Treatment of water contaminated with dimethyl phthalate by Fenton, Photo-Fenton and UV/H_2O_2 processes

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Civil Engineering

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Abstract

This study showed that the application of hydrogen peroxide

(H_2O_2) alone was not sufficient to oxidize Dimethyl phthalate (DMP) in water. Fenton process was found to be effective in removing DMP from pure water and seemed to follow a pseudo-first order reaction, however, it did not show any removal of DMP when the water was spiked with appreciable amount of methanol. The results indicated that increasing the concentration of Fe^{2+} caused an increase in the removal od DMP from pure water by Fenton process, while, increasing the initial concentration of H_2O_2, did not always lead to improving the efficiency of the Fenton process. A high temperature and a pH value of 3 to 4 were found to be best for achieving an efficient removal of DMP from pure water. The study also showed that DMP could be partially degraded by direct photolysis (i.e. UV light only), and that a great enhancement of the removal efficiency was achieved when the action of UV light was combined with the action of Fenton's reagent (i.e. photo-Fenton).

On the other hand, the UV/H_2O_2 process was found to be effective in removing DMP from the pure and methanol-spiked water and the DMP removal seemed to be a pseudo first-order reaction. Similar to Fenton, the high temperature and low pH resulted in enhancing the removal efficiency of DMP by the UV/H_2O_2 process. Lower removal rate of DMP was observed when the initial concentration of DMP (i.e. DMPi) was increased. It was concluded that an optimum molar ratio between DMP, H_2O_2 and Fe^{2+} must be determined in order to obtain the best removal efficiency. The efficiency of Fenton process dropped down drastically when DMP was spiked into local groundwater rather than pure water. However, the efficiency of UV/H_2O_2 dropped only slightly under the same conditions. Due to its many advantages, UV/H_2O_2 process was selected in this study to be the suitable oxidation process for the removal of DMP from water. The optimum conditions required to reach a considerable treatment efficiency of more than 97% of the 0.1 mM DMP at neutral pH value, were: H_2O_2 of 2.0 mM; UV exposure time of 30.6 minutes; and temperature of 33.6 C.

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TREATMENT OF WATER CONTAMINATED WITH DIMETHYL PHTHALATE BY FENTON, PHOTO-FENTON AND UV/H_2O_2 PROCESSES

BY

BASSAM SHAFIQ AL-TAWABINI

A Dissertation Presented to the
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DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
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DOCTOR OF PHILOSOPHY

In

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This Dissertation, written by **Bassam Shafiq Al-Tawabini** under the direction of his Dissertation advisor and approved by his dissertation committee, has been presented and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY IN **CIVIL ENGINEERING.**

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This Dissertation is dedicated

To

The Memory of My Father

And

My Mother, Wife and Children

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Praise and thanks be to **ALLAH**, the Almighty, with whose gracious help it was possible to accomplish this work.

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التخصص : هندسة مدنية (قسم مصادر المياه والبيئة)
تاريخ التخرج : فبراير ٢٠٠٢م

أظهرت هذه الدراسة بأنه لا يمكن معالجة المياه الملوثة بمادة الدايميثايل فثاليت (DMP) باستخدام مركب بروكسيد الهيدروجين المؤكسد فقط بينما نجحت طريقة فنتون (Fe^{2-}/ H_2O_2) بإزالة مادة الفثاليت من الماء النقي ولم تنجح في ذلك عندما كان الماء ملوثا بمادة كحول الميثانول . ويبدو أن التفاعل باستخدام طريقة الفنتون كان من الدرجة الأولى. كما أثبتت الدراسة أن زيادة تركيز المادة الحفازة (Fe^{2-}) زاد من فعالية طريقة الفنتون في إزالة مادة الفثاليت بينما وجد أن زيادة تركيز مركب بروكسيد الهيدروجين (H_2O_2) لم يؤد دائما إلى زيادة في الفعالية . وكان لتأثير درجة حموضة السائل ودرجة حرارته أكبر الأثر في تحديد فعالية طريقة الفنتون على إزالة المادة العضوية . فقد وجد أن درجة حموضة بين ٣ و ٤ ودرجة حرارة عالية تؤديان إلى زيادة في فعالية طريقة الفنتون . كما أن استخدام الأشعة الفوق بنفسجية قد أدى إلى تحسن كبير في قدرة طريقة الفنتون على معالجة المياه الملوثة بمادة الفثاليت سواء أكانت هذه المياه نقية أو ملوثة أصلا بمادة كحول الميثانول .

كما أظهرت هذه الدراسة نجاح طريقة الأشعة الفوق بنفسجية مع مركب بروكسيد الهيدروجين المؤكسد (UV/H_2O_2) في معالجة المياه الملوثة بمادة الدايميثايل فثاليت وتفوقها على طريقة الفنتون وذلك لعدم تأثرها كثيرا بدرجة حموضة السائل أو لوجود مادة كحول الميثانول . كما أثبتت الدراسة أن استخدام الأشعة الفوق بنفسجية فقط كان كفيلا بإزالة المادة العضوية الملوثة جزئيا . ويبدو أن التفاعل باستخدام طريقة (UV/H_2O_2) كان أيضا من الدرجة الأولى مثل طريقة الفنتون . وقد بينت التجارب أن زيادة تركيز مادة الفثاليت المراد إزالتها بالطرق السافة الذكر أثر سلبا على فعالية هذه الطرق في معالجة المياه من المادة العضوية . كما بينت التجارب أيضا أن فشل طريقة الفنتون في إزالة مادة الفثاليت من المياه الجوفية بينما نجحت طريقة (UV/H_2O_2) بانخفاض بسيط في الفعالية .

درجة الدكتوراة في الفلسفة
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DISSERTATION ABSTRACT

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TITLE OF STUDY:	TREATMENT OF WATER CONTAMINATED WITH DIMETHYL PHTHALATE BY FENTON, PHOTO-FENTON AND UV/H_2O_2 PROCESSES
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CHAPTER 1

INTRODUCTION

The high standard of living in modern societies has resulted in continuous generation of huge amounts of waste. Such waste may contain harmful substances that have adverse effects on human health if they are introduced into the environment. The hazardous effect caused by these substances, also called pollutants, is due to the fact that some of these pollutants can be persistent, toxic, flammable, corrosive or even explosive. All waste materials, whether in solid, liquid or gaseous form, that contain one or more of these harmful pollutants are considered hazardous wastes. It is the responsibility of environmental scientists and engineers to treat such wastes and clean the environment using the most effective and economical method available.

Even though traditional waste treatment methods such as the physicochemical (i.e. coagulation-flocculation, sedimentation, and filtration) and biological (i.e. activated sludge and trickling filters) processes are used for treating wastewater, the treatment of industrial and hazardous wastes is usually more complex. This can be attributed mainly to the huge number of pollutants that are potentially present at hazardous waste sites and the wide variations in their concentrations and characteristics.

In recent years, there has been a growing interest in advanced waste treatment methods that may replace or can be combined with traditional methods (1 - 8). These treatment methods have been found to be effective in removing certain pollutants, which were not efficiently removed by physicochemical methods alone. Furthermore, advanced treatment methods were attractive in cases where traditional treatment methods were not economically feasible. This is basically true for highly contaminated wastewaters of low volume.

Hazardous waste treatment and disposal technologies have been developed to handle several types of waste, and new technologies are still emerging. In general, the advanced treatment processes used for the treatment of hazardous wastes include, but not limited to, sorption (e.g. ion-exchange, stabilization, soil washing, thermal desorption and granular activated carbon (GAC) resins); volatilization (e.g. air stripping and soil vapor extraction); membrane processes (e.g. reverse osmosis, microfiltration, and nanofiltration); abiotic transformation (e.g. substitution, oxidation/reduction, hydrolysis, elimination reactions, photochemical reactions and advanced oxidation processes) and biotic transformation (e.g. bioventing, and landfarming).

Advanced Oxidation Processes (AOP), a part of the abiotic processes, have been defined as those processes, which involve the generation of hydroxyl radicals (OH^{o}) in sufficient quantity to destroy the toxic organic pollutants (9 – 18). AOPs have been found to be effective in destroying bio-refractory compounds. Fenton, photo-Fenton, and ultraviolet-oxidation (UV/H_2O_2) processes were commonly applied in the treatment of industrial wastewater (19 - 26) , contaminated soil (27 - 30), ground water (31 - 34) and landfill leachate (35 - 40). In addition, these processes were also used for the removal of organics measured by Total Organic Carbon (TOC), (41), Biological Oxygen Demand (BOD) (42), or Chemical Oxygen Demand (COD) (43, 44) of various industrial wastes. Moreover, the growing interest was focused on the usage of advanced oxidation and photochemical techniques for the sake of detoxification of a number of organic pollutants. Examples of organic compounds that can be treated by AOPs include: phenols (44, 45 - 51), poly aromatic hydrocarbons (PAHs) (52), polychlorinated biphenyls (PCBs) (53 – 55), pesticides and herbicides (56 – 60), dyestuff (61 - 65), 2,4-dinitrophenol (2,4-D) (66 - 69), 2,4,6-trinitrotoluene (TNT) (70, 71), aniline and hexamine (72, 73), benzene, toluene and xylene (BTX) (74), disinfection by products (14, 75), surfactants (76, 77), amines (78) and methyl-tertiary butyl ether (MTBE) (34).

Phthalic acid esters (PAEs), or phthalates, are one of the organic compounds that have received a great attention recently. These compounds are heavily used in the manufacturing of many products that we use in our daily life. For example, they are used in the production of a variety of household and consumer goods including plastic polymers, PVC, lubricating oils, and carriers for perfumes in cosmetics (79 - 82). As a matter of fact, due to their widespread use, phthalates have become one of the most abundant industrial pollutants in the environment (35, 83 - 87). In addition to their widespread use, phthalates are chemicals that are suspected of being toxic to aquatic life (88 - 94) and many of these phthalates are classified as toxic chemicals by the EPA's Toxic Release Inventory (95).

Several studies have shown that while short alkyl chain phthalates can be degraded biologically under aerobic and to a lesser extent under anaerobic condition, long chain alkyl phthalates showed moderate to high resistance to bacterial degradation in the environment (80, 96 - 101). Unfortunately, studies have also shown that most of these processes suffer from a number of drawbacks such as size of reactor needed, toxicity of the phthalates to the microorganisms and the high cost (102, 103). Other studies have reported the treatment of phthalate esters using polymeric ligand exchange (IEX) (104), adsorption (105, 106), photo-catalytic process (16), and oxidation (107).

The extensive literature search conducted in this study revealed the lack of comprehensive research in using advanced oxidation techniques for treating water contaminated with phthalate esters. Thus, the main objective of this study was to investigate the removal efficiency of phthalates from contaminated water using advanced oxidation processes such as Fenton, photo-Fenton and ultraviolet-oxidation (UV/H_2O_2). Dimethyl Phthalates (DMP) was used as a target organic compound.

CHAPTER 2

LITERATURE REVIEW

2.1 Advanced Oxidation Processes (AOPs)

These processes are defined as the oxidation processes that involve the generation of the highly reactive hydroxyl (OH^o) radicals. The generated radicals quickly attack organic pollutants and degrade them. In some cases, hydroxyl radicals, which will be discussed in the following section, may be able to completely degrade the pollutants and convert them into carbon dioxide (CO_2) and water.

2.1.1 Hydroxyl Radical (OH^o)

Radicals, in general, are unstable fragments of molecules with one or more unpaired electrons. Radicals are capable of independent existence and act as intermediates in chemical reactions. They are formed either by the breakage of a single bond or by an electron transfer from (or to) an ion. The energy required to form radicals is usually supplied either thermally (i.e. thermolysis) or photochemically (i.e. phtoloysis) (108). The main reactions that involve radicals include: combination, disproportionation, fragmentation, radical transfer, addition, one-electron transfer and homolytic substitution reactions. Normally radical transfer and addition reactions predominate and these usually involve a chain process, which include: initiation, chain propagation and chain termination (109).

Hydroxyl radical (OH^{o}) is one of the most important oxidants found in air, water, and biological systems. It is a species that is characterized by a one-electron deficiency compared to the thermodynamically stable species hydroxide ion (OH^{-}). It has a very high oxidation potential (2.8 V) compared to other oxidants as shown in Table 2.1. The data show that (OH^{o}) radical comes second to Fluorine, which has the highest oxidation potential of 3.0 Volts (108). Once generated, the hydroxyl radicals aggressively and rapidly attack a wide variety of compounds and react with them. It is the key oxidant in the degradation of pollutants by the advanced oxidation processes (AOPs).

The most common chemical reaction mechanisms of the hydroxyl radical in water include: addition, hydrogen abstraction, and radical interaction. However, only the first two mechanisms are the ones usually involved in advanced oxidation processes. In the addition mechanism, the OH^{o} adds to an unsaturated compound, aliphatic or aromatic, to form a free radical product, while in the hydrogen abstraction mechanism, OH^{o} can abstract a hydrogen atom to form organic free radical and water as with alkanes and alcohols. In applying Fenton's process for industrial waste treatment, the conditions of the reaction are adjusted so that hydrogen abstraction and oxygen addition become the dominant radical reactions (110, 111).

TABLE 2.1: Oxidation Potentials of Several Oxidants

Oxidant	**Oxidation Potential, V**
Fluorine	3.0
Hydroxyl radical	2.8
Ozone	2.1
Hydrogen peroxide	1.8
Potassium permanganate	1.7
Chlorine dioxide	1.5
Chlorine	1.4

The rate of pollutant oxidation by hydroxyl radicals may be described by a second-order reaction:

$$-\frac{d[C]}{dt} = k_{OH^o} [C][OH^o] \qquad (2.1)$$

Where:

$[C]$ = pollutant concentration (M)

$[OH^o]$ = hydroxyl radical concentration (M)

k_{OH^o} = second-order rate constant for the reaction of OH^o with the pollutant (M^{-1} sec^{-1})

Rate constants provide a good indicator of the reactivity of hydroxyl radicals with organic contaminants. The upper limit of k_{OH^o} is approximately 10^{10} M^{-1} sec^{-1}, which is governed by the rate of diffusion of hydroxyl radicals into water. Second-rate constants (k_{OH^o}) of some pollutants including phthalates are listed in Table 2.2. Rate constants in Table 2.2 indicate that highly chlorinated alkenes, such as triachloroethylene (TCE) react rapidly with OH^o radical while chlorinated alkanes, such as carbon tetrachloride, are considered non reactive (17). It is widely accepted that chemical compounds with reaction rates (k_{OH^o}) above 10^9 M^{-1} sec^{-1} are considered good candidates for degradation by OH^o radicals. However, compounds with rate constants below 10^8 M^{-1} sec^{-1} have been found to show inefficient degradation (17).

TABLE 2.2: Second-Order Rate Constants of Selected Compounds for Reactivity With Hydroxyl Radical

Organic Group	**Compound**	**k_{OH°($M^{-1}sec^{-1}$)**
Monocyclic Aromatic Hydrocarbons	Benzene	7.8×10^9
Polyaromatic Hydrocarbons	PAHs	1×10^{10}
Chlorinated Solvents	Carbon Tetrachloride	$< 2 \times 10^6$
Chlorinated Solvents	Trichloroethylene (TCE)	4×10^9
Insecticides	Lindane	7.8×10^8
Insecticides	Carbofuran	7×10^9
Herbicides	Atrazine	2.6×10^9
Fungicides	Pentachlorophenol	4×10^9
Industrial Intermediates	Phenol	6.6×10^9
Industrial Intermediates	Chlorobenzene	5.5×10^9
Industrial Intermediates	Diethyl Phthalate (DEP)	4×10^9
Industrial Intermediates	Dimethyl Phthalate (DMP)	4×10^9
Polychlorinated Biphenyls	PCB (1254)	5×10^9
Chlorinated Dioxins	TCDD	4×10^9

(Extracted from reference 17)

Thus, phthalates such as dimethyl phthalate (DMP) and diethyl phthalate (DEP) with reaction rates of 4 x 10^9 M^{-1} sec^{-1} are expected to exhibit efficient degradation by AOPs. However, very limited work has been conducted towards utilizing AOPs for the removal of such compounds from contaminated waters.

