed by HPLC. The analysis was performed with the same HPLC with the one used in formaldehyde analysis. The mobile phase consisted of 40 % water, 30 % methanol and 30 % acetonitrile (volume %) at a flow rate of 1 mL/min. The sample injection volume and detection wavelength was set at 20 µL and 236 nm, respectively. Separation through a 10 µm, Adsorbosphere, C-18 reversed phase column and corresponding 5-μm guard column (Alltech, Deerfield, IL) at 25°C, resulted in retention time of 4.1 min (RDX) and 3.6 min (HMX), respectively.

2.2.8 Total Organic Carbon (TOC)

A Beckman Model 915B TOC analyzer was used following procedures described in Standard Methods (APHA, 1989). Samples were clarified by centrifugation, filtered through membrane filters, and acidified to pH 2 using phosphoric acid to liberate inorganic CO₂. Organic carbon was determined by injecting 1 mL of the acidified sample.

2.3 Results and Discussions

2.3.1 Stoichiometry

Denitrification is classically considered to be a heterotrophic process by microorganisms that require a reduced organic substrate for respiration and cell synthesis (Gayle et al., 1989; Knowles, 1982). Nitrate (NO₃⁻) is normally used as the terminal electron acceptor and it is sequentially reduced to NO₂⁻ and finally to N₂ (Payne, 1973).
Heterotrophic denitrifying bacteria can use a wide variety of organic compounds, such as methanol, ethanol, glucose, and acetate as well as the myriad of compounds found in municipal wastewaters.

RDX hydrolysates contain formate, formaldehyde, and nitrite that are carbon sources and electron acceptor. However, only a few studies exist where nitrite is used as the electron acceptor (EPA 1975; Kamath et al., 1991). A possible reason is that high concentrations of nitrite are seldom found in municipal wastewaters, and nitrifying activated sludge plants usually completely convert ammonia to nitrate. Nitrite is reduced to nitrogen gas in a fashion similar to nitrate in accordance with the following half equation:

\[ \text{NO}_2^- + 4 \text{H}^+ + 3 \text{e}^- \rightarrow 0.5 \text{N}_2 + 2 \text{H}_2\text{O} \]  \hspace{1cm} (1)

The reduced organic carbon compounds present in the hydrolysates (acetate, formaldehyde, and acetate) are oxidized according to the following half reactions:

\[ \text{HCOO}^- \rightarrow \text{CO}_2 + 2 \text{e}^- + \text{H}^+ \]  \hspace{1cm} (2)

\[ \text{HCHO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4 \text{e}^- + 4 \text{H}^+ \]  \hspace{1cm} (3)

\[ \text{CH}_3\text{COO}^- + 2 \text{H}_2\text{O} \rightarrow 2 \text{CO}_2 + 8 \text{e}^- + 7 \text{H}^+ \]  \hspace{1cm} (4)
The combined equations for bacterial oxidation, ignoring cell synthesis can be written as follows:

\[
\begin{align*}
\text{NO}_2^- + 1.5 \text{ HCOO}^- + 2.5 \text{ H}^+ & \rightarrow 0.5 \text{ N}_2 + 1.5 \text{ CO}_2 + 2 \text{ H}_2\text{O} \quad (5) \\
\text{NO}_2^- + 0.375 \text{ CH}_3\text{COO}^- + 1.375 \text{ H}^+ & \rightarrow 0.5 \text{ N}_2 + 0.75 \text{ CO}_2 + 1.25 \text{ H}_2\text{O} \quad (6) \\
\text{NO}_2^- + 0.75 \text{ HCHO} + \text{ H}^+ & \rightarrow 0.5 \text{ N}_2 + 0.75 \text{ CO}_2 + 1.25 \text{ H}_2\text{O} \quad (7)
\end{align*}
\]

As indicated earlier, Heilmann et al. (1996) found that RDX hydrolysis yields 1.6 M \text{NO}_2^-, 1.5 M \text{HCOO}^-, 0.1 M \text{CH}_3\text{COO}^-, 1.1 M \text{HCHO}, 0.9 M \text{NH}_3, 1.1 M \text{N}_2\text{O}, and 0.34 M \text{N}_2 per M of RDX hydrolyzed. Equation 8 shows this relationship:

\[
\begin{align*}
1 \text{ RDX} (\text{C}_3\text{H}_6\text{N}_6\text{O}_6) & \rightarrow 1.6 \text{ NO}_2^- + 1.5 \text{ HCOO}^- + 0.1 \text{ CH}_3\text{COO}^- + 1.1 \text{ HCHO} \\
& + 0.9 \text{ NH}_3 + 1.1 \text{ N}_2\text{O} \uparrow + 0.34 \text{ N}_2 \uparrow \quad (8)
\end{align*}
\]

In the following section we describe the stoichiometry and experiments for denitrifying hydrolysates.

2.3.2 Denitrification of Nitrite using Acetate and Formate
For simplicity, the system was first started with acetate, formate and nitrite. First the stoichiometric relationship (Equation 9) was constructed by adding Equation 5 to 0.27 (0.1/0.375) times Equation 6:

\[
\begin{align*}
1.6 \text{NO}_2^- + 1.5 \text{HCOO}^- + 0.1 \text{CH}_3\text{COO}^- + 2.9 \text{H}^+ \rightarrow 0.33 \text{NO}_2^- + 0.63 \text{N}_2 \\
+ 1.7 \text{CO}_2 + 2.33 \text{H}_2\text{O}
\end{align*}
\]

According to this stoichiometry, the amount of nitrite exceeds the amount required for complete oxidation of the organics. Therefore, acetate and formate should be oxidized completely; excess nitrite is present and only 80% can be removed if cell synthesis is neglected. However, some organic matter is always converted into cell material, which will require less electron acceptor, and will further reduce the nitrite removal efficiency.

The biological column was operated for three months to demonstrate this conversion and to show that the system could effectively use nitrite as an electron acceptor at the concentrations anticipated. Figure 2-3 shows removal efficiencies of nitrite and formate. At the time of this experiment, we were not monitoring acetate removal. Until about 1800 hours in this figure, formate removal averaged 95%, but nitrite removal averaged only 55.4%, which we attributed to cell synthesis.

The partial removal of nitrite can be used to approximate the cell yield, which generally cannot be measured in packed-bed reactors, due to the difficulty in weighing the biomass that is attached to the column packing. Only 55.4% or 0.89 out of 1.6 moles of nitrite were reduced in the acetate/formate system (For simplicity, we base our
Figure 2-3. Removal efficiencies of hydrolysates and RDX: RDX was introduced at 1800 hours. HMX has similar removal as RDX’s. Acetate concentration was increased at 4600 hours to get high removal of nitrite.
discussion on the coefficients from Equation 9, as opposed to the actual molar concentrations). The amount of substrate used for cell synthesis can be estimated by balancing the amount of nitrite reduced with formate (acetate is neglected due to its low concentration and to simplify calculations). Equation 5 can be multiplied by 0.89 to obtain this result, which shows that 1.33 moles of formate can be reduced. If we subtract this amount from Equation 9, we see that 0.17 out of 1.5 moles of formate are not reduced and therefore must be used for cell synthesis. Stoichiometrically, this amount of formate could produce maximum 0.034 moles of cells ($C_5H_7NO_2$). Therefore, the observed cell yield (mass basis) using this ratio (0.034/1.5) is 0.057-mg cells/mg formate, or 0.21-mg cells/mg TOC, or 0.16-mg cells/mg COD, or 0.31-mg cells/mg NO$_2^-$-N. These results compare to an observed cell yield of 0.18 mg VSS/mg COD for nitrate reduction with methanol in an anoxic slurry reactor at 20 °C (Stensel et al., 1975), and a theoretical yield of 0.4 - 0.9 mg VSS/mg NO$_3$-N for typical denitrification processes (Metcalf and Eddy Inc., 1991).

We next added acetate to balance the carbon source and electron acceptor to maximize nitrite removal (a short experiment to assess the culture's ability to biodegrade RDX was performed in the intervening period, and is reported later in the paper). The stoichiometric relationship that best describes the reaction for this balanced condition using Equation 5 and 6 is shown in Equation 10.

$$1.6 \text{NO}_2^- + 1.5 \text{HCOO}^- + 0.1 \text{CH}_3\text{COO}^- + 0.13 \text{CH}_3\text{COO}^- + 3.33 \text{H}^+$$

$$\rightarrow 0.8 \text{N}_2 + 1.95 \text{CO}_2 + 2.75 \text{H}_2\text{O}$$

(10)
Using this stoichiometry, acetate concentration was increased from 6.53 mg C/L to 17.6 mg C/L (the theoretical amount is 14.5 mg C/L; but more acetate was added for cell synthesis) at approximately 4600 hours in Figure 2-3. As shown in this figure, nitrite removal increased from 40% to over 80%, suggesting that it is possible to balance the carbon sources and the electron acceptor. Acetate was completely removed while maintaining over 90% formate removal from GC analysis.