Reactivity of OH^o radicals with organic pollutants is usually proportional to their solubility in the liquid phase (i.e. water). Many important hazardous chemicals such as chlorinated dioxins (TCDD), which react rapidly with hydroxyl radicals are highly hydrophobic (water hating), with log $K_{ow} > 5$. These compounds exhibit significantly lower reactivity with OH^o radicals when they exist in the sorbed phase (17). There is also a group of inorganic chemicals, which inhibit the action of OH^o radicals, such as chloride anions (112, 113), dissolved organic material (114), Fulvic acid (115), bicarbonate (k_{OH^o} = 1.5 x 10^7 M^{-1} sec^{-1}) and carbonate (k_{OH^o} = 4.2 x 10^8 M^{-1} sec^{-1}) (17). These inhibitors are involved in competing quenching reactions. Although the rate reaction of OH^o radical (k_{OH^o}) for most quenching species is in the range of 10^6 to 10^8 M^{-1} sec^{-1}, their concentrations are often up to 1000 times greater than the concentrations of the contaminants. In fact, the property of quenching OH^o radicals by chemicals such as benzoic acid and 1-propanol has been used by some researchers to quantify the amount of hydroxyl radical generated during AOP processes (111, 116).

2.1.2 AOP Techniques

In principal, there are numerous processes that have been developed to generate hydroxyl radicals including homogeneous photolysis, heterogeneous photocatalysis (9, 10, 117 - 119), sonolysis, radiolysis and electrolysis (12). In this study, the homogeneous photolysis techniques, which include: Fenton, Photo-Fenton and UV/H_2O_2 were used to remove phthalates from the contaminated waters.

The homogeneous photolysis approach to generate OH^o radicals uses the ultra violet (UV) light in conjunction with standard oxidant and / or a catalyst. The standard oxidants used are the hydrogen peroxide or ozone, while the catalyst used is usually ferrous ion (Fe^{2+}). Thus, the chemistry of advanced oxidation involves both oxidation and photolysis mechanisms. Oxidation, which is defined as the chemical conversion of a compound to a more oxygenated form by means of reactions with oxidizing agent such as oxygen (O_2), ozone (O_3), hydrogen peroxide (H_2O_2) and chlorine (Cl_2), plays a significant role in the chemical treatment of wastewaters (120, 121). However, simple oxidation by these oxidants alone, are usually too slow and insufficient to be applied broadly for wastewater treatment in the degradation of many bio-refractory contaminants.

In addition to its wide application as a water disinfectant, UV light has been utilized in the degradation of organic pollutants in a process called photolysis. Photolysis involves the interaction of light with molecules to initiate their dissociation into fragments. If the absorption of photon (i.e. units of light energy) by a molecule is to cause photolysis (dissociation), the photon energy must exceed the energy of the bond to be broken. This requires that the wavelength employed should be within the ultraviolet region of the spectrum for most photolytic reactions (15, 122). Compounds that absorb UV light and have high quantum yields of photolysis are good candidates for photodegradation. Similar to simple oxidation, photolysis alone may not be enough to degrade certain types of organic compounds.

In advanced oxidation technology, the overall rate of oxidation of a contaminant is greatly increased over that obtained by the simple addition of oxidizing agents, and if UV light is involved, photolysis will enhance the degradation process even more (11). The most common advanced oxidation techniques that are commonly applied to wastewater treatment include: Fenton/photo-Fenton and UV/H_2O_2 processes. The basic principals of these techniques will be discussed in the following sections.

2.1.2.1 Fenton and Photo-Fenton Processes

The combination of ferrous ions (Fe^{2+}) with hydrogen peroxide (H_2O_2) was first discovered by a scientist called H.J.H Fenton in 1894 (123). Fenton's reagent has proven to be an efficient hydroxyl radical (OH^o) generation method according to the following reaction:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^o \qquad (2.2)$$

In the presence of substrate, such as a target contaminant, the hydroxyl radicals generated are sometimes capable of detoxifying the contaminants via oxidation. Numerous competing reactions, which involve Fe^2, Fe^{3+}, H_2O_2, OH^o radicals, super-oxide radicals (HO_2^o) derived from the substrate, are also possible during Fenton's reagent treatment [93]. Other possible reactions in the Haber-Weiss process (124) include:

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^o + H^+ \qquad (2.3)$$

$$Fe^{3+} + HO_2^o \longrightarrow Fe^{2+} + H^+ + O_2 \qquad (2.4)$$

$$H_2O_2 + OH^o \longrightarrow H_2O + HO_2^o \qquad (2.5)$$

$$Fe^{2+} + HO_2^o \longrightarrow Fe^{3+} + HO_2 \qquad (2.6)$$

$$Fe^{3+} + R^o \longrightarrow Fe^{2+} + R^+ \qquad (2.7)$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad (2.8)$$

As the reaction in equation 2.2 proceeds, most of the ferrous (Fe^{2+}) species will be converted into ferric (Fe^{3+}) species. However, Fe^{2+} species can be regenerated using equations 2.3 to 2.8.

One or both of the reactants in Fenton process (i.e. H_2O_2 or Fe^{2+}) can be generated within the cell rather than direct application. For example, Fe^{2+} and or H_2O_2 can be generated by electrochemical methods and this process is called electro-Fenton process (20, 39, 45, 48, 73). In a study by Mckinzi and Dichristina, microorganisms were used in driving the Fenton reaction for the transformation of Pentachlorophenol (125).

The catalytic effect of Fe^{2+} can be also enhanced by solution irradiation with ultraviolet (UV) light (i.e. h_v). The so-called Photo-Fenton process can produce a large regeneration rate of Fe^{2+} as well as more species of hydroxyl radicals as shown by reaction 2.10 and this is expected to enhance the oxidation process (126). Thus, the photo-Fenton process can be represented by a combination of reactions 2.2 and 2.9.

$$Fe^{3+} + h_v \longrightarrow Fe^{2+} + OH^o \qquad (2.9)$$

It was shown that several pollutants could be degraded or even mineralized (i.e. completely converted into CO_2 and water) using Fenton's or photo-Fenton processes, mostly, in the aqueous phase. Research studies using Fenton's reagent have demonstrated the oxidation of several organic compounds present as pure compounds in solution such as: phenol (46), chloroaliphatic (127, 128), chlorophenols (50, 129), atrazine (130), herbicides (2, 4-D) (69), trihalomethanes (THMs) (75), PCBs (54, 55), nitrophenols and chlorobenzene (131), and xylidines (110). Various types of treatment of wastewaters containing photographic developers (132), 2,4,6-trinitrotoluene (70, 71), anthracene (133) and azodyes (63, 134, 135) using Fenton's reagent have been also reported.

In a study carried out by the USEPA / Urban Watershed Management Branch (UWMB), Fenton's reagent was used to treat contaminated potable water (136). The study showed that Fenton's reagent was effective in destroying 2-methylnaphthalene, n-hexadecane and diesel fuel in ground water. In another research by the same group (137), Fenton's reagent effectively destroyed diesel fuel in contaminated soil and the methyl tertiary butyl ether (MTBE) in both soils and water at neutral pH. A study by Chen et al. (27) showed that Fenton's reagent was a suitable method for treatment of contaminated soils with 2-methylnaphthalene, n-hexadecane and diesel fuel. They reported that no pH adjustment was necessary. Chemical oxidation of BTX using Fenton's reagent was studied by Lou and Lee (74). They found that at a H_2O_2: BTX: Fe^{2+} ratio of 12:1:60 (ppm), the dissolved BTX can be completely removed in less than 10 minutes.

More recently, Kuo (62) used Fenton's reagent to decolorize simulated dye wastewaters. An average de-colorization of over 97% was obtained with concomitant COD removal of about 90% in 30 minutes or less. The most effective pH for treating dye wastewater was 3.5 and below. Different dosages of H_2O_2 and Fe^{2+} were required for different types of dyes. Complexes of ferric iron and hydroxide ions could also coagulate the dyes. The results of the simulated wastewaters were confirmed with actual wastewaters obtained from dyeing mills. In another study, H_2O_2 and iron were used to treat wastewater containing phenol and/or formaldehyde produced in phenol and coke in gas plants and coal distillation plants, and in the production of phenol/formaldehyde resins. Approximately 8 moles of H_2O_2 for phenol degradation and an additional 2 moles for formaldehyde degradation were required in a reaction time of 30-60 min. This process was only practical and economical for concentrations of phenol up to 5000 ppm (16).

Basu and Wei (138) studied the kinetics of oxidation of 2,4,6 trichlorophenol (TCP) by Fenton's reagent. They found that TCP degradation was a multi-step oxidation process consisting of de-chlorination and aromatic bond cleavage, followed by progressive oxidation reactions, ultimately leading to the formation of CO_2 and water. They also found that the degradation follows a second order kinetics rate.

Casero et al. (78) investigated the chemical degradation of aromatic amines by Fenton's reagent. Their study revealed that complete removal of these pollutants took about 1 and 3 hours. Lin et al. (139, 140), used a coupled ultrasound / Fenton reagent process to treat 2-chlorophenols (2-cp). They found that more than 99% of 2-cp was decomposed and 86% of 2-cp was mineralized using this technique. In another study by Li et al. (63), Fenton's reagent was successfully used in decolorizing a dye chemical wastewater. In their study, the basic oxygen furnace waste slag generated from steel making plants was added to the hydrogen peroxide. Surfactant wastewater treatment by Fenton's reagent was also investigated by Lin et al. (141). A first-order kinetic model was adopted to represent the Fenton oxidation of surfactant wastewater.

2, 4-dinitrotoluene (2,4, DNT) was chosen by Mohanty and Wei (69), as a model compound to be oxidized by Fenton's reagent. Results showed that at a H_2O_2: DNT: Fe^{2+} ratio of 20:1:2.5 (molar), 2, 4-DNT was completely removed in 5 hours. Potter and Roth (46) indicated that oxidation of chlorinated phenols using Fenton's reagent both oxidize and de-chlorinate phenol species.

The photo-Fenton process has also been studied by a number of investigators. In their study, Chen and Pignatello (142) examined the oxidation of phenol (2mM) by Fenton systems in the dark (Fe^{3+}/H_2O_2, Fe^{2+}/H_2O_2, and mixed $Fe^{3+}/H_2O_2/Fe^{2+}$ systems) and under UV/visible light ($Fe^{3+}/H_2O_2/UV$). Photo-assisted Fenton reaction was also studied by Huston et al. (143) in the degradation of selected pesticide active ingredients and commercial formulations in water. Kiwi et al (68) reported that Fenton-type reactions accelerated nitrophenols degradation in comparison with direct photolysis. In a similar study, Wang et al. (69) compared several Fenton-related oxidative processes in removing 2,4-dinitrophenol (DNP). These processes were UV/H_2O_2, Fenton reaction, and Photo-Fenton. Results showed that Photo-Fenton process was the most effective process compared to others.

In a recent study by Fukushima et al. (72), the fate of aniline after a photo-Fenton reaction in an aqueous system containing Fe^{3+}, humic acid and H_2O_2 was investigated. The study showed that the degradation of aniline ($ArNH_2$) was facilitated by light radiation ($\lambda > 370$ nm). Photo-Fenton system was also used for the degradation of ethylene glycol in a study carried out by McGinnis et al. (144).

In general, the reactions that involve Fenton and photo-Fenton processes are governed by a number of factors including doses of H_2O_2 and Fe^{2+}, initial dose of the target compound, pH, temperature, dissolved oxygen (D.O.), reaction time, light intensity and the existence of inhibitors. Several studies have been carried out to evaluate these factors. In their investigation of the 2,4,6 trichlorophenol oxidation by Fenton's reagent, Basu and Wei (145) examined the effects of various reaction parameters such as temperature, pH, oxidation state of catalyst (ferrous versus ferric), mode of addition of oxidant to the reactor, and the presence of dissolved oxygen. They concluded that reaction rate increases significantly with the increase of temperature within the range of 15 to 35°C and the optimum range of pH was 2 to 3.5. They also concluded that dissolved oxygen (D.O.) participates in the reaction and enhances oxidation, however, it was not necessary since normal D.O. level in the industrial wastewater, open to the atmosphere is sufficient to drive the reaction forward. In the first part of their research, Basu and Wei (47) reported that optimum molar ratios between H_2O_2 and substrate level, and between Fe^{2+} and H_2O_2 were 5.5:1, and 0.1:1, respectively. Factors affecting the degradation of p-chlorophenol compound, which is the main photographic developers used in white and black processes, by Fenton's reagent was also assessed by Lunar et al. (146). They found that under optimal conditions of 0.2 M H_2O_2, 9.0×10^{-4} M Fe^{2+}, pH 3 - 5 and room temperature, 50% removal of the target compound was attained in 3 hours.

Kang et al. (147) investigated the efficiency of Fenton's oxidation process on the removal of organic substances by oxidation and coagulation in the treatment of the non-biodegradable landfill leachate. Results of their study showed that chemical oxygen demand (COD) removal was most efficient in the pH range of 2.5 – 4.

2.1.2.2 UV / H_2O_2 Process

Ultraviolet (UV) / H_2O_2 oxidation process involves the single-step dissociation of H_2O_2 to form two hydroxyl radicals (OH^o). Hydroxyl radicals can oxidize organics (RH) by abstraction of protons producing organic radicals (R^o), which are highly reactive and can be further oxidized. The various reactions, which occur during UV/ H_2O_2 oxidation, are as follows:

$$H_2O_2 \xrightarrow{UV} 2\,OH^o \qquad (2.10)$$

$$H_2O_2 \longrightarrow HOO^- + H^+ \qquad (2.11)$$

$$OH^o + H_2O_2 \longrightarrow HO_2^o + H_2O \qquad (2.12)$$

$$OH^o + HOO^- \longrightarrow HO_2^o + OH^- \qquad (2.13)$$

$$2\,HO_2^o \longrightarrow H_2O_2 + O_2 \qquad (2.14)$$

$$2\,OH^o \longrightarrow H_2O_2 \qquad (2.15)$$

$$OH^o + HO_2^o \longrightarrow O_2 + H_2O \qquad (2.16)$$

$$OH^o + RH \longrightarrow H_2O + R^o \longrightarrow \text{further oxidation} \qquad (2.17)$$

It is worth mentioning that in UV/H_2O_2 process, degradation of organics can also take place directly by activation caused by UV (i.e. photolysis), which improves the ability of the organics to be oxidized either by H_2O_2 or by the generated hydroxyl radicals. The activation of the organic compounds can involve direct oxidation by UV or the formation of organic radicals or other reactive intermediates. UV wavelengths of 200-280 nm lead to dissociation of H_2O_2, with mercury lamps emitting at 254 nm being the most commonly used. If the concentration of the H_2O_2 is not limiting, the organics can be completely destroyed by full conversion to CO_2 and water (16).

Ultraviolet / H_2O_2 systems can effectively oxidize recalcitrant organics such as trichloroethylene (TCE), tetrachloroethylene (PCE; perchloroethylene), butanol, chloroform, methyl isobutyl ketone, 4-methyl-2-pentanol, methyl ethyl ketone, and carbon tetrachloride (148). Laboratory-scale UV/H_2O_2 systems were successfully used to demonstrate the oxidation of Metol (149), humic acid (150), MTBE (33, 34, 151). UV/H_2O_2 systems were used for the degradation of formic, acetic and propionic acids

(152). The removal of methanol and various phenolic and chlorinated aliphatic compounds (107) by these systems has also been reported. Other studies showed that UV/H_2O_2 systems were effective in removing nitrobenzenes and nitrophenols (122).

Partial removals of methanol, phenol, p-cresol, alkyl alcohol, benzene, dimethyl phthalate, and toluene were reported with efficiencies ranging from 25% to 60% using UV/H_2O_2 as reported by Mansour et al. (153). According to Weir et al. (154) as high as 98% of benzene was degraded by UV/ H_2O_2 to intermediate organics. They also found that the intermediate organics could also be degraded by supplemental H_2O_2 addition and continued treatment. Removal efficiencies of 85-100% of mono-, di- and trichlorophenols were achieved in a 3-hour reaction period (155).

Ultraviolet process was also used to remove naturally present organics from distilled and tap water. Malaiyandi et. al. (156) reported that 88% and 98% reduction in TOC was achieved by UV/ H_2O_2 treatment of organics in tap and distilled water, respectively. Chang et. al. (157) showed that up to 90% reduction of TOC of tannery waste was achieved in a pilot system using UV irradiation for 2 min. Prat et al. (158) demonstrated that only 70% of color was removed in bleaching wastewaters.

Liao et al. (159) used UV/ H_2O_2 oxidation process for the advanced treatment of secondary effluent of textile wastewater. The results showed that under the conditions of about 650 mg/L of H_2O_2 and a UV lamp power of the 14 W, color was removed completely within 20 minutes. The study also showed that 90% removal of COD was achieved within 40 minutes. In a laboratory-scale reactor, Pinto et. al. (160) investigated the efficiency of UV/ H_2O_2 oxidation process on the degradation of 1,2-dichlorobenzene. They found that the rate of degradation using UV/ H_2O_2 was twice that obtained with UV light alone. The effects of molar ratio of H_2O_2 to butyl chloride, hydraulic retention time, UV intensity, pH, inorganic carbon, and humic substances on the removal of butyl chloride were investigated by Gurol et al. (161). They concluded that the higher UV intensity plays a significant role in degrading the target compound.

Sundstrom et al. (107) evaluated the destruction of aromatic pollutants by UV light catalyzed oxidation with H_2O_2. They studied the degradation of benzene, toluene, chlorobenzene, phenol, 2-chlorophenol, 2,4,6-trichlorophenol, dimethylphthalate, and diethylphthalate. Results of the study showed that oxidation with UV combined with H_2O_2 works much better than using UV alone. Results also showed that chlorophenols have the highest reaction rate while phthalates have the lowest rates of reactions of all the compounds tested. However, in their study, Sudstrom et al. tested only the effect of H_2O_2 to pollutant ratio on the reaction rate while keeping other parameters such as pH, temperature and initial concentration of pollutant constant throughout the experiments. It is worth mentioning here that Sundstrom et. al. study was the only study found in the literature on the degradation of phthalates by UV/H_2O_2 system.

2.2 Phthalic Acid Esters (PAEs)

Phthalic acid esters have recently received a great attention by many researchers who investigated their suspected health effects on human health. The chemical and physical characteristics of these compounds are discussed below. The fate of PAEs in the environment and their degradation pathways are also discussed below.

2.2.1 Chemical Structure

The term "phthalate esters" is used to describe the mono-and di-esters of the isomeric benzene dicarboxylic acid, which is called the phthalic acid. The most widely used of these, and the most studied toxicologically, are the esters of ortho-phthalic (o-phthalic) acid shown in Figure 2.1. Diesters may be symmetrical (e.g. diethyl phthalate) or asymmetrical (e.g. butyl benzyl phthalate). There are other types of phthalate esters such as the isophthalic acid and terephthalic acid but these are not produced or used in the same large volumes as those of o-phthalic acid.

Esters of phthalic acid (PAEs) are formed by linkage of an alkyl groups (R) to the carboxylic groups as shown in Figure 2.2. The alkyl group (R) can be a methyl (CH_3^-), ethyl ($C_2H_5^-$), butyl ($C_4H_9^-$), or other groups. The chain length of the alkyl group can vary from 1 to 13 carbons. The most common industrial phthalates of interest to environmental researchers include Dimethyl Phthalate (DMP), Diethyl Phthalate (DEP), Di-n-Octyl Phthalate (DOP), Di-n-Butyl Phthalate (DBP), Butyl Benzyl Phthalate (BBP) and the Di-(2-ethylhexyl) Phthalate (DEHP). The chemical structures of these esters are shown in Figure 2.3 (17). Phthalate compounds have different alkyl chain lengths and thus different molecular weights. A list of the molecular weights, molecular formula and alkyl chain lengths of the most common phthalate esters is given in Table 2.3 (80).

Phthalate esters are widely used industrial chemicals serving as important additives or plasticizers to plastics and polyvinyl chloride (PVC) resins. Due to their stability, fluidity and low volatility, most of the mid- to high molecular weight phthalate esters (e.g. DOP and DEHP) are used in the manufacturing of PVC. Their performance advantages include high performance, good cold temperature properties and high absorption efficiency (82). In fact, plasticizers hold 65 % of the 7.5 million ton world market for plastic additives, accounting for 4.9 million tons, with a value of approximately $ 7.6 billion. About 2.7 million tons/year of total phthalates were produced in the early eighties (162). The majority of plasticizers (about 90%) are used for PVC, which is heavily used in diverse applications such as coatings, plumbing, construction materials, plastic bottles, home furnishings, transportation, clothing, and to a limited extent in food packaging and medical products and (35, 85). On the other hand, low molecular weight phthalates such as dimethyl and diethyl phthalate esters are typically used in cellulose ester-based plastics. Dimethyl phthalate (DMP) is mainly used in resins, rubber materials and in solid rocket propellants. It is also used in lacquers, plastics, coating agents, safety glasses, molding powders, insect repellent and perfumes. Diethyl phthalate (DEP) has similar uses as DMP and in addition it can be used as wetting agent, camphor substitute and alcohol denaturant. Dibutyl phthalate (DBP) can be used as a textile lubricating agent, printing inks, resin solvent, paper coatings and explosives (80).

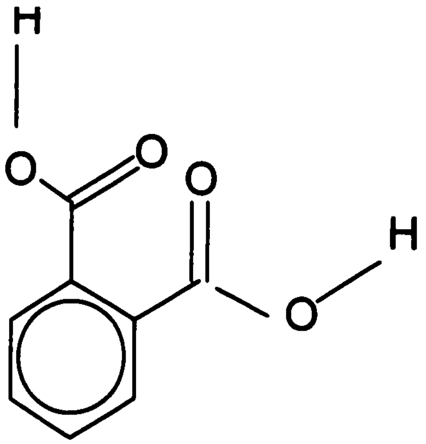


Figure 2.1: Chemical Structure of the o-Phthalic acid

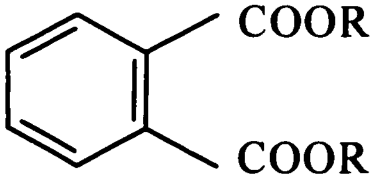
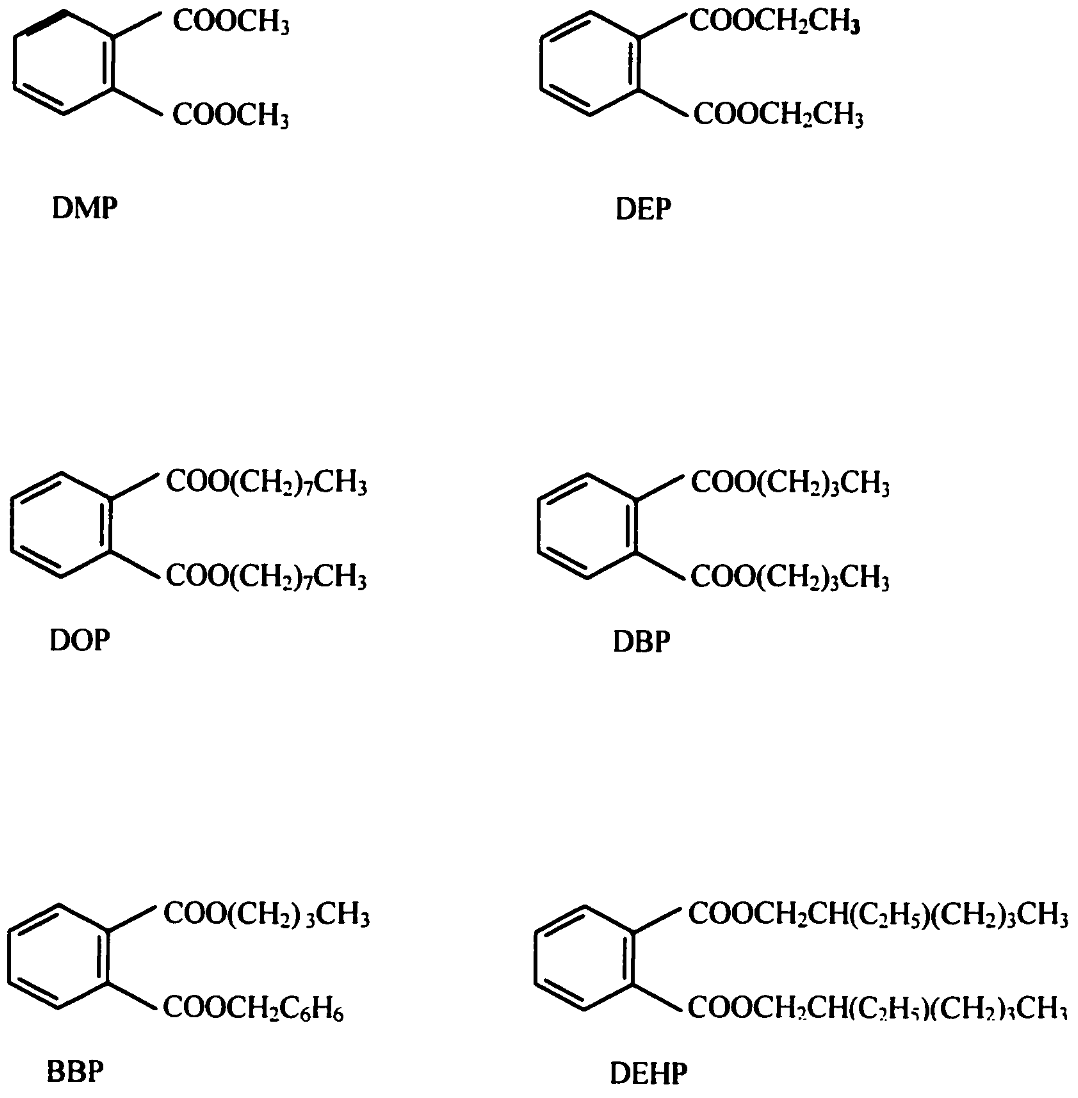


Figure 2.2: o-Phthalic Acid linked to an Alkyl Group



DMP DEP DOP DBP BBP DEHP

Figure 2.3: Chemical Structures of the Most Common Phthalate Esters.

TABLE 2.3: A List of The Most Common Phthalate Esters

Description	Compound	Molecular Formula	Alkyl Chain Length	Molecular Weight (gm)
Di Methyl Phthalate	DMP	$C_{10}H_{10}O_5$	1	194.18
Di Ethyl Phthalate	DEP	$C_{12}H_{14}O_5$	2	222.23
Di-n- Butyl Phthalate	DBP	$C_{16}H_{22}O_5$	4	278.35
Butyl Benzyl Phthalate	BBP	$C_{24}H_{38}O_6$	4, 6	312.39
Di-n-Octyl Phthalate	DNOP	$C_{24}H_{38}O_5$	8	390.54
Di (2-ethylhexyl) Phthalate	DEHP	$C_{24}H_{20}O_4$	8	390.54

2.2.2 Physical and Chemical Properties

Phthalate diesters are derived from the lower alcohols. For example, DMP is synthesized from methanol, while n-butanol is used in the production of DBP, in the presence of concentrated sulfuric acid catalyst (163). Phthalates are colorless or yellowish fluids of low viscosity and exist as liquids at room temperature. However, their viscosities increase with increasing length of the side chain. The majority of phthalates have low melting points (-25 to – 47^0C) with the exception of DMP which has a melting point of + 5.5^0C. These phthalates have relatively high boiling points (280 to 370^0C). The low melting point and high boiling point of these phthalate esters contribute to their usefulness as plasticizers, heat transfer fluids, and carriers. Specific gravities of these compounds range from 0.98 to 1.192. The diesters have low vapor pressures generally below 0.01 mmHg (1.3 Pa) at room temperature.

Due to its importance in assessing the treatment of soil and groundwater, water solubility of phthalate esters has been studied by a number of investigators (80). In fact, determination of water solubility of phthalates is essential since some hydrophobic (water-hating) phthalate esters may partition onto solids, form emulsions, float at the air-water interface or sink to the bottom of aquifers. These partitioning mechanisms decrease the effectiveness of biological and physicochemical treatment processes. The portioning mechanisms of phthalate esters in the environment are discussed in section 2.2.3.

In general, most of the studies carried out on this subject concluded that water solubility of phthalates is inversely proportional to sorptivity, bioaccumulation, and volatilization from aqueous solutions (164). They also concluded that water solubility of phthalates could influence the biodegradation, photolysis, and chemical oxidation process. These studies also found that precise water solubility measurements for phthalates with moderate to high water solubilities can be obtained easily with conventional methods such as shake-flask procedures (165), however, measurements for more hydrophobic compounds can be confounded by a variety of experimental problems. One of these problems is the difficulty in separating colloidal emulsions of un-dissolved chemicals from the aqueous phase (166). For this reason, different water solubilities of phthalates were reported in the literatures. In his paper, Staples et al. (80) reported the most correct water solubilities of phthalate esters as listed in Table 2.4. Data in this Table show that lower molecular weight phthalates (DMP and DEP) are more soluble in water than the higher molecular weight phthalates (DOP and DEHP). For example, water solubility of DMP is more than 4000 ppm while that for DEHP is less than 0.003 ppm. In this study, the higher solubility of DMP in water compared to other phthalates was one of the reasons behind the selection of DMP as a target compound to be oxidized by advanced oxidation processes.

Vapor pressure is another physical parameter that plays a significant role in the fate of fugitive emissions and other releases of phthalate esters to the atmosphere. Vapor pressure is typically determined by direct pressure measurement at elevated temperatures. Vapor pressure measurements reported in the literature (80) for phthalate esters are summarized in Table 2.4. Similar to the case of measuring water solubility values for phthalates, measured values of vapor pressure obtained in different studies often vary by more than one order of magnitude. However, a general trend is apparent showing that the vapor pressure of phthalate esters declines more with increasing alkyl chain length.