2.3.3 Formaldehyde Addition

After developing stable conditions with acetate and formate, we added formaldehyde, which simulates the total hydrolysate system. The first step was to make a mass balance equation including formaldehyde. However, if the same hydrolysate mole ratio (Equation 8) is used, nitrite becomes limiting, and it is not possible to predict carbon oxidation. Therefore, additional nitrite was added to allow all carbon sources to be oxidized. The stoichiometric balance for treating hydrolysates including additional nitrite can be written as follows, using Equation 5 through 7:

\[(1.13\text{NO}_2^-) + 1.6\text{NO}_2^- + 1.5\text{HCOO}^- + 0.1\text{CH}_3\text{COO}^- + 1.1\text{HCHO} + 4.33\text{H}^+ \rightarrow 1.37\text{N}_2 + 2.8\text{CO}_2 + 4.17\text{H}_2\text{O} \] (11)
Figure 2-4. Removal efficiency of each hydrolysates after adding formaldehyde: formaldehyde was analyzed later in this experiment, and completely removed.
Equation 11 shows that insufficient nitrite is present and 1.133 moles (underlined) must be added to complete the carbon oxidation. Cell growth will reduce the required electron acceptor (nitrite); therefore, we initiated our experiment with 10% less nitrite.

Figure 2-4 shows the percentage removal of each hydrolysate in the bioreactor with this ratio. During one month, we obtained very stable removals over 90% of all hydrolysates. This result was confirmed by checking total organic carbon (TOC). As also shown in Figure 2-5, inlet total organic carbon is approximately 100 mg/L, and effluent is approximately 10 mg/L. Table 2-2 also shows the agreement between “Calculated TOC” and “Measured TOC”. In this table, “Calculated TOC” indicates the sum of all carbon sources. All data show that denitrification performed well in accordance with the mass balance equation.

2.3.4 Degradation Kinetics of Carbon Sources

We anticipate that in a commercial facility, upset conditions may occasionally allow breakthrough of one or more substrates. Therefore, it is desirable to know which carbon sources are preferentially degraded. In order to evaluate the reactor’s preference among the three different carbon substrates, degradation efficiency was measured along the length of the reactor for each carbon source. Samples were collected with the reactor operating at 0.6 mL/min (twice the normal flow rate was used to stress the reactor) and an inlet feed concentration ratio of 197.4 mg of NO₂⁻-N, 97.9 mg HCOO⁻-C, 71.8 mg of HCHO-C, and 13.1 mg of CH₃COO⁻-C per 1 L. The samples were taken over time over
Figure 2-5. Comparison of influent and effluent total organic carbon (TOC).
<table>
<thead>
<tr>
<th></th>
<th>Formate</th>
<th>Formaldehyde</th>
<th>Acetate</th>
<th>Calculated TOC</th>
<th>Measured TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent</td>
<td>49.9</td>
<td>35.6</td>
<td>6.5</td>
<td>92.1</td>
<td>100.2</td>
</tr>
<tr>
<td>Effluent</td>
<td>7.5</td>
<td>0.3</td>
<td>0.0</td>
<td>7.8</td>
<td>12.3</td>
</tr>
</tbody>
</table>

*Compounds are expressed in units of mg organic carbon /L.
time from the inlet (x = 0 cm), the outlet (x = 20 cm) and from 5 ports along the reactor's length.

The degradation for the carbon sources is shown in Figure 2-6. The results indicate that acetate and formaldehyde are preferentially degraded over formate. Acetate and formaldehyde degradation rates are approximately equal.

2.3.5 Influent Concentration Effect

We next investigated the treatment capability of the biological reactor at increased influent concentrations. The concentration of each hydrolysate was increased by two and four times its original concentration (original composition is 98.7 mg/L of NO$_2$-N, 49.0 mg/L of HCOO$^-$-C, 35.9 mg/L of HCHO-C, and 6.53 mg/L of CH$_3$COO$^-$-C). Region A in Figure 2-7 corresponds to the original concentration. Region B corresponds to double the influent concentration. The removal of formate, the compound which is degraded last among organic hydrolysates, initially decreased, but recovered after approximately 1000 hours; the effluent pH was approximately 7.5. Region C corresponds to a quadrupling of the original concentration. At this loading, removal efficiency of each hydrolysate dropped to 30 % or less and did not recover, even after two months. Reactor effluent pH increased to 8 to 8.5. Therefore, the concentration of hydrolysates was decreased back to twice the original concentration, and the reactor efficiency recovered to over 90 %, as shown in region D in Figure 2-7.

The result suggests that this reactor can treat hydrolysates up to twice original concentration. The alkalinity produced during conversion of nitrite to nitrogen gas and
Figure 2-6. Degradation profile of carbon sources along the column length: nitrite removal is 78%, flowrate is 0.6 ml/min and reactor inlet is located at 0 cm.
Figure 2-7. The change of hydrolysates and RDX removal efficiencies under various conditions. (A; original concentration system is acetate: 6.53 mg C, formaldehyde 35.9 mg C, formate 49.0 mg C, nitrite 98.7 mg per L. B; 2 times original concentration system. C; 4 times original concentration system. D; 2 times original concentration system. E; keeping 2 times original concentrations system, nitrate [51.8 mg NO$_3^-$-N/L] as an additional nitrogen source was added instead of nitrite [75.7 mg NO$_2^-$-N/L]. F; keeping 2 times original concentration of hydrolysates system and nitrate, trace amounts of RDX/HMX [5 mg RDX and 3 mg HMX/L] were added in the system containing nitrate as the additional nitrogen source.
the oxidation of the organic acids was sufficient to raise the pH and inhibit the reactor (the optimum pH range for denitrification is 7 to 7.5; US EPA, 1975). Equation 11 predicts that 4.33 moles of hydrochloric acid are needed to balance the alkalinity produced from the biological oxidation of the hydrolysates of one mole of RDX.

2.3.6 Changing Electron Acceptor

In a full-scale installation, it may be more desirable to use nitrate as opposed to nitrite as the additional electron acceptor for balancing the carbon sources. Nitrate is more commonly found in wastewater treatment, and is less toxic. Region E in Figure 2-7 shows the results when using nitrate instead of nitrite. At 3600 hours, the additional nitrite was replaced with nitrate, and was effectively used as an electron acceptor without any adaptation period. The culture's ability to use nitrate as an electron acceptor has implications for full-scale systems. The hydrolysates contain ammonia, which is untreated in the anoxic system. An aerobic, biological process could be used after the anoxic process. This process could be operated to nitrify the ammonia and remove any untreated organic compounds. The produced nitrate could be used as the additional electron acceptor for anoxic process if it were recycled back to the anoxic column influent. The recycle might also help with pH control.

2.3.7 RDX and HMX Biodegradation

The ability to degrade high explosives is a desirable property for the hydrolysate treatment. If so, it could degrade trace amounts of RDX or HMX that inadvertently
escaped alkaline hydrolysis. The inoculum used to start this culture (Wilkie, 1994) was also able to transform RDX and HMX to non-explosive byproducts using the same reactor system, but with nitrate as the electron acceptor and ethanol as the co-substrate. Chiou et al. (1997, 1998) showed mineralization of $^{14}$C RDX and $^{14}$C HMX using the parent culture, with $^{14}$C recovery (as $^{14}$CO$_2$) as high as 40%. Hesselmann and Stenstrom (1992) observed RDX biodegradation using acetate as a co-substrate with nitrate as the electron acceptor.

To test for RDX and HMX biodegrading ability, low concentrations of RDX and HMX were added to the influent. The first experiments were performed when nitrite was being used as an electron acceptor. Initially 5 mg/L of RDX and 3 mg/L of HMX were added. No biodegradation of RDX and HMX were observed, and the culture's ability to oxidize the organic compounds was severely impacted (at 1800 hours in Figure 2-3). The concentrations of both RDX and HMX were decreased to 1 mg/L after 45 days (about 3000 hours in Figure 2-3). However, gradual decline in organic carbon removal efficiency continued, and no explosive transformation was observed. The results suggest that RDX and HMX cannot be degraded by the culture under these conditions, and RDX and HMX can inhibit carbon oxidation. The culture quickly recovered its ability for treating hydrolysates after the explosives were removed from the system (at 3700 hours in Figure 2-3).

A second set of experiments was performed after adding nitrate as the electron acceptor. The results are shown in region F in Figure 2-7. Approximately 30% of the RDX were biodegraded and there was no impact on carbon oxidation. The culture
retained its ability to biodegrade RDX even after long periods when it was absent from the feed.