In order to predict the tendency of phthalates to partition into water, animal lipids, sediment, and soil organic matter, a number of predictive methods have been developed in order to estimate octanol-water partition coefficients (K_{ow}) (167). The simplest and currently most reliable method for determining K_{ow} for low solubility, hydrophobic compounds is the "slow-stir" method (168, 169). Values of log (K_{ow}) of phthalate esters are presented in Table 2.4 (80).

It is clear that water solubility is inversely proportional to K_{ow}. In general, the major portion a chemical compound would be in the solid phase if it has a log K_{ow} value greater than 5. Thus, DMP, which has a log K_{ow} value of less than 2, is more suitable for oxidation by advanced oxidation processes than those of higher alkyl chain such as DOP and DEHP, which have log K_{ow} values of 8 and 7.5 respectively. This is another reason behind the selection of DMP as a target compound in this study.

2.2.3 Environmental Partitioning

In the environment, phthalates can partition between air, water and aerosols. The extent at which phthalates can partition between these matrices is measured by a number

TABLE 2.4: Some Physical Properties of Common Phthalates

Compound	Boiling Point (°C)	Melting Point (°C)	Specific Gravity	Solubility in H_2O (ppm)	Log K_{ow}	VP (mmHg)
DMP	283.7	5.5	1.192	4200	1.61	2.0E-3
DEP	295	-40	1.118	1100	2.38	1.0E-3
DBP	340	-35	1.042	11.2	4.45	2.70E-5
BBP	370	-35	1.111	2.7	4.59	5.0E-6
DNOP	-	-25	0.978	0.0005	8.06	1.0E-7
DEHP	384	-47	0.986	0.003	7.5	1.0E-7

of parameters such as Henry's Law constant (H), fraction of chemical on the aerosol (Φ) and the sediment to water partition coefficients (K_{oc}).

Henry's Law constant (H), which is the measure of the equilibrium distribution coefficient of a chemical between water and air serves as a guide in estimating the tendency of a substance to escape from water into air. The ratio of the vapor pressure to the molar water solubility estimates the coefficient (H).

Henry's constants (H) for six phthalate esters are shown in Table 2.5. Chemical compounds with (H) values in the range of 1×10^{-7} atm-m^3/mole are generally considered to have negligible volatility (80). This implies that most of the low molecular weight phthalates are practically nonvolatile and most probably will remain in the liquid phase (i.e. water).

In the atmosphere, the distribution of organic chemicals between gaseous and particulate phases can be estimated by the parameter (Φ), which represents the fraction of chemical on the particulate (i.e. aerosol) phase (170). Higher values of Φ indicate that the large portion of the chemical is more likely to be attracted to the aerosol rather that the vapor phase. Results indicate that phthalate esters with alkyl chain lengths of less than six carbons (DMP through BBP) exist primarily in the gas phase (vapor) whereas compounds with longer alkyl chains (DOP and DEHP) are mainly adhered to the aerosols as shown in Table 2.5 (80).

TABLE 2.5: Environmental Partitioning Coefficients of Common Phthalate Esters

Compound	H (atm-m^3/mol)	Φ	K_{oc} (L/kg) (sediment)
DMP	1.22E-07	0.00019	55-360
DEP	2.66E-07	0.00039	69 - 1726
DBP	8.83E-07	0.014	1375 - 14900
BBP	7.61E-07	0.072	9000 - 17000
DNOP	1.03E-04	0.8	-
DEHP	1.71E-05	0.8	87420 - 510,000

The sorption of phthalates to soil, sediment, or suspended solids is partially governed by the relative hydrophobicity of the chemical. These hydrophobic chemicals adsorb mainly to the organic matter in the solid. Several researchers (171, 172) have reported that soluble soil humic material associates strongly with phthalate esters, increasing their apparent water solubility and decreasing their apparent degree of soil sorption. The soil (sediment) to water partition coefficients (K_{oc}) for a number of phthalates are shown in Table 2.5 (80). The K_{oc} levels vary on a wide range due to various types of soils or sediments used in various studies. Table 2.5 clearly indicates that low alkyl chain phthalates, such DMP and DEP have lower K_{oc} levels than the high alkyl chain ones such as DEHP. This is expected since DMP and DEP have higher water solubilities than DEHP.

A number of authors have examined the dissolved versus suspended particulate-bound fraction of phthalate esters in surface water samples. Germain and Langlois (173) collected surface water samples from the St. Lawrence River. Both dissolved phthalate ester and phthalate ester bound to suspended particulate matter-bound (SPM) were analyzed. The SPM concentration was estimated to be 3.0 mg/L. About 14% of the DBP concentration was sorbed to SPM and 86% was dissolved. For DEHP, 53% was SPM-bound while only 47% was dissolved. No other phthalate ester had detectable SPM-bound fractions.

The adsorption behavior of DMP and DEP at near saturation conditions on two sandy soils was investigated by Hunter and Uchrin (106). The results of their study showed that both esters were adsorbed to the high organic content soil, while little adsorption was displayed to the low organic matter soil. The study also revealed that DEP showed a greater tendency to adsorb than DMP. In another study, Klug and Forsling (105) conducted a spectroscopic study of phthalate adsorption on gamma and alumina oxide. The study results showed the formation of two different types of complexes: outer and inner sphere. The relative concentrations of these complexes were shown to vary considerably with pH but very little with increasing ionic strength.

2.2.4 Occurrence in the Environment

The phthalate esters are of concern because they are the most abundant artificially made chemicals in the environment. Release of phthalates into environment may occur during manufacturing, usage or disposal. They occur in natural waters at levels ranging between nanograms (ng) and milligrams (mg) per liter. They are widely used to impart flexibility to plastics. Butyl benzyl phthalate (BBP) is found in vinyl floor tiles and adhesives, while di-n-butyl phthalate (DBP) occurs in food packaging and PVC. The monomeric esters tend to permeate foodstuff within the packaging, and levels in the USA are 50-500 ppb. In the UK, the intake in foodstuff is typically 230 μg/day and in chocolate bars wrapped in polypropylene reached 14 ppm. Consumers are also exposed to epoxy resins used to line water pipes and tin cans (2, 88).

In their survey of the distribution of semi-volatile organic compounds in streambed sediments, United States from 1992 – 1995, Lopes et al. (87) indicated that phthalate esters are among the organic compounds usually encountered in streambed sediments. In 1994, Vitali et al. (84) conducted a sampling campaign for the determination of phthalate acid esters levels in freshwaters and sediment of rivers and lakes of the Rieti District (central Italy). They found that there is a direct relation between phthalates levels and the input to urban or industrial treated wastewaters near the sampling point. They concluded that the concentration of phthalates in fresh waters could be considered as markers of contamination sources. In another survey, Furtmann K, (86) gathered a database of phthalate concentrations over a two years period of time in all matrices of the aquatic environment in Northrhine-Westfalia (Germany). The database included levels of phthalates in surface waters, sediments, suspended particulate matter rainwater, wastewater and sewage sludge. He concluded that sewage sludge contains the highest concentration of phthalates.

In a survey of residue levels of phthalate esters in water and sediment samples from Klang River basin Malays, Tan, G. H. (83) found that levels of PAEs correspond to those reported from North America and Western Europe. He found that DEHP levels in freshwater sediment samples ranged from 180 ppb to 30.0 ppm. The sediment samples, however, are found to contain DEHP ranging from 493 ppb to 15.014 ppm. Phthalates levels were high around a station where direct discharge points are found. Atlas and Giam (174) measured trace organic compounds in air and rainfall at a rural site in Texas. They found that chlorinated hydrocarbons and phthalic acid esters (PAEs) were present at concentrations of ng/m^3 in air and ng/L in precipitation. Their results showed that the most abundant compounds measured in air and rainfalls were PAEs. Their study also showed that PAEs were found in concentrations higher than other compounds such as toxaphene, chlordane and hexachlorocyclohexanes (HCHs).

Below the Vaal River Barrage in South Africa. Van Steenderen et al. (175) identified a number of point source contamination sites, which could affect the water quality for users further down the river. After checking 25 points, they found that DBP and phenol were found at all the sampling points. Thuren and Larson (176) measured the levels of DBP and DEHP in airborne fallout and in air at 14 localities in Sweden to determine whether their distribution is governed by local or long-range transport processes. The results indicated that a total deposition of DBP and DEHP to the ground in Sweden is about 220 tons per year and is of a similar order of magnitude as the emissions.

Bauer and Herrmann (85) tried to determine the percentage of PAEs transported in the leachate solutions of a number of landfills. The results showed that the maximum concentration of DEHP was 235.9 ppb and of DBP was 62.7 ppb in the leachate solutions. Suspended particles contained maximum concentrations of 167.6 µg/g and 126.0 µg/g for DEHP and DBP respectively. Their results also indicated that 85% of the total PAEs and a mean of 87% of the hydrophobic DEHP was detected in the dissolved phase. The amounts of PAEs in solution were correlated to dissolved organic carbon (DOC) concentrations. Moreover, there was a negative correlation of the contents of suspended solids with PAEs in dissolved form. They concluded that in municipal landfill leachates the DOC is much more important as a transport vehicle for hydrophobic phthalate esters than the suspended particles present.

A study of organic contamination in Oso Bay, Texas, by Hollyfield, and Sharma (177) was carried out by analyzing sediments from 9 sites in the bay by GC/MS. They found that in most of the sites, sediments contained about 40-193 mg/kg of phthalates. They indicated that these contaminants originated from a variety of sources, including a landfill, military facilities, municipal discharges, and industrial discharges. The USEPA water quality database STOrage and RETrieval (178) contains a survey of surface water monitoring data from the year 1988 to 1993. The database shows that a total of 4448 DMP observations including 17 detected values were reported (0.38%). For DEP, 4458 observations were reported, including 56 detected values (1.3%). For DBP, 4544 observations including 98 detected values were reported (2.2%), while for BBP, 4399 results were reported including 55 detected values (1.7%). The very low percentages of detectable concentrations are attributed to the relatively high detection limits that generally ranged from 1 to 10 ppb. Staples et al. (95) reported that most detected concentrations of DMP, DEP, DBP and BBP ranged from 0.01 to 1.0 ppb.

2.2.5 Health Effects

As indicated earlier phthalate esters are widespread in the environment. Major part of the phthalates entering the environment are suspected to come from anthropogenic sources with disposal of phthalates-containing products where landfills and incineration being the major source. In recent years, the health effect of phthalate on human and animals has been subjected to an intensive research in Europe and United States of America.

A number of toxicological studies conducted on phthalates have indicated that these chemicals have been implicated in mammalian hepatotoxicity (179), mammalian testicular atrophy (180), mammalian teratogenicity (181), and plant toxicity (182). Animal data indicate that phthalates are absorbed after oral administration, inhalation or after dermal contact. Orally administrated diesters are hydrolyzed to the respective monoesters and alcohols in the gut. The diesters and monoesters are widely distributed in organisms without showing accumulation. For example, ingestion of an unspecified quantity of DMP resulted in moderate toxicity characterized by tachycardia, marked hypotension and loss of consciousness. Ingestion of about 10 g of DBP resulted in ocular toxicity and nephrotoxicity. (183 – 185).

In a study involving a Swedish PVC-processing factory, peripheral nervous system symptoms and signs were investigated among 54 male workers exposed mainly to DEHP, and BBP. The workers were divided into three groups of approximately equal size and with mean phthalate exposures of 0.1, 0.2, and 0.7 mg/m^3. Some workers displayed various peripheral nervous system symptoms and signs, but these were not related to the level of exposure. None of the workers reported symptoms indicating work-related obstructive lung disease. Conventional lung function tests also showed no association with exposure. However, some biochemical parameters (hemoglobin, a-1-antitrypsin, immunoglobulin A) showed associations with exposure (91).

Generally, the acute toxicity of the phthalates is low in rats and mice. Phthalate esters derived from the shorter, saturated carbon chain alcohols appear to be more toxic to rats and mice than the esters derived from longer-chain alcohols (91).

For DMP, oral lethal dose (LD_{50}) values of around 7-8 g/kg have been reported for rats and mice. Lethal doses of around 9 g/kg DEP in rats and mice have also been reported. Signs of acute oral toxicity in rats included reduced activity, difficulty in breathing and lack of co-ordination. (91).

Parkerton and Konkel (92) reported that the predicted no-effect concentration (PNECs) for DMP, DEP, DnBP and BBP ranged from 3109 to 4708, 865 to 1173, 43 to 62, and 38 to 60 ppb, respectively.

A number of researches have directed their research towards the determination of contamination levels of phthalates in baby food and infant formula in plastic packaged food such as milk, cream, butter and cheese (93). Others studied the migration of phthalates from PVC films during home-use and microwave cooking (81, 89, 90, 186).

Recently, Stringer, et al. (81) conducted a survey on the presence of phthalate esters and other components in children's toys. The results of their survey indicated that the majority of soft PVC toys contain substantial proportions of phthalate esters that have been the potential to leach out during use and therefore present an exposure risk to infants.

US Environmental Protection Agency (USEPA) has listed six of the phthalates shown in Table 2.3 in the water priority list, which consist of the hazardous compounds that need to be removed from waters. These phthalates were included in the EPA priority list because of their carcinogenic or xenoestrogenic properties (187, 188). Furthermore, in 1999, many European countries banned the use of phthalates in baby toys because the chemicals can leach out of plastic (89). Even though this move have been opposed by a number of companies that deal with plasticizers, many of these companies started to look for other types of plasticizers that do not pose health effect on human.

2.2.6 Degradation Pathways

Due to the recent findings of a number of studies on phthalates potential risk on health of biota, a great interest has been given to the removal of these compounds form the environment. Even though some studies were conducted on the removal of phthalates from air, the majority was directed towards the removal from water and sediments. Several studies have been carried out in the area of treating phthalates based on the degradation pathways of these compounds via sorption, aqueous hydrolysis, photooxidation and biodegradation (80).

As mentioned earlier, hydrophobic organic pollutants have low aqueous solubility and tend to be adsorbed by suspended particulates, leading eventually to their storage in bed sediments. Thus, long chain (hydrophobic) phthalates can be adsorbed easily. A number of scientists tried to make use of this phenomena and suggested treatment units for phthalates based on this pathway. Zhou and Rowland (164) studied the interactions between hydrophobic organic pollutants and suspended particles in estuarine waters. Results of their research showed that partition coefficient of DEHP decreased with pH but increased with salinity, due to increased chemical hydrolysis in higher pH waters and decreased solubility in saline waters.). In another study, Zhao and Sengubta (104) used a polymeric ligand exchanger (PLE) for selective removal and recovery of phthalates among other anionic trace contaminants. They found that compared to traditional sorbents, the PLE can selectively remove these contaminants, and yet it is amenable to efficient regeneration with brine. Klug and Forsling (105) conducted a spectroscopic study of phthalate adsorption on gamma and alumina oxide. The study results showed the formation of two different types of complexes: outer and inner sphere. The relative concentrations of these complexes were shown to vary considerably with pH but very little with increasing ionic strength.

Phthalate esters are also susceptible to aqueous hydrolysis. The products of hydrolysis are acid and an alcohol. Phthalate esters can undergo two hydrolytic steps, producing first the monoester and one free alcohol moiety and a second hydrolytic step creating phthalic acid and a second alcohol. Ester hydrolysis may be either acid or base catalyzed, with, in some instances, metal ions, anions, or organic materials serving as catalysts. Phthalate esters are hydrolyzed at negligible rates at neutral pH as shown in Table 2.6. Acid hydrolysis of phthalate ester is possible, but is estimated at four orders of magnitude slower than alkaline hydrolysis. Hydrolysis rates decrease and corresponding half-lives increase with increasing alcohol chain length. Half-lives ranged from about 3 years for DMP to 2000 years for DEHP. Gledhill et al. (189) estimated a hydrolysis half-life of >100 days for BBP. Hydrolysis is unlikely to be an important fate process for phthalate esters under typical environmental conditions.

Degradation by light (i.e. photodegradation) is another method of degradation of phthalates in the environment. Aqueous photolysis occurs through absorption of UV light in the region of 290-400 nm. Shorter wavelengths are attenuated by passage through the atmosphere and water column, while longer wavelengths lack the sufficient energy to break bonds (80). Photolysis can be mediated via either direct or indirect mechanisms. Direct mechanism involves direct absorption of UV radiation by the chemical, while indirect mechanism occurs by absorption of UV light radiation by water with the formation of activated species such as hydroxyl radicals (108).

Direct irradiation of organic micro-pollutants by high-intensity UV light provides a significant destruction pathway. For example, contaminants such as trichloroethylene (TCE), up to 30% of the reaction occurs via direct photolysis during typical UV/Oxidation treatment. Few studies on phthalate ester photolysis are available. Gledhill et al. (189) reported that a 1.0 mg/L solution of BBP exposed to sunlight for 28 days resulted in less than 5% degradation.

TABLE 2.6: Degradation Half-Lives of Common Phthalate Esters

Compound	Aqueous Hydrolysis Half-Lives (years)	Atmospheric Photooxidation Half-Lives (days)
DMP	3.2	9.3 - 93
DEP	8.8	1.8 - 18
DBP	22	0.6 – 6.0
BBP	> 0.3	0.5 - 5.0
DNOP	107	0.3 – 3.0
DEHP	2000	0.2 – 2.0

Wolfe et al. (190) estimated a maximum near-surface phthalate ester photolysis half-life of 144 days for phthalate esters. This estimate was based on unpublished experiments with DMP spiked into surface water that was irradiated with sunlight for one week. Photooxidation of phthalate esters in sunlit surface waters does not appear to represent an important transformation process. Based on the data of Wolfe et al., Howard (191) estimated that aqueous photooxidation half-lives range from 2.4 to 12 years for DEP and DnBP and from 0.12 to 1.5 years for DEHP.

In contrast to the minor role of photodegradation in natural waters, these reactions appear to be much more important in the atmospheric fate of phthalate esters. Reaction with hydroxyl radicals is generally the most important photodegradation process for organic chemical pollutants in the atmosphere. Predicted photooxidation half-lives for phthalate esters are listed in Table 2.6 (80).

Biodegradation is a critical process affecting the environmental fate of phthalate esters. Considerable research has been conducted on the biodegradability of phthalates over the last few decades. Microbes from diverse habitats have been shown to degrade phthalate esters and resulting intermediates (101, 187, 192).

Representatives from both aerobic and some anaerobic environments include gram-positive and gram-negative bacteria have been used for the degradation of phthalates. Although some individual microbes are capable of completely mineralizing phthalate esters, more efficient metabolism appears to result from mixed microbial populations, typically found in the environment (193, 194).

Research suggests that the metabolic pathway for the microbial metabolism of phthalates under both aerobic and anaerobic conditions begins by ester hydrolysis to form monoester and the corresponding alcohol. Under aerobic conditions, further enzymatic degradation of the monoester proceeds via phthalic acid by either a 3,5 or 4,5 dihydroxyphthalate pathway to procatechuate. Aromatic ring cleavage of procatechuate can then occur via either an ortho pathway that results in the formation of pyruvate and oxaloacetate or a meta pathway yielding a β-ketoadipate that is further degraded to acetyl CoA and succinate (195).

Although less is known about the pathways of anaerobic catabolism, it appears that the monoester is degraded to phthalic acid and then further degraded by the same pathway used for benzoate (194). Benzoate has been shown to be readily degraded anaerobically (196). Primary degradation for the lower molecular weight phthalates DMP, DEP, DBP and BBP occurred rapidly, typically exceeding 90% degradation within a week. Most higher molecular weight phthalate esters demonstrated primary degradation in excess of 90% after 12 days. Madsen et al. (102) studied the kinetics of phthalate mineralization in sludge amended soil and indicated that aerobic mineralization was 4 to 5 times faster than anaerobic mineralization. The data of this study suggested that in the absence of oxygen, which was the case with sludge-amended soil, a significant fraction of the phthalate escaped mineralization under the in-situ conditions.

Despite the fact that biodegradation of phthalate esters is an important pathway and biotreatment is a promising technique for their removal form the environment; there exist a number of limitations that might prevent its widespread application. Among the drawbacks to bioremediation are inhibition by non-pollutant metabolites, toxicity of contaminants at high concentration, inability to deal with contaminant mixtures, long residence time needed and high cost. For example, in their study, O'Connor et al. (197) evaluated phthalates for their anaerobic biodegradability and toxicity to methanogenesis. They concluded that even though phthalates were metabolized under methanogenic conditions, their fate was significantly influenced by their concentration and residence time in methanogenic habitats. In another research, Kleerebezem et al. (100) investigated the anaerobic biodegradability of phthalic acid isomers. Results of the study showed that 17 to 156 days were required for only 50% degradation of these compounds. They concluded that the time needed for the startup of anaerobic bioreactors treating wastewaters containing phthalic acid isomers depends little on the microbial composition but may take several months.

In 1998, Bauer et al. (35) published the results of their work on the degradation of phthalates in municipal landfill leachates. They observed that large amount of phthalates were leached from plastic dumped at municipal landfills. This leachate transports phthalates either adsorbed on particulate matter or in the dissolved phase. Dissolved organic materials such as humic substances enhance the solubility of PAEs. The results of their work also showed that in the biochemical environments of municipal landfills, short chain PAEs can be degraded by microorganisms, however, there was no cleavage of the aromatic ring. Long chain PAEs are neither degraded abiotically nor by microorganisms and hence they can be leached and washed out of the landfills into the groundwater and continue to be a threat to the environment.

Ejlertsson et al. (166) studied the influence of some factor on the degradation of phthalates under methanogenic conditions. These factors included water solubility, side-chain degradability and side-chain structure. Their investigation strongly indicated that phthalates having high water solubility were degraded, whereas those having low water solubility were not. The results of their study also showed that all alcohols, commonly used in the production of phthalates and enhances their solubilities, were degraded to methane and carbon dioxide. The effect of solubility of PAEs was also investigated by Wang and Grady (97). They studied the effects of biosorption and adsorption on biodegradation of DnBP. The data indicated that when the initial DnBP concentration was lower than the solubility limit, biosorption before biodegradation decreased the biodegradation rate by lowering the soluble DnBP concentration.

In their investigation of the inhibition of methanogenic activity of starch-degrading granuals by aromatic pollutants, Fang et al. (103) found that phthalates were among the group of chemicals that can be considered toxic to the microorganisms. To show how sensitive the biotransformation mechanism of PAEs is, Chauret et al. (198) conducted a research on the biotransformation of DnBP by subsurface microorganisms. They found that factors such as nutrient depletion, lowering of the redox potential under sulfate-reducing conditions, and buildup of toxic intermediates reduced the biotransformation rate significantly.

In their study, Wang et al. (192) suggested pretreatment step for wastewater discharged from a phthalic acid production factory that consist of several physicochemical treatment processes. Their proposed treatment process included flocculation-clarification, followed by filtration and finally by neutralization with lime. They claimed that this process is very effective in reducing the PAEs form 2000 ppm to 50 ppm. They claimed that after treatment, the water would become degradable by biological process.

Furthermore, membrane processes are among the new processes that are considered promising in the treatment of complex wastewater. Reverse osmosis is one of the most widely used treatment method in the Northwestern Europe countries while nanofiltration has gained popularity during the last 5 years (199). Unfortunately, the literature search did not reveal any study on the treatment of phthalate acid esters by membrane processes alone.

In summary, the extensive literature search conducted in this study has clearly indicated that phthalate esters are among these contaminants that are very complex and difficult to treat by the traditional methods. Their chemical and physical characteristics such as the high molecular weight and hydrophobicity pose many difficulties in treating these chemicals. For example, air stripping and adsorption of phthalates do not destroy the contaminants, but only transfer it form one phase to another, while biological treatment is susceptible to poisoning of microorganism by the heavy metals and the phthalates themselves. It is clear that there is a need to explore the feasibility of using other treatment techniques that are capable of destroying the phthalates in the contaminated water in an efficient manner. In addition, the literature search has showed a lack of work on the treatment of phthalates when they exist in the dissolved form of aqueous media. Therefore, it was the main objective of this study to assess the treatability of water contaminated with phthalates using the advanced oxidation technology, which has been applied successfully on many types of organic pollutants.

CHAPTER 3

OBJECTIVES

The primary objective of this study is to investigate the removal efficiency of one of the phthalate esters from water using two of the Advanced Oxidation Processes (AOPs). The two AOPs selected are: Fenton/photo-Fenton and UV/H_2O_2 processes. These two AOP processes were selected since they represent two different mechanisms in which hydroxyl radicals are generated as discussed in Chapter 2. Dimethyl phthalate (DMP) was selected as a target compound that represents the low alkyl chain phthalate esters, which are characterized by the high solubility in water. It was indicated in the previous chapter that the extent of solubility of the compound in water influences its removal efficiency by the AOPs. This is due to the fact that hydroxyl radicals (OH^o) react mainly with dissolved organic pollutants. Furthermore, previous studies showed that DMP and other low alkyl chain phthalate esters could be more toxic to microorganisms during the biotreatment process than the high alkyl chain phthalates.

The following objectives have been set for this study:

(1) To study the effect of initial concentrations of ferrous ion (Fe^{2+}), H_2O_2, temperature, pH and UV exposure time on the efficiency of Fenton process in removing DMP from water.

(2) To study the effect of initial concentrations of H_2O_2, temperature, pH and UV exposure time on the efficiency of UV/H_2O_2 system in removing DMP from water.

(3) To compare the Fenton and UV/H_2O_2 processes with respect to their treatment efficiencies of DMP in the presence of methanol.

(4) To optimize the parameters of the selected process that will give the best removal efficiency of DMP.

CHAPTER 4

MATERIALS & METHODS

4.1 The Photo-Reactor

All experiments were conducted in a locally fabricated bench-scale photo-reactor of approximately 1.2 Liter capacity made of Pyrex-glass equipped with an outer Plexiglas cylindrical vessel. A sketch of the reactor is shown in Figure 4.1. The internal diameter of the inner reactor is 9.0 cm with a height of 19 cm while the outer cylinder has a diameter of 14.0 cm and a height of 25 cm. A low-pressure ultraviolet (UV) lamp with an average diameter of 2.0 cm, irradiating at the wavelength of 254 nm with an output intensity of about 100 mWatt is used for illumination purpose. The lamp is placed 2.5 cm above the base of the reactor to avoid breakage by the magnetic stirrer, which is used to mix the reactants inside the reactor.

The starting volume of the solution in the reactor is 400 ml. At this point, the lamp will be immersed up to 5.5 cm inside the solution. The reactor works in a batch mode and samples were withdrawn from a sampling point using a pipette. Samples were withdrawn from the reactor at 0, 15, 30, 45 and 60 min respectively. A preliminary investigation showed that the temperature of the solution would be increased by a maximum of 10°C

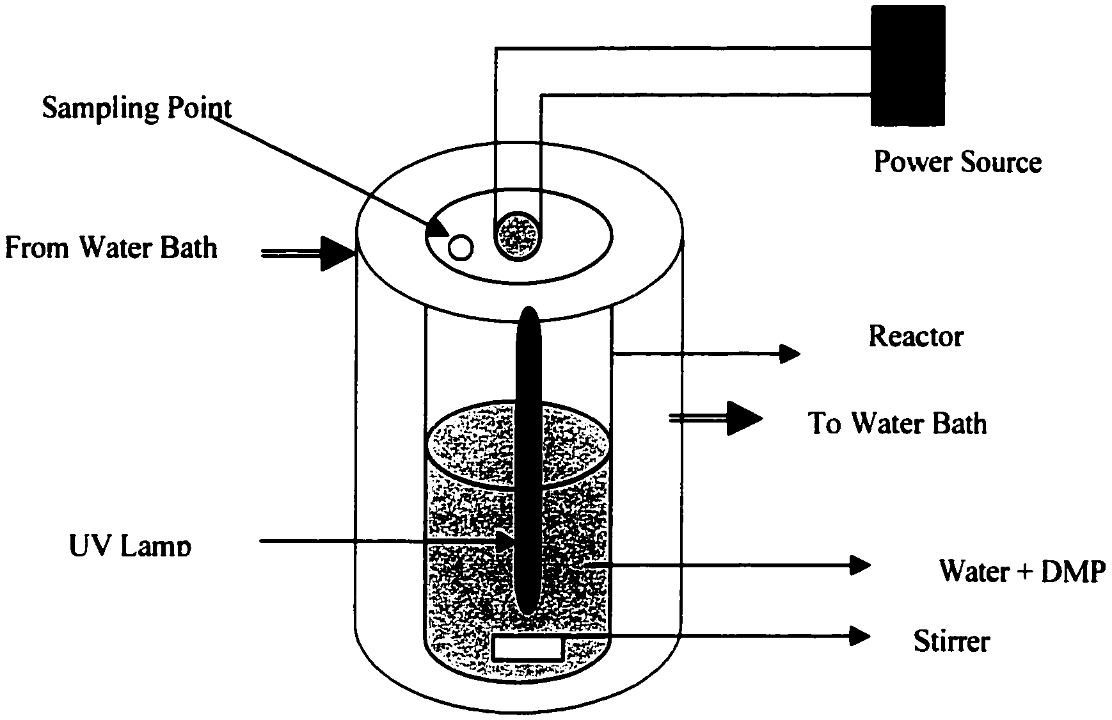


Figure 4.1: Bench-Scale Photo-Reactor

after exposed to the UV lamp for one hour. Thus, an outer cylinder was used as a water jacket to adjust the temperature of the solution and to overcome the problem of heating due to the UV lamp. An adjustable-temperature water bath was used to control the temperature of the cooling water. The variation of the temperature after the usage of the water jacket was only ± 2°C.

4.2 Preparation of the Solutions

4.2.1 Dimethyl Phthalate (DMP) Standard

As was stated earlier, methanol (CH_3OH) is the alcohol used in the production of DMP. However, in the environment, phthalates can be detected in water with or without the designated alcohol. If the contamination of water with DMP occurred during the production stage, methanol is most likely to be detected along with DMP. However, if the contamination occurred after usage of products that contain DMP, methanol is not likely to exist.

For this reason, one set of experiments consisted of preparing stock standard solutions of DMP initially in methanol before spiking into the water, while the other set of experiments involved spiking DMP directly into the water without introducing methanol as the solvent for DMP. The DMP was purchased from Chemical Service, England with purities of approximately 99 %. Approximately 200 mg of DMP was dissolved in 100 mL CH_3OH forming a stock DMP standard solution of approximately 2000 ppm. Methanol used was HPLC grade with 99.99 assay from Fisons Co.. Aliquots of this stock were spiked into a distilled and de-ionized water to prepare the "DMP-contaminated water". Water samples with initial DMP concentrations of 0.1 and 0.2 mM (i.e. 20 and 40 ppm) were prepared. In these water samples, methanol concentration was about 80mM (2560 ppm).