2.4 Conclusion

The application of biological denitrification for treating synthetic hydrolysates of RDX was successfully demonstrated. The results show that post-denitrification of HE hydrolysates is feasible. The following specific conclusions are made:

- The nitrite produced during alkaline hydrolysis can be used as the electron acceptor in the biological oxidation of the acetate, formate and formaldehyde produced in the hydrolysis.
- Experimental results very closely match calculated stoichiometric conversions. The removal efficiency of each byproduct as well as TOC was over 90%. The observed cell yield (mass basis) with acetate/formate oxidation and nitrite reduction was 0.21-mg cells/mg TOC or 0.16 mg cells/mg COD.
- The volumetric removal rate was as high as 170 mg/L NO₂⁻-N per day with existing organic carbon sources.
- Acetate and formaldehyde were preferentially degraded over formate.
- In a full-scale system, some form of pH control will likely be required.
- The culture was able to biodegrade RDX when using nitrate as an electron acceptor.
The study shows that the biological denitrification for treating hydrolysates of RDX is a feasible process in spite of the complexity of the system. One contribution of this work is successfully demonstrating denitrification of nitrite using various low molecular weight compounds. The results of this research may be applicable to other industrial wastewaters containing nitrite or nitrate, and multiple carbon sources. Pilot-scale research of this process is underway at the Pantex Plant in Amarillo, TX. Research is also underway to treat hydrolysates from TNT.
2.5 References


CHAPTER 3
Application of a Membrane Bioreactor for Treating High Explosives Process Wastewater

3.1 Introduction

The end of the cold war created a worldwide surplus of both conventional and nuclear weapons. The United States and other countries are destroying large quantities of weapons, which creates the need for safe and reliable disposal technologies for energetic materials and wastewaters associated with their processing. Among the high explosives that are manufactured and are used in weapons, RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine) is the most common, and is classified as a possible human carcinogen (McLellan et al., 1988).
Previous work in our laboratory over the past four years has shown that RDX can be readily destroyed by alkaline hydrolysis regeneration followed by biological denitrification (Heilmann et al. 1996; Zoh and Stenstrom, 1997). The hydrolysis process produces large quantities of concentrated wastewaters containing acetate, formaldehyde, formate, ammonia and nitrite. These byproducts can not be directly released to the environment, and require further treatment. To treat these RDX hydrolysis byproducts (hydrolysates), anoxic denitrifying process was developed that converts the hydrolysates to end products. Nitrite, which is produced during hydrolysis was used as the electron acceptor. Over 90% of each organic carbon source was removed and the results closely match the stoichiometry predicted by the empirical redox equations describing the process.

Recently, membrane separation processes have been applied to treat municipal and industrial wastewaters. Combining membranes with biological treatment is an attractive technique and has resulted in a new concept: the membrane bioreactor (MBR). The recent development of a new generation of more productive and less expensive ultra (UF) and microfiltration (MF) membranes make this possible. The MBR is defined as the combination of two basic processes-biological degradation and membrane separation-into a single process where suspended solids and microorganisms responsible for biodegradation are separated from the treated water by a membrane filtration unit (Manem and Sanderson, 1996). The entire biomass is confined within the system, providing both perfect control of the residence time for the microorganisms in the reactor (solid retention time) and the disinfection of the effluent.
In this study, the operational performance of the bench-scale MBR system, consisting of a biological denitrification reactor coupled to a ceramic ultrafiltration membrane module, was investigated for treating hydrolysates of RDX and removing biomass.

3.2 Experimental

3.2.1 Denitrifying Culture

The microorganisms were obtained from an anaerobic digester sludge at Hyperion wastewater treatment plant in El Segundo, CA. The feed contains basic growth medium containing $\text{NH}_4\text{Cl} \ 0.2 \text{ g/L}$, $\text{MgCl}_2 \cdot \text{H}_2\text{O} \ 0.1 \text{ mg/L}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O} \ 0.04 \text{ g/L}$, $\text{Na}_2\text{SO}_3 \ 0.02 \text{ g/L}$. This basic medium was supplemented with hydrolysates and trace mineral solution. The pH was maintained between 7.0 and 7.5, the optimum range for denitrification, by the adding small amount of 0.5 M $\text{H}_3\text{PO}_4$ daily to compensate pH increase from the denitrification and to provide phosphorus as a nutrient.

3.2.2 Experimental Design of MBR Unit

The performance of a ceramic ultrafiltration membrane module in the denitrification process was done in a bench-scale cross-flow ceramic membrane test unit. Figure 3-1 shows the schematic diagram of the MBR unit. This unit consists of ceramic zirconia tubular membrane with cut-off of 200 kilodalton (pore size: 0.02 μm) in a stainless steel housing (U.S Filter Co. Warrendale, PA). This membrane was 250 mm
Figure 3-1. Schematic diagram of Membrane Bioreactor.
long, and had a 7-mm channel diameter. The total membrane surface area was 0.0055 m². Membrane pressure between 21-105 kPa was tested.

The anoxic bioreactor was a Plexiglas unit with continuous stirring and an external jacket. A constant volume (1.2 L) of mixed liquor in the anoxic bioreactor was maintained using a liquid sensor situated on the surface of the mixed liquor. A Plexiglas cover was provided so that the dissolved oxygen concentration would be no more than 0.05-mg O₂/L. The two feed tanks that contain carbon sources and nitrogen sources had a volume of 5 L each. The feed solution from the bioreactor was pumped from a solution reservoir, through a membrane tube, The biomass was recycled to the bioreactor. The desired pressure was controlled by a backpressure valve. Permeate was collected from the membrane tube. The membrane was backwashed by pumping deionized water or 2% NaClO solution followed by rinsing with deionized water) through the module and then rinsing with deionized water. The regeneration procedure usually takes about 30 minutes. The first portion of backwashed water before the washing with 2% NaClO is recycled back into the bioreactor to avoid biomass loss.

### 3.2.3 Analytical Methods

Formate (HCOO⁻), nitrite (NO₂⁻), and nitrate (NO₃⁻) were analyzed using a Dionex Ion Chromatograph (basic chromatography module CMB-2, gradient pump GPM-1; Dionex, Sunnyvale, CA) with suppressed conductivity detection (conductivity detector CDM-1). An Ion Pac AS9-SC analytical column (4 mm I.D.) was used with a subsequent suppressor column. The mobile phase consisted of 0.75 mM NaHCO₃ and 2
mM Na₂CO₃ dissolved per 1L of milli-Q water. The eluent flow rate was set to 2 mL/min. Samples were manually injected into a 50-μl sample loop. Peaks were detected at retention times 1.45, 2.03 and 2.85 min. for HCOO⁻, NO₂⁻, and NO₃⁻, respectively.

For the detection of formaldehyde, a modification of the technique reported by Kuwata et al. (1979) was used. The reaction solution for formaldehyde was prepared by dissolving 0.5 g of 2,4-dinitrophenylhydrazine (DNPH) in 500 mL of 2 N hydrochloric acid and purified by shaking with 5 mL of chloroform. Formaldehyde in the sample (0.4 mL) was first allowed to react with DNPH in acidic solution (4 mL) in order to form 2,4-dinitrophenylhydrazone and solid phase extraction (SPE) method (Richard and Junc, 1986) was used to change solvent from acidic water to acetonitrile, and the solution was analyzed by High Performance Liquid Chromatography (HPLC). HPLC analysis was performed with a Hewlett Packard 1500 Series variable wavelength detector (Avondale, PA) equipped with an autosampler. An Adsorbosphere C-18 micron reversed-phase column (Altech, Deerfield, IL) was used with a mobile phase consisting of 50% acetonitrile and 50% water (volume %) at a flow rate of 1.5 mL/min. An UV detector set to 254 nm was used to detect dinitrophenylhydrazone peak at a retention time of 5.89 min.

The MBR system was monitored with daily measurements of pH, Dissolved Oxygen (DO) and temperature. Chemical oxygen demand (COD), total organic carbon (TOC), suspended solid (SS) were measured on a weekly basis. All analyses were
performed according to Standard Methods (APHA, 1992). Bacteria in the permeate were counted using a heterotrophic surface-plate counting method (Winne et al., 1996).

3.3 Results and Discussions

3.3.1 Bioreactor Performance

Zoh and Stenstrom (1997) found that the hydrolysis byproducts of RDX, consisting of acetate, formaldehyde, formate, nitrite, could be removed by using a denitrifying (anoxic) biological process, that converts the hydrolysates to harmless end products, such as N₂ and CO₂. Over 90 percent of each organic compound was removed in a packed-bed, upflow reactor. The same culture was used for the application of MBR for treating RDX hydrolysates wastewater. Feed solution was prepared using the ratio of 1.6 M NO₂⁻, 1.5 M HCOO⁻, 0.1 M CH₃COO⁻, 1.1M HCHO which is the same as RDX hydrolysates (Heilmann et al., 1996). Nitrate was added as the electron acceptor to allow all carbon sources to be oxidized. The stoichiometric balance for treating hydrolysates using biological denitrification including additional nitrate can be written as follows;

\[
(0.68 \text{NO}_3^-) + 1.6 \text{NO}_2^- + 1.5 \text{HCOO}^- + 0.1 \text{CH}_3\text{COO}^- + 1.1 \text{HCHO} \\
+ 3.88 \text{H}^+ \rightarrow 1.14 \text{N}_2 + 2.8 \text{CO}_2 + 3.94 \text{H}_2\text{O} \tag{1}
\]

Using this stoichiometry, synthetic wastewater containing these compounds was prepared as substrates (13.1 mg/L of CH₃COO⁻-C, 98.0 mg/L of HCOO⁻-C, 71.8 mg/L
Table 3-1. Original composition of the synthetic hydrolysates of RDX wastewater.

<table>
<thead>
<tr>
<th>Contribution</th>
<th>Concentration (mg COD/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetate</td>
<td>35.0</td>
</tr>
<tr>
<td>Formate</td>
<td>130.5</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>191.5</td>
</tr>
<tr>
<td>Total COD</td>
<td>357.0</td>
</tr>
</tbody>
</table>
of HCHO-C) and electron acceptors (51.9 mg/L of NO$_3^-$-N and 121.9 mg/L of NO$_2^-$-N).

The organic compound contribution to COD is shown in Table 3-1. The MBR unit was operated with this ratio for three months.

The concentration of each compound, chemical oxygen demand (COD) and total organic carbon (TOC) of the feed and permeate from the membrane were measured in order to determine removal rate. As shown in Figure 3-2 and Table 3-2, over 90% of formaldehyde, formate and nitrate were removed, but nitrite removal was only about 55%. The low nitrite removal shows the impact of cell synthesis. Insufficient carbon exists to react with the electron acceptor. Table 3-2 also shows that over 97% of COD and TOC removal (205 mg TOC/L for feed and 5 mg TOC/L for the permeate) and almost complete removal of suspended solids from the permeate.

3.3.2 Effect of Transmembrane Pressure on Flux

The transmembrane pressure was increased from 21.0 to 105.0 kPa to observe its impact on flux pattern. As shown in Figure 3-3, the flux exhibits an initial rapid decrease, followed by a slow, almost linear, decrease with time. The curve may thus be divided into two regions - Period I, where the flux decrease rapidly, and Period II, where flux decrease slowly. It is concluded that the initial rapid decrease in flux is due to a rapid increase in foulant on the surface of the membrane. Thereafter the foulant becomes limited to a constant, steady value. Changes in the characteristics of the foulant are responsible for the long-term decline.
Figure 3-2. Removal Efficiency of Each Hydrolysate Component.
### Table 3-2. The MBR process performance for hydrolysates of RDX wastewater

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Permeate</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>357</td>
<td>10.5 ± 3.0</td>
<td>97.2</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>205 ± 10</td>
<td>5.0 ± 1.5</td>
<td>97.6</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>125</td>
<td>&lt;5</td>
<td>&gt; 96</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>53 ± 2</td>
<td>&lt;0.1</td>
<td>&gt; 99.8</td>
</tr>
<tr>
<td>pH</td>
<td>7.0 ± 0.1</td>
<td>7.4 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>NO$_3^-$ (mg/L)</td>
<td>230</td>
<td>15.5</td>
<td>93.3</td>
</tr>
<tr>
<td>NO$_2^-$ (mg/L)</td>
<td>400.5</td>
<td>180.5</td>
<td>55.0</td>
</tr>
</tbody>
</table>
Figure 3-3. Effect of Transmembrane Pressure on Flux (SS= 200-250 mg/L).
There are two theories for the phenomena — pressure controlled model (concentration polarization), and mass transfer controlled model (film theory) (Cheryan, 1986). As shown in Figure 3-3, after a short time (within 20 min), the flux is independent of transmembrane pressure, therefore, mass-transfer is dominant. Equation 2 shows this theory.

\[ J = \frac{D}{\delta} \ln \frac{C_g}{C_b} = k \ln \frac{C_g}{C_b} \]  

(2)

Where \( J \) is the permeate flux and \( C_B \) is the bulk concentration of bacteria, \( C_G \) is the "gel" concentration at the membrane surface, \( D \) is the diffusion coefficient and \( k \) is the mass transfer coefficient. Note in this model, there is no pressure term, and increase in transmembrane pressure does not increase flux. This model is valid only in the pressure-independent region, and fits this MBR system.

3.3.3 Temperature Dependence of Flux.

In general, higher temperatures will increase flux. Cheryan (1986) found that as temperature increased, the beneficial effects (lower viscosity, higher diffusivity) result in a net increase in flux. In the mass transfer-controlled region, temperature is expected to have a significant effect since diffusivity increases with temperature according to the modified Stokes-Einstein equation:
Figure 3-4. Temperature dependence of Flux (steady-state flux chosen at $t = 30$ minutes).
\[ D_i = \frac{D \eta_2 T_1}{T_2 \eta_1} \]  

where \( D \) is the diffusion coefficient, and \( \eta \) is the dynamic viscosity of the permeate, \( T \) is the absolute temperature, and the subscript 1 and 2 refer to two different temperature.

Temperature experiment was accomplished only between 15 and 40 °C (287-313 °K) because the microbial culture is also limited by temperature. High temperature operation will result in bacteria denaturation and other heat damage to bacteria. As shown in Figure 3-4, a small increase in steady-state flux (from 0.22 to 0.27 \( \text{m}^3/\text{m}^2/\text{day} \)) was observed in this temperature range. An operating temperature is in the 25-35 °C for the MBR is probably the best.

3.3.4 Effects of Suspended Solids and Hydrolysates Concentration

The flux showed a strong dependence on the suspended solids concentration. According to the mass transfer model in Equation 2, as \( C_B \) (bulk concentration of bacteria) increases, the permeate flux \( (J) \) decreases. Figure 3-5 shows the results. The change in suspended solids concentrations markedly affect the absolute value of the flux. We also investigated maximum loading rate of the MBR by increasing the concentrations of hydrolysates. From the results, the MBR reactor can treat hydrolysates up to 2 time’s original concentration system (26.3 mg/L of CH\(_3\)COO⁻-C, 196.0 mg/L of HCOO⁻-C, 143.6 mg/L of HCHO-C, and 245.0 mg/L of NO\(_2\)⁻-N) corresponding 0.72 kg COD/m\(^3\)/day with HRT of 20-24 hours.
Figure 3-5. The Impact Biomass Concentration on the Permeate Flux.
Figure 3-6 shows the effect of increasing hydrolysates concentration on suspended solids concentration. When the loading rate is increased, the biomass concentration increases as well. At day 120, the concentration of the feed was doubled. From then, suspended concentration increased slowly from around 300 mg/L to up to 550 mg/L. F/M ratio only increased from 0.33 to 0.50 kg N/kg SS/day due to increasing suspended solids concentration.

3.3.5 Filtration Performance

The biomass population in the bioreactor and from the MBR permeate were analyzed using the bacteria counting method. This assay was carried out following the heterotrophic surface-plate counting method. This method is a quantitative method for the direct measurement of viable numbers of bacteria in a water environment. None of the plates inoculated with permeate samples showed colonies. This test was repeated and the same observation was made. The few colonies observed at the end of the cyclic run in the treated water probably come from the detachment of some bacteria that are able to grow on the inner surface of the housing.

3.3.6 Membrane Fouling and Cleaning

Concentration polarization and the fouling of membranes are problems inherent to high recovery in membrane process. To overcome these problems, crossflow membrane (MF or UF) filtration was used (Chaize and Huyard, 1991). Maintaining a high cross flow velocity and high pressure to improve flux without cleaning membranes
Figure 3-6. Changes in biomass concentration in the MBR.
requires excessive energy. Therefore, an efficient and inexpensive cleaning technique is usually required to make a membrane process as cost-effective.

Figure 3-7 shows long-term flux change and cleaning cycle of the membrane. The membrane was washed during these experiments, and the washings resulted in an increase in the permeation flux. During a typical cycle (3-4 days), suspended solids accumulated on the membrane surface, and the permeation flux decreased to 7-15% of the initial value. At the end of the cycle, the permeation flux stabilized at about 0.10–0.15 m³/m²/d (4.17-6.25 L/m²/h). Average permeate flux was obtained by measuring permeate volume over certain time interval, and was 0.20 m³/m²/d. Depending on the membranes used, filtration performances vary from 0.05 to 10 m³/m²/d (Manem and Sanderson, 1996).

Various methods have been proposed to reduce fouling. These methods can be classified into two general categories: chemical and physical. Several cleaning methods were attempted to recover water flux including acid-base washing, backwashing. From the results, a backwashing procedure was selected to recover membrane flux. The backwashing were performed by pumping with deionized water or chlorine solution (2% NaClO solution) through the membrane module. Figure 3-7 shows original flux recovery from backwashing with both methods. As shown in this figure, the original recovery flux (about 2.0 m³/m²/day) was accomplished by backwashing with chlorine solution; only 50% of original flux was obtained by backwashing with deionized water. This shows chlorine solution backwashing is more effective for cleaning a membrane to recover original flux. However, backwashing with deionized water is recommended
Figure 3-7. Permeation Flux as a Function of Time.
(Other flux recoveries are from deionized water backwashing).
because the net cumulative volume with chlorine backwashing was not much different from that of deionized water backwashing. Another reason is that chemical cleaning can hurt the microorganism even though no contact is allowed between chlorinated water and bacteria in the bioreactor. Finally backwashed water containing chlorine is discharged with excess sludge from the bioreactor, which may present a problem in some cases.

The membrane cleaning process with deionized water backwashing restored most of the membrane flux. It is necessary to use the chemical cleaning procedure for complete flux restoration. Therefore the membranes should be occasionally backwashed with chlorine solution in order to prevent internal and external fouling.

Considering the recovery of permeates flux and net cumulative permeate volumes, 1-day filtration and 30-minutes of backwashing cycle was found to be the optimum operation mode. Therefore the cycle of cleaning membrane was also changed from biweekly to everyday. With the cycle of 1-day filtration and 30-minutes backwashing, the net cumulative permeate volume was increased up to 200% compared to biweekly cleaning operation.