Other sets of "DMP-contaminated water samples" were prepared directly by dissolving the pure DMP compound into distilled and de-ionized water directly. Water samples with initial DMP concentrations of 0.1 and 0.2 mM (i.e. 20 and 40 ppm) were prepared.

4.2.2 Hydrogen Peroxide (H_2O_2) Solution

Stock hydrogen peroxide (H_2O_2) of approximately 35% purity was used to prepare the H_2O_2 solution. The actual concentration of the H_2O_2 solution was determined by standardizing with 0.1N potassium permanganate solution ($KMNO_4$) titration method (200, 201). In this method, approximately 10.0 gm of the original H_2O_2 solution was transferred into a 500 mL volumetric flask. Distilled and deionized water was added to the flask up to the mark. One hundred (100) mL of this solution, acidified with 5 mL of 20% sulfuric acid (H_2SO_4), was titrated with 0.1N $KMNO_4$. Formation of persistent pink color was taken as an indication of the end-point of the titration.

The concentration of the H_2O_2 solution was calculated using the following formula:

$$\% \ H_2O_2 \text{ (by weight)} = (\text{mL } KMNO_4 * 0.1 * 0.01701*1000) / \text{wt of } H_2O_2 \qquad (4.1)$$

In this study, the H_2O_2 stock solution prepared was calculated to have an average concentration of approximately 180 mM (6120 ppm) H_2O_2. Certain volumes of this stock solution were added to the "DMP-contaminated water samples" to the desired concentrations of H_2O_2.

4.2.3 Ferrous Sulfate ($FeSO_4.7H_2O$) Solution

Ferrous sulfate ($FeSO_4.7H_2O$) from Riedel-De Haen AG solution was used to prepare a stock ferrous ions (Fe^{2+}) solution of 100 mM by dissolving 278 mg into 100 mL distilled and de-ionized water. The Fe^{2+} stock solution was prepared on daily basis and few drops of 0.01 M Sulfuric Acid were added to the stock solution in order to prevent oxidation of ferrous ions (Fe^{2+}) into ferric ions (Fe^{3+}).

To stop the reaction at certain time intervals, anhydrous sodium sulfite (Na_2SO_3) reagent from BDH Chemicals Ltd., Poole England, was added to the water samples. Sodium sulfite will immediately quench the reactions by completely removing the residual H_2O_2 reagent.

4.3 Measurement of DMP

4.3.1 Liquid-Liquid Extraction

To measure the residual DMP concentrations after a certain reaction time, 20 mL water samples were extracted with 10 mL mixture of methylene chloride (CH_2Cl_2) and n-hexane (C_6H_{14}) (v/v 1:3 MDC/C_6). The 10 mL extract was then concentrated to 2 mL by gently purging with nitrogen gas. This extraction method is similar to the extraction method applied in EPA 606 Standard method for the analysis of phthalates in wastewater (202).

4.3.2 Analytical Techniques

4.3.2.1 Gas Chromatography (GC)

Varian *3400CX* model Gas Chromatograph (GC) equipped with a Photo-Ionization Detector (PID) was used for the analysis of DMP. A 30 m long, 0.53 mm i.d. DB-5 fused silica capillary column, was used for separation purpose. The oven temperature was programmed from 80°C to 200°C at a ramp rate of 20°C. Both detector and injector temperatures were set at 280°C. Helium gas was used as a carrier at a flow rate of 3 mL and a makeup of 27 mL. One (1) μL of the extract was injected into the GC by splitless mode. The GC instrument was calibrated by analyzing a number of standard solutions of different DMP concentrations. From the prepared stock solution of DMP in 4.2.1, several stock standards of approximately 5, 10, 15, 20, 50, 100 and 200 ppm of DMP was injected into the GC. The area counts of the DMP peak of the various standard concentrations are listed in Table 4.1, and plotted in Figure 4.2.

4.3.2.2 UV/VIS Spectrophotometer

An hp 8451A diode array UV/VIS spectrophotometer from Hewlett Packard was used to measure the absorption of the various solutions.

4.4 Experimental Procedure Layout

The effects of the various parameters including initial concentrations of the reactants (H_2O_2 and Fe^{2+}), UV, pH and temperature on the degradation of DMP were investigated. The effect of the presence of the alcohol was also investigated. Table 4.1 indicates the experimental conditions employed throughout this study.

TABLE 4.1: Calibration Data for Analysis of DMP by Gas Chromatography

DMP ppm	Area Count R_1	Area Count, R_2	Area Count R_3	Average Area Count
201.860	230678.0	230678.0	230678.0	230678.0
134.573	169697.0	169697.0	169697.0	169697.0
100.930	119651.0	119651.0	119651.0	119651.0
50.465	60146.0	60146.0	60146.0	60146.0
20.186	22656.0	22656.0	22656.0	22656.0
13.457	14237.0	14237.0	14237.0	14237.0
10.093	11105.0	11105.0	11105.0	11105.0
5.047	5054.0	5054.0	5054.0	5054.0

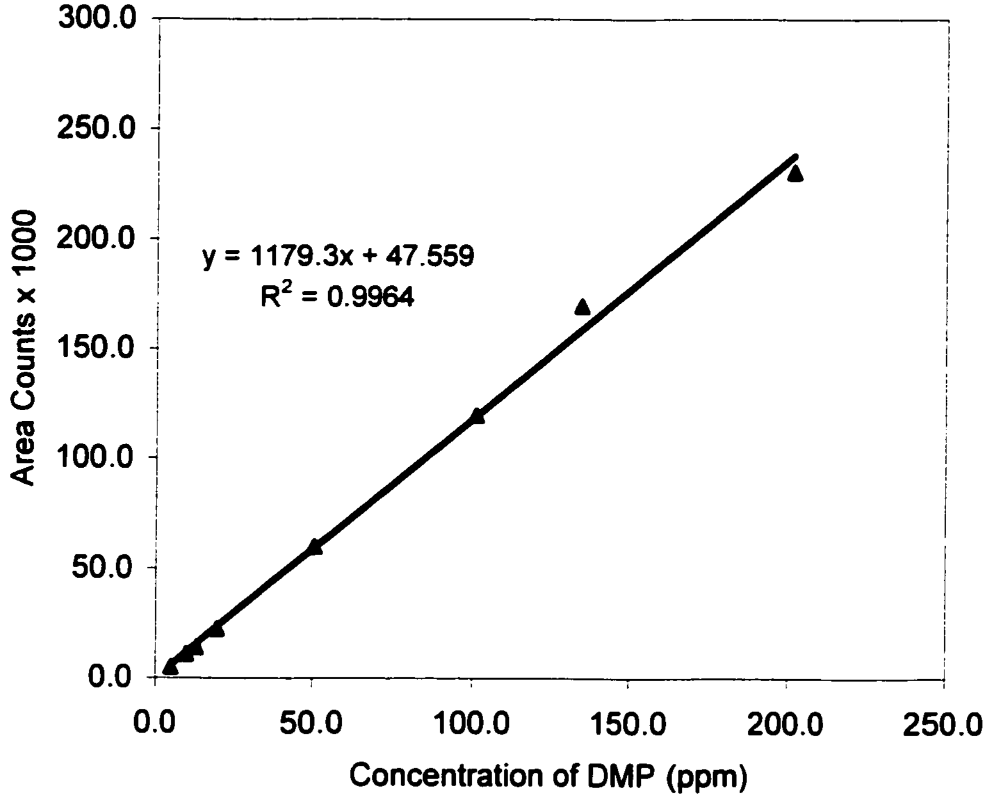


Figure 4.2: GC Calibration Curve for Analysis of DMP.

The following experimental steps were followed throughout the study:

1. Two hundred (200) mL of distilled and de-ionized water samples were spiked with certain amount of DMP to achieve the required concentration. Water samples were then mixed thoroughly for 24 hours to ensure that DMP was dissolved completely into the water samples. These samples were then transferred to the reactor.

2. Temperature and pH of the DMP-spiked water samples were adjusted to the required levels and measured by a thermometer and pH meter, respectively.

3. Ferrous sulfate was then added to the DMP-spiked water samples in certain amounts at the predetermined levels of Fe^{2+} concentrations.

4. Hydrogen peroxide (H_2O_2) solution was then added to the solution gradually at the concentrations required while stirring at constant rate with a magnetic stirrer.

5. In the photo-Fenton experiments, UV source was used to irradiate the solution.

6. Twenty (20) mL samples were then taken from the reactor at times 0, 15, 30, 45 and 60 min and transferred into 25 mL glass brown bottles, which contain few milligrams of sodium sulfite.

TABLE 4.2: Experimental Conditions of the Study

Parameter	**Level**
DMP_i (mM)	0.1, 0.2
H_2O_2 (mM)	0.0 – 4.0
Fe^{2+} (mM)	0.1 - 0.4
UV Time (min)	0 - 60
pH	3 - 9
Temperature (°C)	15, 25, 35
Reaction Time (min)	0, 15, 30, 45, 60

7. These samples were then extracted by liquid-liquid method and the residual concentrations of DMP were measured by GC technique.

8. In the UV/H_2O_2 experiments, the same procedure was followed as in the Photo-Fenton experiment with the exception that no Fe^{2+} was added.

CHAPTER 5

RESULTS & DISCUSSION

The results obtained from a number of experiments to study the removal of DMP by Fenton and UV/H_2O_2 oxidation processes are presented and discussed in this chapter. As stated earlier, there were basically two types of aqueous matrices into which DMP was spiked. The first matrix was pure, distilled and de-ionized water and it is referred to it in the text as "DMP/Water". The second matrix was pure distilled water mixed with a known concentration of methanol (i.e. 80 mM or 2560 ppm) and it is referred to as "DMP/Water/MeOH". The discussion in section 5.1 is on the removal of DMP from "DMP/Water" matrix, while in section 5.2, it is focused on DMP removal from "DMP/Water/MeOH" matrix.

Experiments in this study were designed and conducted in a step-wise manner to understand the removal pattern of DMP under various conditions. The removal of DMP by the action of H_2O_2 alone was investigated first, followed by the Fenton method in which Fe^{2+} was applied in addition to H_2O_2, followed by photo-Fenton in which UV irradiation was introduced in addition to H_2O_2 and $Fe^{2+}$and finally the UV/H_2O_2 processes was studied in which Fe^{2+} was not used.

The following sections discuss the influence of various parameters on the removal efficiency of DMP. These parameters include ferrous ions (Fe^{2+}), hydrogen peroxide (H_2O_2), UV dosage, pH and temperature. Reaction time of 60 minutes was selected since the preliminary investigation carried out in this study showed that an appreciable amount of 0.1 mM of DMP can be removed within 1 hour. Measurements of DMP at 15, 30, 45 and 60 minutes were also taken to determine the removal rates of DMP using various treatment methods under various conditions.

5.1 Removal of DMP from "DMP/Water" matrix

5.1.1 Removal of DMP by H_2O_2 alone

Hydrogen peroxide (H_2O_2) by itself has long been used in industrial applications as a powerful oxidant. It has various environmental applications such as the oxidation of sulfides with respect to odor control, notably in pulp and paper manufacture and textile plant wastes (203). It was used as an additional oxygen source for overloaded activated sludge plants (204). Hydrogen peroxide has also applications in the surface treatment industry involving cleaning, decorating, protecting, and etching metals (16). H_2O_2 is typically injected at concentrations in the range of 50 to 100 ppm for in situ applications with high concentrations in excess of 500 ppm being used to control microbial growth (205).

The literature reviewed in this study revealed a lack of research work on testing the efficiency of H_2O_2 alone on oxidizing phthalate esters. Thus, in this study, it was decided to investigate the efficiency of H_2O_2 alone on removing DMP in water. The initial concentration of DMP used was set at 0.1 mM (i.e. 20 ppm). This value was carefully selected after reviewing the literature, which indicated that levels of phthalate in the water usually ranged from 10 ppb to 10 ppm (91). However, higher levels of phthalates could also be found in the environment especially if accidental spills occur. The DMP concentration level of 20 ppm selected in this study represents a reasonable level that can be tested for its treatability by AOPs. In addition, some experiments were conducted using higher concentrations of DMP (i.e. 40 ppm) to study the effect of the initial concentration of the target contaminant on its removal efficiency by AOPs. The initial concentrations of H_2O_2 used were between 0.0 mM up to 4.0 mM (i.e. 0 to 140 ppm). This means that molar ratio of H_2O_2 to the initial DMP concentrations reached as high as 40:1. This range of H_2O_2 was selected since it represents a practical range beyond which H_2O_2 concentration may not be cost effective. In these set of experiments, pH, temperature and stirring rate were kept constant and the percentage DMP removal was determined after 15, 30, 45 and 60 minutes.

The results of these experiments are shown in Table A.1.1 and Figure 5.1. The results clearly show that H_2O_2 alone was not able to degrade DMP to any appreciable level. It is clear that H_2O_2 alone was not able to oxidize the DMP under the experimental conditions used in this study. The reason behind that can be attributed to the inefficiency

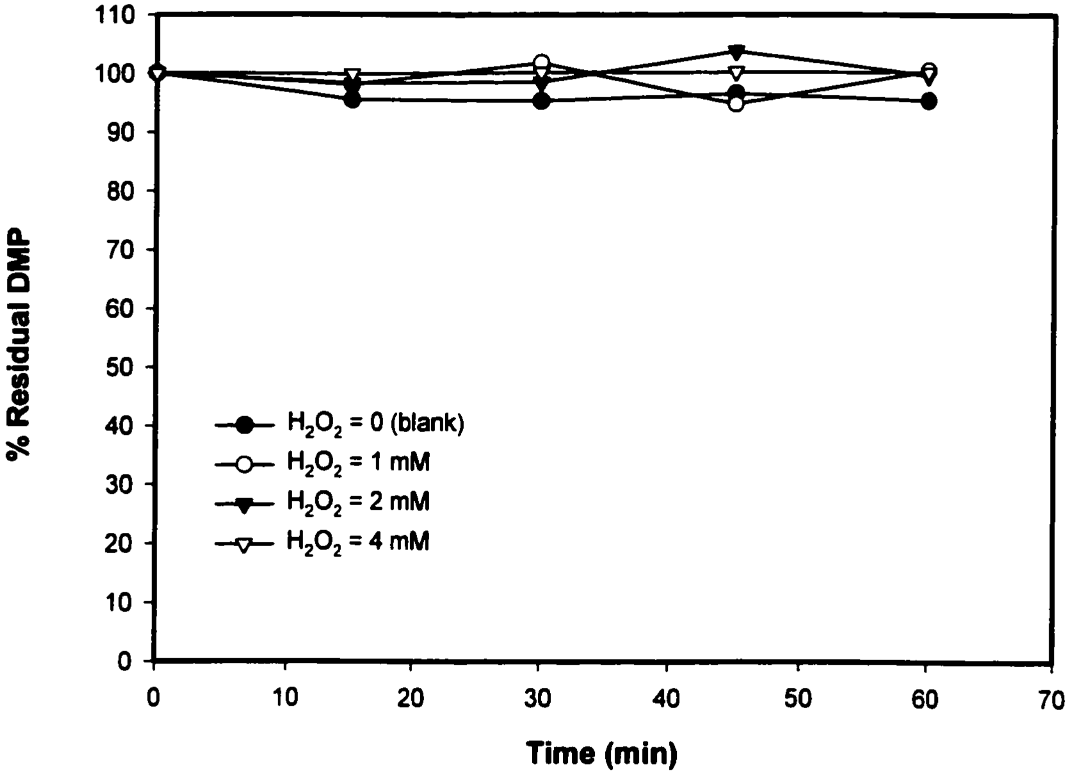


Figure 5.1: Removal of DMP from Water by H_2O_2 Alone.
(DMP$_i$ = 0.1 mM, pH = 6, Temp. = 25°C)

of hydrogen peroxide alone to degrade high concentrations of many refractory contaminants.