3.3.6 Comparison of Performance with Packed-Bed Reactor (PBR)

Zoh and Stenstrom (1997) also treated RDX alkaline hydrolysis byproducts in a denitrifying (anoxic) packed-bed upflow reactor. Over 90% removal of the organic compounds and nitrite were observed in a reactor with three-hour retention time. Table 3-3 summarizes the performance results obtained with the two treatment systems. TOC
Table 3-3. Performance comparison between the packed-bed reactor (Zoh and Stenstrom, 1997) and MBR for treating hydrolysates.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PBR</th>
<th>MBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC Removal (%)</td>
<td>&gt; 90</td>
<td>97.6</td>
</tr>
<tr>
<td>SS of Effluent (mg/L)</td>
<td>55 (±4)</td>
<td>3.5 (±1.1)</td>
</tr>
<tr>
<td>Loading Rate (mg COD/L/day)</td>
<td>357</td>
<td>714</td>
</tr>
<tr>
<td>Phosphate Buffer</td>
<td>used</td>
<td>not used</td>
</tr>
</tbody>
</table>
removals of both treatment systems were almost identical. As expected, MBR was dramatically more efficient than PBR for the removal of SS. The suspended solids concentration of the effluent of PBR was about 55.2 (± 4.0) mg/L, and the permeate from the MBR was 3.5 (± 1.1) mg/L. This means that the MBR effectively retains the biomass and achieves better effluent quality.

The MBR treated hydrolysates with higher loading rate than PBR. While PBR reactor could treat hydrolysates up to COD of 357 mg/L (197.4 mg/L of NO$_2^-$.N, 97.9 mg/L HCOO$^-$.C, 71.8 mg/L of HCHO-C, and 13.1 mg/L of CH$_3$COO$^-$.C) in 28 hours, MBR was able to treat up to 714 mg COD/day (26.3 mg/L of CH$_3$COO$^-$.C, 196.0 mg/L of HCOO$^-$.C, 143.6 mg/L of HCHO-C, and 245.0 mg/L of NO$_2^-$.N) in 24 hours.

The limits to treatment in both systems are probably pH control. Alkalinity is produced during conversion of nitrite to nitrogen gas and the oxidation of the organic acids. It was more difficult to control pH in the PBR reactor. Phosphate buffers consisting of 0.036 M of K$_2$HPO$_4$ and 0.016 M of NaH$_2$PO$_4$.H$_2$O were used in the feed solution to the PBR. However, in a pilot or full scale system, buffering is not practical because of cost and effluent quality. However, the MBR system has a completely mixed reactor that can be easily maintained between 7.0 and 7.5 by the adding small amounts of 0.5 M H$_3$PO$_4$. This should make the MBR system more practical in a pilot or full scale system.

3.4 Conclusions
The MBR system effectively treated wastewater containing RDX hydrolysates with high removal efficiencies. Approximately 97% COD and 93% of nitrate, and 55% of nitrite were removed in the MBR. The MBR was capable of very efficiently separating the biomass and effluent, which produced a clear final effluent. The following conclusions are presented:

- Treated water is free of suspended solids and evidenced by low TSS (~1 mg/L) and low heterotrophic surface bacteria counts.
- Increasing transmembrane pressure did not help the permeate flux.
- Increase of temperature affected flux, but was not significant.
- Increase of suspended solids concentration decreased the permeate flux significantly.
- The MBR allows HRT and SRT to be controlled independently.
- The maximum loading rate was 0.50 kg N/kg SS/day or 1.82 kg COD/kg SS/day with an F/M of 0.5 kg N/kg SS/day.
- Membrane backwashing is required to maintain flux.

The MBR process is well suited to applications that require small reactors, and improvements obtained by optimizing filtration performance will help extend its application for treating other wastewaters.
3.5 References


CHAPTER 4

The Kinetics of Fenton Oxidation of RDX and HMX

4.1 Introduction

Wastewaters generated at former munitions production facilities contained high explosives compounds such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 2,4,6-trinitrotoluen (TNT) (Urbanski, 1964). RDX and HMX are the most important high explosives used by the U.S. and European munitions industry. During World War II, RDX production in the United States and Germany averaged from 15,200,000 to 7,100,000 kg per month, respectively.

The US EPA (McLellan et al., 1988) classifies RDX as a Possible Human Carcinogen (Class C). A lifetime health advisory for exposure to this compound in
drinking water is set to and 0.002 mg/L by EPA. HMX is often found together with RDX as an environmental contaminant. RDX and HMX are more energetic than TNT, and they are used in both conventional and nuclear weapons. Past disposal of these wastewaters to the surrounding environment has resulted in numerous acres of contaminated soils and groundwater (Comfort et al., 1995; Spalding and Fulton, 1988).

Bioremediation, although possible, may require excessive time or too costly to oxidize RDX and HMX in aqueous solution. Strong oxidants may be a useful treatment technique for these applications. Products resulting from chemical oxidation might be more amenable to biological treatment than the parent compound.

Advanced oxidative processes are commonly used for remediating water contaminated with organic compounds (Sedlack and Andren, 1991; Venkatadri and Peters, 1993). The Fenton reaction is the one of the oldest and most powerful oxidative treatment available. This reaction has been used to treat wastewater containing recalcitrant organic pollutants.

Li et al. (1997a; 1997b) previously showed that the Fenton reaction could effectively destroy TNT in water and soil. TNT destruction involved denitrification and hydroxylation of the nitroaromatics to yield oxalate, carbon dioxide, and nitrate (Li et al., 1997b). TNT mineralization by Fenton oxidation was photocatalyzed with greater than 90% mineralized within 24 h.

The objective of this study is to determine the potential to use the Fenton reaction to destroy RDX and HMX. In this paper, we investigated the chemical kinetics of Fenton oxidation of RDX and HMX under acidic aqueous conditions. Various factors
that are important to maximizing oxidation were studied, and the principal reaction byproducts were also determined.

4.2 Experimental

4.2.1 Reagents

Technical grade hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) was obtained from Lawrence Livermore National Laboratory (Livermore, CA). Reagent grade 30% H$_2$O$_2$, FeSO$_4$·7H$_2$O, (Fisher Scientific, Pittsburgh, PA) were used as purchased.

4.2.2 Experimental Section

Experiments were performed in a water bath between 20 and 50 °C, and were held at constant temperature for at least one hour prior to start of a kinetic run. The reactions were conducted in a 500-mL flask in the dark condition. The ferrous ions were added in the form of FeSO$_4$·7H$_2$O, and the calculated amounts of 30% H$_2$O$_2$ solution. The reaction was started by adding FeSO$_4$·7H$_2$O, and the calculated amounts from 30% H$_2$O$_2$ stock solution to a known aqueous solution of RDX (10 mg/L) or HMX (4.5 mg/L). Molar ratio of 4600:48:1 was maintained for Fe$^{2+}$, H$_2$O$_2$, and RDX (or HMX). RDX and RDX are sparingly soluble in water. The solubility limits at 25 °C are ~5mg of HMX/L (Rosenblatt et al., 1991) and ~45 mg of RDX/L (Gibbs and Popolato, 1980), respectively. The initial pH of the solution was fixed at 3 using 1N H$_2$SO$_4$ to maximize reaction rates (Sedlak and Andren, 1991; Watts et al., 1990a, 1990b; Kuo 1992). The 500-mL flask was stirred using a stainless steel mixer. One mL samples were taken at
predefined times using 1 cc-microsyringes. Samples collected in less than 2 seconds, and were immediately filtered into cooled (0 °C) HPLC vials for analysis. Another 10-ml aliquot was collected for TOC analysis using a Beckman Model 915B TOC analyzer.

4.2.3 High performance liquid chromatography (HPLC) analysis – RDX and HMX

Liquid samples were filtered through 0.2 μm membrane filters and analyzed by HPLC. A Hewlett Packard 1500 Series instrument equipped with a variable wavelength detector and an autosampler. An Adsorbosphere C-18 10-μm reversed-phase column (Alltech, Deerfield, IL) with prefilter element and guard column (C18, 5-μm, Alltech) were used with a mobile phase consisting of 30 % methanol, 30 % acetonitrile, and 40 % water (volume %) at a flow rate of 1.0 mL/min. A UV detector set to 236 nm was used, and RDX and HMX peaks at retention times of 3.6 min and 4.1 min were observed.

4.2.4 Ion chromatography - Nitrate

Nitrate (NO₃⁻) was analyzed using a Dionex Ion Chromatograph (basic chromatography module CMB-2, gradient pump GPM-1; Dionex, Sunnyvale, CA) with suppressed conductivity detection (conductivity detector CDM-1). An Ion Pac AS9-SC analytical column (4 mm I.D.) was used with a subsequent suppressor column. The mobile phase consisted of 0.75 mM NaHCO₃ and 2 mM Na₂CO₃ dissolved in deionized water from Millipore Co. (Freehold, NJ). The eluent flow rate was set to 2 mL/min. Samples were manually injected into a 50-μl sample loop.
Peaks were detected at retention times between 4.9 and 5.0 minutes for $\text{NO}_3^-$. The peak area was a linear function of the concentration between 1.0 to 15.0 mg $\text{NO}_3^-$/L. For the external calibration, at least three data points were gathered for each standard concentration. The mean was then used for the calibration curve. All samples were filtered through sterile Acrodisc-13 0.2-μm syringe-microfilters (Gelman Sciences, Ann Arbor, MI) before injection.

### 4.2.5 Gas Chromatography/Mass Spectroscopy (GC/MS)

Samples were analyzed using a GC/MS, consisting of a Finnigan gas chromatograph Model 9610 equipped with a Grob-type splitless injector and a Finnigan quadrupole mass spectrometer Model 4000 with an INCOS Model 2300 data system. The GC/MS was operated with electron energy of 70 eV, a source temperature of 240 °C, and a scan speed of 1s scan-1 from 50 to 550 amu. A 30-m DB5-MS (0.25 mm I.D., 25-μm film thickness, J&W Scientific, Folsom, CA) fused silica column was programmed for 4 min at 30 °C.