Highly chlorinated aromatic compounds and inorganic compounds (e.g. cyanides) are among those organics that were not degraded by H_2O_2 alone. Researchers have found that at reasonable H_2O_2 concentration, the reaction rates of H_2O_2 with these compounds are very low (16).

The comprehensive literature search carried out on this subject did not lead to any previous work on the decomposition of DMP by H_2O_2 alone. Thus, the results of this study proved that DMP could be included among these compounds that are difficult to decompose by H_2O_2 alone within the condition used. The difficulty of DMP decomposition may be justified by the fact that phthalate esters belong to a group of chemicals that are highly stable with high molecular weight.

It seems that the chemical bonds within the chemical structure of the ortho-phthalic acid diesters, shown in Figures 2.1 through 2.3 are fairly strong and hard to break. A stronger oxidant with a higher oxidation power is needed to break these bonds. The highly reactive hydroxyl radicals (OH^{o}) generated by the advanced oxidation processes (AOPs) represent a good candidate that may be able to degrade phthalates.

5.1.2 Removal of DMP by Fenton Process

In Fenton process OH^o radicals are generated after mixing of an oxidant (H_2O_2) and ferrous ions (Fe^{2+}). Ferrous ions (Fe^{2+}) work as a catalyst according to equation 2.2. The influence of various parameters like the concentration levels of H_2O_2 and Fe^{2+}, pH and temperature on the efficiency on the DMP removal from pure water samples were investigated by conducting several experiments. The results of these experiments are discussed in the following sections.

5.1.2.1 Effect of Fe^{2+} Concentration

According to equation 2.2, one mole of Fe^{2+} will produce one mole of OH^o radicals, and an increase in the concentration of Fe^{2+} will increase the generation rate of OH^o radicals and may enhance the removal efficiency of the DMP. To explore the effect of Fe^{2+} on the removal of DMP, the concentration of Fe^{2+} was varied while keeping other parameters constant. In these set of experiments, the initial H_2O_2, pH and temperature were set at 2 mM (68 ppm), 3 and 25°C respectively. The value of pH was selected after reviewing the literature, which claim that Fenton works more efficient under acidic conditions. The results are listed in Table A.1.2 and plotted in Figure 5.2, which shows that, in the first 15 minutes, the removal of DMP increased from 45% to more than 90 % when the initial concentration of Fe^{2+} was increased from 0.2 to 0.4 mM (11.2 to 22.4 ppm).

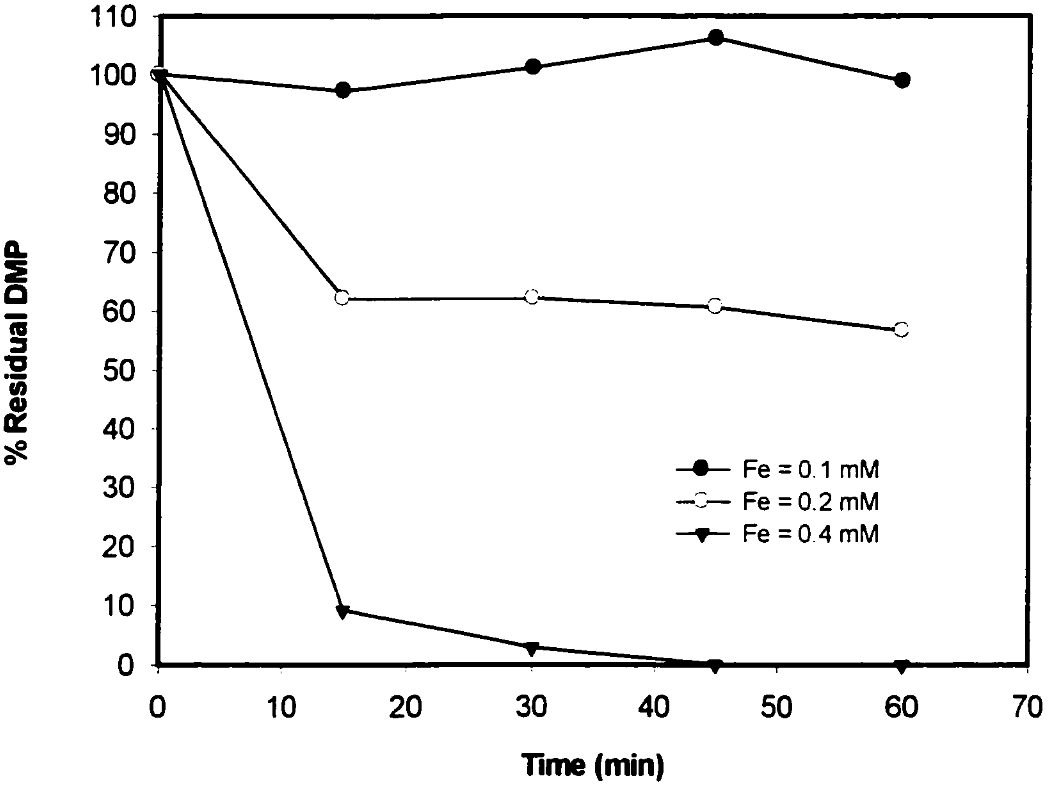


Figure 5.2: Removal of DMP by Fenton Process at Various Fe^{2+} Concentrations (DMP_i = 0.1 mM, H_2O_2 = 2 mM, pH = 3, Temp. = 25°C)

After a reaction time of 45 minutes, complete removal of DMP was observed at Fe^{2+} concentration of 0.4 mM (22.4 ppm). It can also be noted from Figure 5.2 that there was basically no appreciable removal of DMP even after a reaction time of 60 minutes. This could be due to that the 0.1 mM of Fe^{2+} was not high enough to produce sufficient OH^o radicals to degrade DMP. It seems that the ratio of $DMP_i : Fe^{2+}$ of 1 : 4 represents a reasonable starting concentration of Fe^{2+} that should be supplied in order for Fenton system to be able to remove DMP from water at this concentration of DMP and H_2O_2.

Figure 5.2 also shows that the removal of DMP follows a similar trend at Fe^{2+} concentrations of 0.2 and 0.4 mM, respectively. Obviously, at Fe^{2+} concentrations of 0.1 mM, there was basically no removal of DMP and thus there is no trend of removal. At the Fe^{2+}concentration levels of 0.2 and 0.4 mM, a higher removal rate is observed in the first 15 minutes of reaction time followed by a much slower rate. This behavior can be explained by referring to the reaction in equation 2.2, which shows that as the Fenton reaction proceeds, ferrous ions (Fe^{2+}) will be depleted and transformed into ferric ions (Fe^{3+}). The latter may not be as good as ferrous ions in the production of OH^o radicals. As a matter of fact, it was noticed during running the experiments that the color of the water has gradually changed from light greenish to light brownish, which is a clear indication that Fe^{2+} ions are consumed and more of Fe^{3+} are formed in the form of ferric oxides ($Fe(OH)_3$) which tend to precipitate. From engineering point of view, the formation of excessive amounts of ferric oxides is considered a disadvantage. This is because an additional treatment step is needed following the treatment by Fenton system in order to remove the precipitated material. The additional treatment step requires an additional cost that must be taken into consideration.

Another reason of the initial higher rate of DMP removal can be attributed to the mechanism of OH^o radicals formation in an aqueous medium. It is well known that the formation of OH^o radicals is very fast, however, most of it is consumed very quickly by the reaction with H_2O_2 as shown in equation 2.2 or with super-oxide radical (HO_2^o) as shown in equation 2.6. As reaction between Fe^{2+} and H_2O_2 and HO_2^o proceeds, more OH^o radicals will be formed and more DMP will be removed but with a slower rate. The reaction continues until one of the reactants is consumed or converted to another form. The formation of intermediates, which might have different reaction rates with (OH^o) radicals, could be responsible for such high rates of DMP removal.

The experimental results clearly demonstrate the significant role that the catalyst (Fe^{2+}) plays in the Fenton process. The catalytic effect of Fe^{2+} is vital in determining the extent of DMP removal by Fenton process. In general, any additional dosage of Fe^{2+} applied can react with H_2O_2 and produce larger amounts of hydroxyl radicals in the solution provided that enough concentration of H_2O_2 is supplied. Many research studies that investigated the efficiency of Fenton process on the removal of organic compounds other than DMP have arrived to a similar conclusion (46). For example, in his study of the oxidation of 2-Chlorophenols in water by Fenton method, Lin et al. (139) found that better removal efficiency of the compound was achieved when Fe^{2+} concentration was increased from 0.5 ppm to 10 ppm.

In order to determine the removal rate of DMP by Fenton system, a plot of the ratio of DMP at certain time t, (DMP_t) to the initial DMP concentration (DMP_i) is plotted with time a in semi-logarithmic scale as shown in Table A.1.3 and Figure 5.3. From Figure 5.3, it seems that removal of DMP by Fenton process follow a pseudo-first order reaction with a rate coefficient calculated to be 0.0989/min according to the following equation of the best fit formula:

$$\text{Ln}\,[DMP / DMP_i] = -0.0989 * t \qquad (5.1)$$

$$r^2 = 0.9092$$

Similar order of reaction rates has been found by a number of researchers. For example, Nedoloujko and Kiwi (118) found that mineralization (i.e. complete decomposition into CO_2 and water) of Tert-Butylpyridine (tBP) due to Fenton reaction in homogeneous media followed a pseudo-first order decay kinetics.

5.1.2.2 Effect of H_2O_2 Concentration

To study the effect of H_2O_2 concentration level on the formation of OH^o radical, another set of experiments were conducted. In these experiments, the initial concentration of ferrous ions (Fe^{2+}) was kept constant at 0.2 mM (11.2 ppm). In addition, pH and

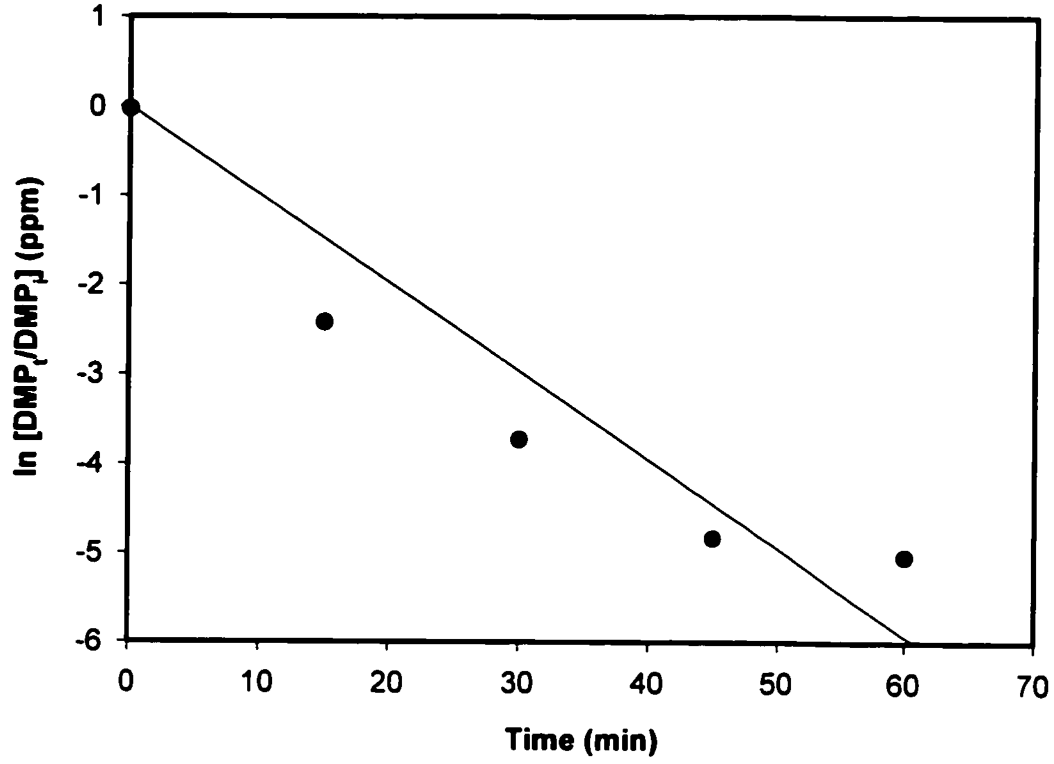


Figure 5.3: Ln (DMP$_t$/DMP$_i$) versus time in Fenton process. (DMP$_i$ = 0.1 mM, H_2O_2 = 2 mM, Fe^{2+} = 0.4 mM, pH = 3, Temp. = 25°C)

temperature levels were set at 3 and 25°C respectively. Initial concentrations of H_2O_2 used were 0.5, 1.0, and 2.0 mM. The results are shown in Table A.1.4 and Figure 5.4. The data depicted from Figure 5.4 show that a remarkable reduction of DMP concentration occurred when H_2O_2 concentrations increased from 0.5 to 1 mM. It can be noted from Figure 5.4 that after a reaction time of 60 minutes, only 20% of DMP was removed when H_2O_2 was 0.5 mM, while more than 80% was removed at H_2O_2 of 1.0 mM. This is expected since according to equation 2.2, H_2O_2 is one of the reactants and more OH^o radicals are expected to form as H_2O_2 concentration increases. However, when H_2O_2 concentration was raised from 1.0 to 2.0 mM, the removal of DMP dropped down after 25 minutes of reaction time.

About 56% of residual DMP was left un-removed after a reaction time of 60 minutes at an initial H_2O_2 concentration of 2.0 mM while only 20% of residual DMP was found when initial H_2O_2 concentration of 1.0 mM. The reason behind this may be attributed to the fact that some of the OH^o radicals formed will react with H_2O_2 according to the reaction in equation 2.5. H_2O_2 in this case will act as inhibitor for the OH^o radicals. This means that the initial concentration of H_2O_2 has to be optimized for a certain Fenton process in order to achieve a better removal efficiency of DMP.