### 4.2.6 Liquid-Liquid-Extraction (LLE)

Prior to GC/MS analysis, samples were extracted and concentrated with dichloromethane (Optima-grade, Fisher Scientific). A total of 500 mL of the sample was contacted with 100 mL of dichloromethane in a Pyrex accelerated one-step extractor (Pyrex, Corning, NY). The concentrator tube was kept in a water bath at 80 °C. Recondensation of the recirculating dichloromethane was achieved with a condenser on
top of the extractor body that was operated at 2-4 °C. After 5.5 h, the extraction was complete, and the solvent was concentrated to 1-5 mL. The sample volume was then further reduced by evaporation to 500 μL with 99.999% helium gas. The concentrated sample was transferred into an autosampler vial using a gas-tight syringe with attached luer-tip needle. The vial was closed and sealed with a Teflon-lined cap. The final sample concentration was 1:2000 with this method.

4.2.7 TOC Measurement

TOC was measured with a Beckman Model 915B TOC analyzer was used following procedures described in Standard Methods. Samples were filtered through membrane filters, acidified to a pH lower than 2 using phosphoric acid to liberate inorganic CO₂ and refrigerated prior to analysis.

4.2.8 Gas Analysis

A special series of experiments were performed to analyze the gas produced during the reaction. 5-mg of RDX and HMX were put into a gas tight glass reactor; total reactor volume was 250 mL. The system was then sealed and purged with 99.999% helium gas for 10-15 minutes in order to remove air inside the reactor. The reactor was sealed, and kept at a constant temperature (T = 25 °C) and continuously stirred. The calculated amounts of FeSO₄ · 7H₂O and 30 % H₂O₂ were added into the sealed system by using syringes. Gas samples were taken at the end of the reaction (after 6 hours). The liberated gas volume was measured using attached syringes, and the gas samples
were analyzed with gas chromatograph. A Varian 3400 Series chromatograph was used with a thermal conductivity detector and a 2m x 2mM Pyrex column packed with 80/100 mesh Porapak QG (Alltech Associates, Inc.). Carrier gas was helium (99.9995% purity at 80 mL/min). Temperatures were 100 °C (injector), 60 °C (column), and 110 °C (detector). Samples were collected with a 1-mL glass Pressure-Lok series A-2 syringes equipped with a Teflon plunger and push-button valve (Precision Scientific).

4.3 Results and Discussions

4.3.1 Mechanisms

Understanding the reaction mechanism for the oxidation of RDX and HMX under conditions relevant to wastewater treatment is an essential step in the design of an efficient, cost-effective Fenton's reagent treatment systems. These factors are especially important in order to determine appropriate pH and oxidant concentrations. Identification and quantification of intermediate and byproducts are also important because a successful RDX or HMX treatment system must be free of harmful byproducts.

According to Walling (1975), the basic mechanism of the Fenton treatment process consists of chemical oxidation and chemical coagulation of organic compounds. In an acidic environment, Walling (1975) proposed that hydrogen peroxide in the presence of excess ferrous ions reacts in the following way:

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}^\cdot
\]  

(1)
The products of the reaction are the ferric ion, the hydroxyl radical (·OH), and the hydroxide ion (OH\(^-\)). The OH radical produced in Equation 1 is capable of reacting with a variety of organic compounds. Hydroxyl radicals are nonspecific oxidants that react with most organic contaminants at rates close to diffusion in water [\(-10^{10} \text{ l/(M's)}\)] (Kakarla and Watts et al., 1997).

Oxidation products of organic substrate obtained via addition of ·OH, or via hydrogen atom abstraction, are presented in the following two equations (Yang and Carberry, 1994):

\[
\begin{align*}
\text{HO}^- + \text{R} & \rightarrow (\text{HO}) \rightarrow \text{hydroxylated product} \quad (4) \\
\text{HO}^- + \text{RH}_n & \rightarrow (\text{RH}_{n-1}) + \text{H}_2\text{O} \rightarrow \text{oxidized product} \quad (5)
\end{align*}
\]

### 4.3.2 Kinetic Models

The following reaction can represent the chemical oxidation of the Fenton treatment process reaction kinetics. A second-order rate equation was applied to fit the data:

\[
\frac{dC_{\text{HE}}}{dt} = -k_{\text{HE}} C_{\text{HE}} C_{\text{OH}^-} \quad (6)
\]
Figure 4-1. Fenton oxidation of RDX under different temperature.

(RDX = 0.045 mmol, Fe$^{2+} = 0.72$ mmol, H$_2$O$_2$ = 210 mmol/L)
where $C_{HE}$ is the concentration of high explosive compound (RDX or HMX), $C_{OH}$ is the hydroxyl radical concentration, and $k_{HE}$ is the second order rate constant. In the case of constant hydroxyl radical concentration, or in excess concentration compared to substrate (high explosives), equation 6 can be reduced to a pseudo first-order rate equation:

$$\frac{dC_{HE}}{dt} = -k_{HE}' C_{HE} \quad (7)$$

where $k_{HE}'$ is the pseudo first-order rate constant. If $t = 0$, then $C_{HE}$ is equal to $C_{HE, t=0}$ and integration from 0 to $t$, the solution of the differential equation (Equation 7) is:

$$\ln \frac{C_{HE}}{C_{HE, t=0}} = -k_{HE}' t \quad (8)$$

Pseudo first-order rate constants can be obtained through a linear least square fit of the sample data to Equation 8.

To determine whether this model fits, first, batch reactions of RDX and HMX with Fenton’s reagents constant conditions of 0.045 mmol/L for RDX and 0.015 mmol/L for HMX; $[H_2O_2]_0$ and $[Fe^{2+}]$ is 69.2, and 2.16 mmol/L for RDX, and 23.0 mmol/L, 0.72 mmol/L for HMX, respectively. The pH was fixed to 3.0 and temperature was 20, 25, 30, 40, 50 ºC.

Figure 4-1 and shows the results of RDX Fenton oxidation. At 25 ºC and pH 3, Fenton oxidation of RDX is very fast, and after 70 min, only 10% of RDX remains. At
Figure 4-2. Temperature dependence of rate constant of Fenton oxidation of RDX (RDX = 0.045 mmol, Fe$^{2+}$ = 0.72 mmol, H$_2$O$_2$ = 210 mmol/L).
Figure 4-3. Temperature dependence of rate constant of Fenton Oxidation of HMX (HMX = 0.015 mmol, Fe$^{2+}$ = 0.72 mmol, H$_2$O$_2$ = 69.2 mmol/L).
Table 4-1. Pseudo-first-order rate constants (min$^{-1}$) of Fenton oxidation of RDX and HMX for different temperatures.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>RDX</th>
<th>R$^2$</th>
<th>HMX</th>
<th>R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.0167</td>
<td>0.994</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.0241</td>
<td>0.998</td>
<td>0.0080</td>
<td>0.994</td>
</tr>
<tr>
<td>30</td>
<td>0.0294</td>
<td>0.997</td>
<td>0.0119</td>
<td>0.995</td>
</tr>
<tr>
<td>40</td>
<td>0.0647</td>
<td>0.998</td>
<td>0.0239</td>
<td>0.999</td>
</tr>
<tr>
<td>50</td>
<td>0.1159</td>
<td>0.999</td>
<td>0.0358</td>
<td>0.996</td>
</tr>
</tbody>
</table>
higher temperatures, the rate is much faster. From all temperature ranges (20 to 50 °C), the pseudo first-order reaction mechanism fits the data well with R² values were between 0.994-0.999 (Figure 4-2). Similar results were obtained on HMX oxidation (Figure 4-3), but the rate of HMX oxidation is much slower.

The rates of Fenton oxidation of RDX are approximately 2.8 times greater than the rates for the Fenton oxidation of HMX at similar temperature, the difference in rates increases at higher temperature (Table 4-1). An increase in temperature of 10 °C produces an increase in the rate of 1.4-2.2 fold for the Fenton oxidation of RDX and 1.5-2.0 fold for HMX over the investigated temperature range.

4.3.3 Arrhenius Plot of Rate Constant

The effect of changing temperature on the reaction rate of RDX and HMX can make us to calculate activation energy using Arrhenius Equation (Equation 9). The temperature dependency of pseudo first-order reaction rate coefficient can be represented using the Arrhenius equation:

$$\ln k_{HE}(T) = \ln A - \frac{E}{R \cdot T}$$ (9)

where $A$ is the empirical Arrhenius factor or pre-exponential factor; $E$ is the activation energy (J mol⁻¹), $T$ is the absolute temperature (°K) and $R$ is gas constant (8.314 J mol⁻¹). The Arrhenius factor $A$ and the constant $E/R$ can be determined from a linear-squares fit of the logarithm of the rate constant and the reciprocal of the absolute temperature.
Table 4-2. Temperature dependency of pseudo-first order rate constants of Fenton oxidation of RDX and HMX: Arrhenius parameter and Activation Energy.

<table>
<thead>
<tr>
<th></th>
<th>In A</th>
<th>E (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDX</td>
<td>16.95</td>
<td>51.3</td>
</tr>
<tr>
<td>HMX</td>
<td>14.77</td>
<td>48.6</td>
</tr>
</tbody>
</table>
Figure 4-4. Arrhenius plot of pseudo-first order rate constants of Fenton oxidation of RDX and HMX.
With respect to our results we consider the activation energy to be temperature independent over the range from 20 to 50 °C. The values of the activation energies were 51.3 (RDX) and 48.6 (HMX) kJ·mol⁻¹, respectively (Table 4-2 and Figure 4-4). This result suggests that RDX and HMX Fenton oxidation occurs with a similar reaction mechanism.

4.3.4 Impact of Changing H₂O₂ and Fe²⁺ concentration

Fenton’s reagent is most likely to be effective in on-site treatment application rather than in situ because the reaction would require through mixing of the contaminants and co-substrates. The possibility exists that iron which is naturally present in soils and groundwater catalyzes Fenton’s reaction when H₂O₂ is added in situ. However, because the optimum pH for oxidation of organics by Fenton’s reaction is in the acidic range, significant reaction rates may not occur in groundwater and in situ remediation cases involving H₂O₂ injection without pH modification (Venkatadri and Peters, 1993).

The investment costs for application of Fenton’s reagent is usually expected to be low. The primary factor contributing to the chemical costs of Fenton’s reagent is the cost of H₂O₂ ($1.72/gallon for 50 wt % aqueous solution) (Watts et al., 1990a). For this reason, it may be important to optimize the amount of H₂O₂ required, especially in the treatment of contaminated soils.

For these reasons, the impact of changing Fe²⁺ or H₂O₂ concentration on Fenton oxidation should be investigated. First, the concentration of Fe²⁺ was maintained at 0.72
Table 4-3. The impact of the $\text{H}_2\text{O}_2$ concentration on pseudo-first-order rate constants of Fenton oxidation of HMX with constant concentration of $\text{Fe}^{2+}$ ($\text{Fe}^{2+} = 0.72 \text{ mmol/L}$, HMX = 0.0152 mmol/L, pH = 3).

<table>
<thead>
<tr>
<th>$\text{H}_2\text{O}_2$ concentration (mmol/L)</th>
<th>k (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.92</td>
<td>0.0154</td>
</tr>
<tr>
<td>34.6</td>
<td>0.0136</td>
</tr>
<tr>
<td>69.2</td>
<td>0.0128</td>
</tr>
</tbody>
</table>

Table 4-4. The impact of $\text{Fe}^{2+}$ concentration on pseudo-first-order rate constants of Fenton oxidation of HMX with constant concentration of $\text{H}_2\text{O}_2$ ($\text{H}_2\text{O}_2 = 69.2$ mmol/L, HMX = 0.0152 mmol/L, pH = 3).

<table>
<thead>
<tr>
<th>$\text{Fe}^{2+}$ concentration (mmol/L)</th>
<th>k (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.36</td>
<td>0.0154</td>
</tr>
<tr>
<td>0.72</td>
<td>0.0128</td>
</tr>
<tr>
<td>2.16</td>
<td>0.0195</td>
</tr>
</tbody>
</table>
Figure 4-5. The impact of increasing both $\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}$ concentration on rate constant of Fenton oxidation of RDX ($\text{RDX} = 0.045 \text{ mmol/L}, \text{Fe}^{2+} : \text{H}_2\text{O}_2 = 1 : 95$)
Figure 4-6. The impact of increasing both $\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}$ concentration on rate constant of Fenton oxidation of HMX (HMX = 0.015 mmol, $\text{Fe}^{2+}: \text{H}_2\text{O}_2 = 1:95$)
mmol/L, and \( H_2O_2 \) concentration was increased from 6.92 to 69.2 mmol/L for oxidation of 4.5 mg of HMX/L. Table 4-3 shows that the pseudo first-order rates constant. It implies that increasing \( H_2O_2 \) concentration while keeping \( Fe^{2+} \) concentration for HMX oxidation does not improve the rate. Another experiment was performed with keeping \( H_2O_2 \) concentration at 69.2 mmol/L, while increasing \( Fe^{2+} \) concentration from 0.36 to 2.16 mmol/L (Table 4-4). At this time also, the rate constant did not increase. This suggests that oxidation rate can be increased only by increasing both \( Fe^{2+} \) and \( H_2O_2 \) concentration in the oxidation of HMX.

Therefore, the effect of varying both initial \( Fe^{2+} \) and \( H_2O_2 \) concentration on the reaction of RDX and HMX was investigated as next step. Reagent concentrations were increased with the ratio of \( Fe^{2+}: H_2O_2 =1:95 \). Figure 4-5 and 4-6 shows that as both concentrations are increased, pseudo first order rate constant was increased from RDX oxidation rate was increased from 0.18 to 0.65 min\(^{-1}\), and HMX rate increase was smaller than RDX, but increased from 0.008 up to 0.03 min\(^{-1}\).

### 4.3.5 The Byproducts of Fenton Oxidation

The next step is to investigate the byproducts of Fenton oxidation of RDX and HMX. First, we found nitrate ion in both RDX and HMX endproducts solution from Ion Chromatography analysis. However, no nitrite ions were found in both RDX and HMX solution. Figure 4-7 and 4-8 shows the kinetics of RDX and HMX degradation and \( NO_3^- \) formation by Fenton oxidation. The molar yields are approximately 1.5 M \( NO_3^- \) formed/M RDX oxidized and 1.75 M \( NO_3^- \) formed/M HMX oxidized. These results
Figure 4-7. Kinetics of RDX degradation and \( \text{NO}_3^- \) formation by Fenton oxidation (RDX = 0.045 mmol, Fe\(^{2+} \) = 2.16 mmol, \( \text{H}_2\text{O}_2 \) = 210 mmol/L)
Figure 4-8. Kinetics of HMX degradation and NO$_3^-$ formation by Fenton oxidation (HMX = 0.015 mmol, Fe$^{2+}$ = 0.72 mmol, H$_2$O$_2$ = 69.2 mmol/L).
indicated that $\text{NO}_3^-$ is a direct product from RDX and HMX formed during the first reaction step in timely accordance with RDX and HMX degradation. Therefore, nitrate can be chosen as a surrogate parameter to indicate reaction rate during Fenton oxidation.

Another sets of experiments were performed with TOC analysis of RDX reaction products. An increase in mineralization of RDX was progressively obtained by Fenton oxidation. Figure 4-9 shows TOC removal vs. time during oxidation at pH 3.0 containing 23.0 mmol $\text{H}_2\text{O}_2$ and 2.16 mmol $\text{Fe}^{2+}$/L in 10 mg RDX/L. The Fenton process destroyed 85% of TOC after 8 h of oxidation of a 10 mg/L RDX solution. Almost complete mineralization of RDX was achieved using Fenton reagent. However, we failed to measure the TOC in HMX solution because initial concentration was too low (0.85 mg TOC/L).

Even though we found nitrate as a byproduct from Fenton’s reaction with both RDX and HMX, the recovery of nitrogen from RDX and HMX was only 25% and 22%, respectively. Visible gas evolution suggested gaseous byproducts. To identify and quantify the gas byproducts from RDX and HMX reaction products, 5-mg of RDX or HMX was put into a gas tight glass reactor with total reactor volume of 200 mL. The system was then sealed and purged with 99.999 % helium gas for 10-15 minutes in order to remove the air inside the reactor. Syringes, in the closed portion, were attached after the reactor was sealed to measure gas volume produced after the reaction. The solution was kept at a constant temperature ($T= 25 \, ^{\circ}\text{C}$) and continuously stirred. The calculated amounts of $\text{FeSO}_4\cdot7\text{H}_2\text{O}$ and 30% $\text{H}_2\text{O}_2$ from stock solutions were next added into the
Figure 4-9. Mineralization of RDX by Fenton Oxidation
(pH = 3, RDX = 0.045 mmol, Fe$^{2+}$ = 2.16 mmol/L, H$_2$O$_2$ = 210 mmol/L).
sealed system. Gas samples were taken at the end of the reaction (about after 6 hours). The gas volumes from each reactor were measured using attached graduated syringes.

The gas analysis showed that 0.408 % N₂ and 0.065 % CO₂ from RDX, the remaining 71.0 % were composed of oxygen, argon, water. Using the ideal gas law and the gas volume produced during the reaction, the total moles produced from Fenton oxidation were 0.053 mmol of N₂ and 0.008 mmol of CO₂. The normalized molar yield is 2.36 M N₂ and 0.37 M CO₂/M RDX oxidized. (Table 4-5). The HMX byproducts were 0.3368 % N₂ and 0.0415 % CO₂. The remaining 67.9 % was comprised of oxygen, argon, and water. The total productions were 0.0326 mmol of N₂ and 0.004 mmol of CO₂. The normalized molar yield is 1.94 M N₂ and 0.24 M CO₂/M HMX oxidized. (Table 4-5).

Finally, in order to further determine the byproducts from RDX and HMX. The reaction end products of RDX and HMX Fenton Oxidation were analyzed using liquid-liquid extraction (LLE) and GC/MS analysis. Organic intermediates or end-products, if extractable by dichloromethane and chromatographable, will be detected with this method. The samples were concentrated from 500 mL to 500-uL. A comprehensive set of blank samples was extracted with LLE and analyzed with GC/MS. LLE system blanks (100 mL of dichloromethane with no sample and recirculated for 5.5 h) as well as GC/MS system blanks (GC/MS injection of pure Optima-grade dichloromethane, Fisher scientific) were analyzed at various stages in the experiment to detect any system changes or contamination. Deionized water and HPLC-grade water blanks were also extracted (LLE) and analyzed. Potential contamination from the Fenton's reagents was
Table 4-5. Normalized molar yields for products of Fenton Oxidation of RDX and HMX (Results from liquid analysis and gas analysis)*.

<table>
<thead>
<tr>
<th>Byproducts</th>
<th>RDX</th>
<th>HMX</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃⁻</td>
<td>1.50</td>
<td>1.75</td>
</tr>
<tr>
<td>N₂</td>
<td>2.36</td>
<td>1.94</td>
</tr>
</tbody>
</table>

*M product formed/M RDX (or HMX) oxidized.
determined with a set of blanks (12 mL of 30% H$_2$O$_2$ and 0.4 g of FeSO$_4$ · 7H$_2$O in 500 mL of deionized water or HPLC-grade water, respectively). Finally, RDX and HMX Fenton oxidation samples were prepared with deionized water (10 mg RDX or 4.5 mg HMX, respectively), and stirred for 1 days in 100 mL of water with 12 mL of 30% H$_2$O$_2$ and 0.4 g of FeSO$_4$ at 25 °C. No further intermediates or end products could be detected by GC/MS analysis.

4.3.6 Proposed Mechanism

A general pathway involving mineralization of RDX to CO$_2$ at pH 3.0 from Fenton oxidation is proposed. The main oxidizing species is ·OH, although some reactions with HO$_2^-$ could also take place. Since ·OH is a stronger oxidizing radical than HO$_2^-$, all oxidation reactions are strongly accelerated in the presence of Fe$^{2+}$. The mineralization process is initiated by hydrogen abstraction of carbon. The resulting carbon radical can undergo the destruction of N-N bond, and resulting ·NO$_2$ reacts with ·OH to release of NO$_3^-$. The carbon radical can accept another ·OH, and resulted in formation of HCOOH. This functional group is transformed to CO$_2^-$, and the final product is CO$_2$ (Equations 10, 11).

\[
\begin{align*}
\text{HCOOH} + \cdot \text{OH} & \rightarrow \quad \text{H}_2\text{O} + \text{CO}_2^- + \text{H}^+ & (10) \\
\text{CO}_2^- + \text{H}_2\text{O}_2 & \rightarrow \quad \text{OH}^- + \cdot \text{OH} & (11)
\end{align*}
\]
From the results of gas analysis, we also found high concentration of oxygen. The source of oxygen is HO$_2$· (equation 12 and 13). Either two-hydroxyl radicals undergo fusion to produce H$_2$O$_2$ back and oxygen, or HO$_2$· radical reduces ferric ion to ferrous ion and produce oxygen in this process.

\[
\begin{align*}
\text{HO}_2\cdot + \text{Fe}^{3+} & \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \quad (12) \\
2 \text{HO}_2\cdot & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (13)
\end{align*}
\]

We could not detect nonpolar organic compounds by GC/MS analysis at equilibrium. Therefore we conclude that none of the intermediates are persistent during the reaction. The mass balance for nitrogen for RDX and HMX is 104%, 70%, respectively.

4.4 Conclusions

The results show that RDX and HMX can be effectively oxidized in aqueous solutions with Fenton’s reagents. The following conclusions are made;

- The degradation of RDX and HMX by the Fenton oxidation is rapid at between 20 and 50 °C, and 90 % of RDX can be degraded in 70 min at 25 °C, and similar results is obtained on HMX oxidation with much slower rates.
• Experimental results show that there exists an optimal pH at 3 and an optimal temperature at 30 °C for the Fenton treatment process.

• At a H₂O₂: Fe²⁺: RDX ratio of 4600:48:1, RDX and HMX were completely removed in 3 hours, and all experimental data could be fit to a pseudo first-order rate equation.

• The reaction rate coefficient was strongly dependent on temperature and H₂O₂ and Fe²⁺ concentrations.

• The temperature dependence follows the Arrhenius correlation. The activation energy using Arrhenius equation was determined to be 51.3 (RDX) and 48.6 (HMX) kJ mol⁻¹, respectively.

• Finally, the byproducts (NO₃⁻) and mineralization of the oxidation of RDX and HMX with Fenton's reagent are discussed. No further unknown end-products could be detected by GC/MS.

Bishop et al (1968), who found that purification of water by means of the Fenton reaction was the most effective in the pH range of 3-5, concluded the method to be unattractive for practical application, due to the necessity of low pH. However, the 'natural' pH of the nitrocompounds is low and the pH value is further decreasing during the reaction due to the formation of HNO₂.

The Fenton reaction requires the presence not only of hydrogen peroxide, but also some catalytic amounts of ferrous ion. However, since iron is one of the most abundant metals occurring in nature, the Fenton reaction does not introduce any
secondary pollution. It is also much cheaper than the hydrogen peroxide photolysis, as no source of irradiation is required. Thus, the Fenton reaction is more attractive method for purification of waters and wastewaters containing high explosive compounds where there is enough acidity to maintain homogeneity.
4.5 References


CHAPTER 5

Summary and Conclusions

5.1 Packed-Bed Reactor

Alkaline hydrolysis byproducts of the high explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), consisting of acetate, formate, formaldehyde and nitrite were treated in a denitrifying (anoxic) packed-bed upflow reactor. Additional nitrite or nitrate was added to match the carbon oxidation requirement. In a two-year long study, over 90% removal of the organic compounds and nitrite were observed in a reactor with a three-hour retention time. Removal was quantified by measuring actual compound concentrations as well as total organic carbon. The stoichiometry of the experimental results closely matched the predicted stoichiometry. Formaldehyde and acetate were preferentially removed over formate. The system removed N(nitrite) : C(acetate) : C(formaldehyde) : C(formate) in relative ratio of 1: 0.07 : 0.36 : 0.50, respectively. The volumetric removal rate was as
high as 170 mg/L of NO₂⁻-N per day with existing carbon sources. The observed cell yield (mass basis) of nitrite reduction with acetate/formate was 0.21 mg cells/mg TOC or 0.16 mg cells/mg COD at 20 °C. This culture was also capable of biodegrading RDX and HMX when using nitrate as an electron acceptor.

5.2 Membrane Bioreactor Application

Membrane technology has attracted much attention from scientists and engineers in recent years as a new separation process in water and wastewater fields. A membrane bioreactor (MBR) system, consisting of a bioreactor coupled to a ceramic crossflow ultrafiltration (UF) module, was evaluated at UCLA. This system was used to treat a synthetic wastewater containing hydrolysis byproducts (hydrolysates) of high explosive RDX compound. The synthetic wastewater, consisting of acetate, formate and formaldehyde as carbon sources and nitrite and nitrate as nitrogen sources was fed to the MBR reactor. The bench-scale anoxic MBR system effectively treated these wastewaters. The permeation flux was between 0.15 and 2.0 m³/m²/day and was restored to original flux after backwashing. Heterotrophic bacteria counts method showed that the membrane was very efficient in retaining biomass, which had resulted in the production of a clear final effluent. The reactor was operated over a range of transmembrane pressure, temperature, suspended solids concentration, and organic loading in order to evaluate the influence on the permeation flux and optimize its treatment. Increasing the transmembrane pressure and temperature did not increase flux. Increasing suspended
solids (SS) concentration in the bioreactor decreased the permeate flux significantly. The maximum organic loading rate was 0.72 kg COD/m$^3$/day. F/M ratio was increased up to 0.50 kg N/kg SS/day or 1.82 kg COD/kg SS/day. It was found that 30 minutes DI water backwashing each day gave the best results both in terms of flux stability and net cumulative permeate volume.

### 5.3 Fenton Oxidation

We investigated the feasibility of the Fenton oxidation of high explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetraaza-1,3,5,7-tetranitrocyclooctane (HMX). It was found that the oxidation of RDX and HMX by Fenton’s reagent is rapid at between 20 and 50 °C. At a H$_2$O$_2$: Fe$^{2+}$: RDX ratio of 4600:48:1, RDX and HMX were completely removed in 3 hours. All experimental data could be fit to a pseudo first-order rate equation. The temperature dependence follows the Arrhenius correlation. The activation energy using Arrhenius equation was determined to be 51.3 (RDX) and 48.6 (HMX) kJ mol$^{-1}$, respectively. Experimental results show that there exists an optimal pH at 3 for the Fenton treatment process. The reaction rate coefficient was also strongly dependent on both H$_2$O$_2$ and Fe$^{2+}$ concentrations. Finally, the byproducts (NO$_3^-$ and N$_2$) and mineralization of the oxidation of RDX and HMX with Fenton’s reagent are discussed. During GC/MS analysis of the end products, no further unknown products could be found. The results
of our work show that RDX and HMX effectively oxidized in acidic aqueous solutions with Fenton's reagent.
IMAGE EVALUATION
TEST TARGET (QA–3)

1.0

1.1

1.25

1.4

1.6

1.8

2.0

2.2

2.5

3.2

I.0

1.1

1.25

1.4

1.6

1.8

2.0

2.2

2.5

3.2

150mm

6"

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