Furthermore, some studies investigated the utilization of H_2O_2 in Fenton process and reported that the extent of H_2O_2 utilization decreased with an increasing H_2O_2 concentration. Lin et al (139) found that at 0.5 ppm Fe^{2+}, more than 72% of H_2O_2 was

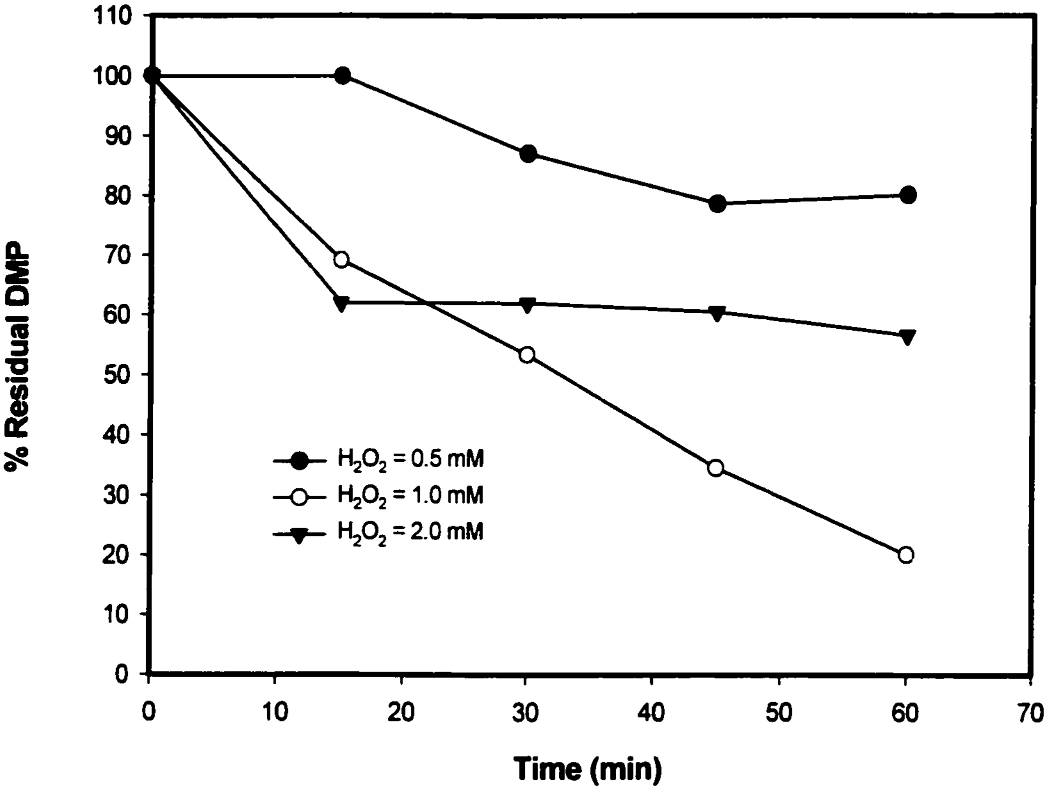


Figure 5.4: Removal of DMP by Fenton Process at Various H_2O_2 Concentrations (DMPi = 0.1 mM, Fe^{2+} = 0.2 mM, pH = 3, Temp. = 25°C)

utilized with an initial H_2O_2 dosage of 10 ppm, but less than 40% was utilized with H_2O_2 of 500 ppm. He noticed that this result is in contrast to the extent of decomposition of 2-Chlorophenol. This supports the claim that optimum conditions of H_2O_2 and Fe^{2+} have to be determined for every case study when using Fenton system for the treatment of organic compounds. However, in their investigation of the decomposition of 2,4-dinitrotoluene by Fenton process, Mohanty and Wei (69) claimed that the consumption of H_2O_2 increased with the amount applied. They stated that at higher H_2O_2 concentrations, there would be a greater amount of self-decomposition because the OH^o radicals generated would react with H_2O_2 and hence reaction 2.5 would gain prominence.

One more thing to observe is that H_2O_2 reacts with Fe^{2+} to form hydroxyl radicals shows a 1 : 1 molar ratio between the two reactants. Therefore according to equation 2.2 a higher dosage of H_2O_2 will not affect the production rate of OH^o radicals. This means that stoichiometrically the molar concentration of H_2O_2 needed is equivalent to that of Fe^{2+}. However, ferric ions (Fe^{3+}) that are produced by the reaction of equation 2.3 will again react with H_2O_2 to produce Fe^{2+} as shown in equation 2.3, which will in turn be used to produce more OH^o radical ready to decompose more of DMP. This can explain the initial higher removal rate of DMP as H_2O_2 concentration increases from 0.5 to 2 mM. Furthermore, the other possible reactions that are involved in Fenton system and which are listed in equations 2.4 to 2.8 also play a role in the mechanism by which a target compound is degraded by OH^o radicals. In fact, some of the reactants play two opposite roles. For example, in equation 2.2, H_2O_2 species promote the production of OH^o radicals, while in equation 2.5; these species deplete some of the OH^o radicals formed before.

Finally, the various organic radicals of the target compounds (R^o) or its intermediates that are formed during Fenton process may largely affect the performance of the process.

It is interesting to note the pattern by which DMP is removed at various initial concentrations of H_2O_2. At initial concentration of 0.5 MM of H_2O_2, DMP started decreasing after 15 minutes and reached a residual of 80% which means that only 20% of DMP was removed after 45 minutes of reaction time after which no DMP removal was observed. A fairly similar pattern was observed when initial H_2O_2 concentration of 2.0 mM was used but with a higher DMP removal. Figure 5.4 shows that about 40% of DMP were removed in the first 15 minutes with no further removal after that. However, at initial concentration of 1.0 mM of H_2O_2, only 20% of DMP remains undecomposed (80% removed) after 60 minutes of reaction time. This behavior can be attributed to the different chain reactions that accompany the main Fenton reaction. These reactions, which are shown in equations 2.3 to 2.8 have different reaction rates. The reaction, which has a higher reaction rates at certain conditions will dominate other reactions.

In brief, it can be concluded that an optimum level of H_2O_2 has to be determined for the DMP removal by Fenton system. Figure 5.4 also shows that at the conditions used of DMP_i = 0.1 mM and Fe^{2+} of 0.2 mM, the optimum level of initial H_2O_2 concentration would be 1.0 mM.

5.1.2.3 Effect of Sequential Addition of H_2O_2

A number of researchers who studied the removal of pollutants by Fenton process have reported that the rate of oxidation by OH^o radicals generated from Fenton is affected by the method and rate of H_2O_2 addition to the solution to be treated. Bowers et al (206) showed that stepwise addition of H_2O_2 is more effective than a large initial dose. Similar conclusion was reached by Basu and Wei (138) who claimed that utilization of H_2O_2 can be enhanced by addition in smaller increments rather than a single addition at the start of the reaction. On the other hand, Mohanty and Wei (69) did not find a major improvement by applying H_2O_2 sequentially.

Thus to investigate this, an experiment was conducted to study how this factor affects the removal efficiency of DMP by Fenton process. One experiment was conducted by introducing the whole amount of H_2O_2 needed initially while the other experiment was carried out by applying H_2O_2 sequentially at five intervals during the first 15 minutes (i.e. 0.2 mM of H_2O_2 was added at every three (3) minutes. In both experiments, an initial concentration of 0.1 mM of DMP was used. Ferrous ion of 0.2 mM was applied. Temperature and pH were kept at 25°C and 3 respectively. The results are given in Table A.1.5 and Figure 5.5. The results show that when the amount of H_2O_2 was added initially, better removal of DMP was achieved than when it was applied sequentially. This finding does not completely agree with the findings of Bowers and others. However, a reasonable explanation could be that conditions used in this study were different from the conditions used in their study. It seems that the amount of H_2O_2 that was available at certain time interval was not sufficient to complete the reaction with Fe^{2+}. The stiochemtric balance between the initial substrate (DMP_i), Fe^{2+} and H_2O_2 concentrations plays a vital role in determining the fate of Fenton process. The type of organic compound to be treated also plays a role. This means that oxidizing DMP by Fenton process may not necessarily follow the same pattern as the oxidation of other compound. The results show that addition of the whole amount of H_2O_2 at the start of the experiments was more effective in removing DMP from water.

5.1.2.4 Effect of pH

The effect of pH on the removal of DMP by Fenton process was also investigated. To study this, a set of experiments was conducted at a constant initial concentration of 0.1 mM DMP. Initial concentrations of H_2O_2 and Fe^{2+} were set at 1.0 and 0.2 mM. Temperature was set at 25°C for all experiments. The initial pH levels of the aqueous solution spiked with the DMP compound were set at several levels before the addition of the reactants (i.e. H_2O_2 and Fe^{2+}) using 0.1N sulfuric acid (H_2SO_4). The pH levels used were: 3, 5, 7 and 9 respectively. The results are listed in Table A.1.6 and plotted in Figure 5.6. The results clearly show that Fenton's reagent works best under acidic conditions in the range of pH = 3 to 4. Basically there was no removal of DMP when pH was greater than 7.

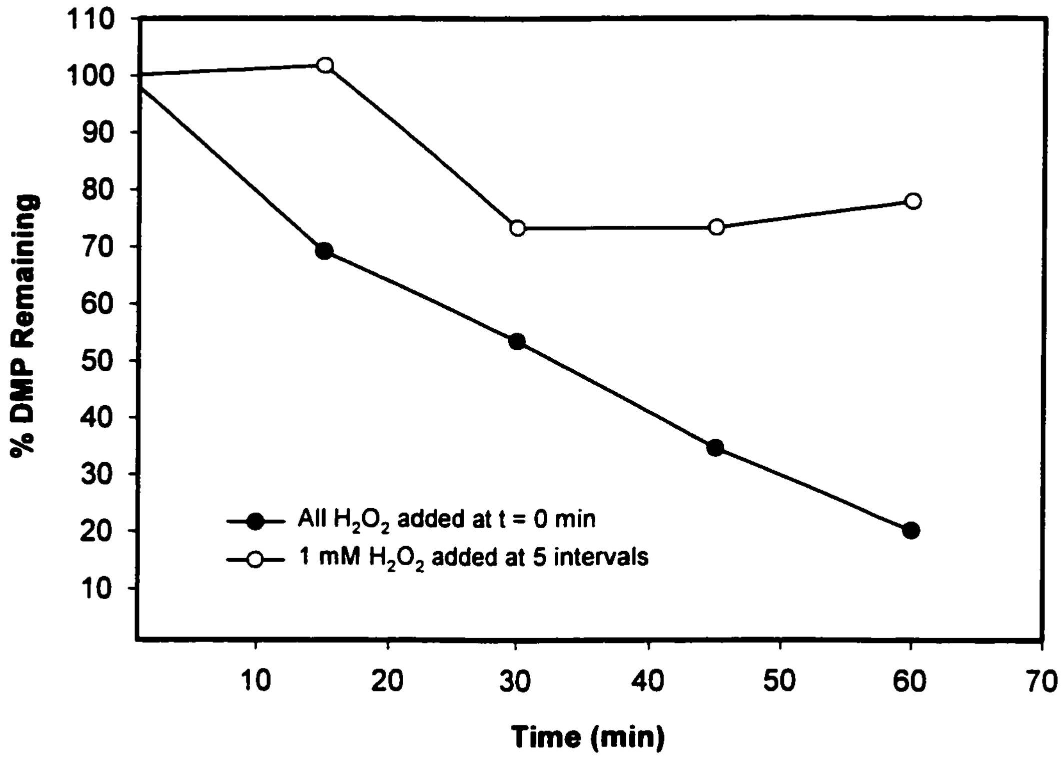


Figure 5.5: Effect of H_2O_2 Addition Mode on the Removal of DMP by Fenton (DMP_i = 0.1 mM, Fe^{2+} = 0.2 mM, pH = 3, Temp. = 25°C)

This result agrees with the results obtained by many researchers who studied the effect of pH on the performance of Fenton system (6, 25, 46, 62, 135, 147). Those researchers found that pH effect to be quite significant and an optimum pH around 3.0 had been observed for the Fenton Oxidation process. They concluded that only in acid conditions, Fe^{2+} would react with H_2O_2 to produce OH^o radicals. The drop in efficiency on the basic side is attributed to the transition of iron from a hydrated ferrous ion (Fe^{2+}) to a colloidal ferric species (Fe^{3+}). In the ferric form, iron catalytically decomposes the H_2O_2 into oxygen and water, without forming hydroxyl radicals. Hence maintaining the pH at its optimum level was adopted for all test runs afterward.

A second aspect of pH deals with its shift as the Fenton reaction progresses. On conducting the Fenton experiments, it was noticed that pH follows a profile that is typical of Fenton reactions. It was noticed that pH drops slightly when Fe^{2+} reagent was added and another small drop occurred when H_2O_2 reagent was added. The pH then continues to drop until it reaches about 3 depending on the catalyst (Fe^{2+}) concentration. The first inflection is caused by the addition of $FeSO_4$ catalyst, which typically contains residual H_2SO_4. The second drop in pH is attributed to the fragmenting of organic material into organic acids. In fact the absence of such pH decrease may mean that the reaction is inhibited and the potentially hazardous build-up of H_2O_2 is occurring within the reaction mixture.

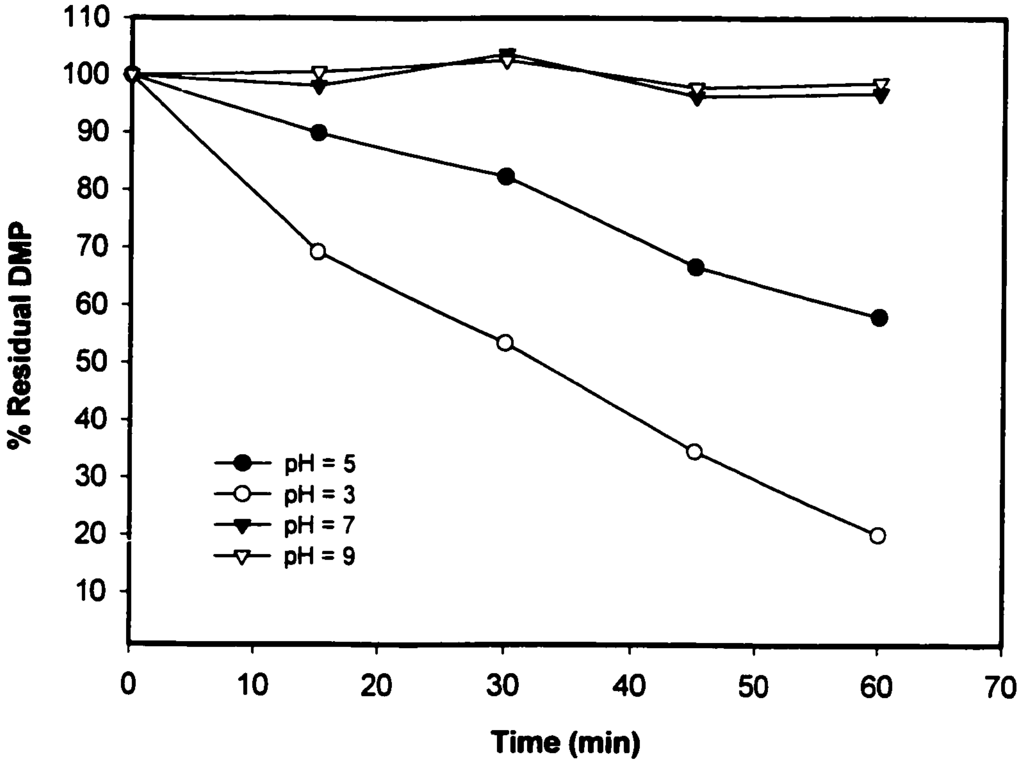


Figure 5.6: Removal of DMP by Fenton Process at Various pH Levels (DMP$_i$ = 0.1 mM, H_2O_2 = 1.0 mM, Fe^{2+} = 0.2 mM, Temp. = 25°C)

5.1.2.5 Effect of Temperature

The reaction in equation 2 is temperature dependent and more OH^o radicals are expected to form at elevated temperatures as has been shown by other studies (78). In this study, temperature of the aqueous solution was raised from 15°C up to 35°C, while other parameters were kept constant. The results of these tests are shown in Table A.1.7 and Figure 5.7, which clearly show that temperature plays a significant role in increasing the reaction rate between OH^o radicals and DMP and thus increased the removal rate of DMP. More than 99% removal of DMP was achieved in 15 minutes of reaction time when the DMP-spiked water was preheated to 35°C prior to the addition of reactants. Under the same conditions, 30% and 2% DMP removal was achieved when the temperature was 25°C and 15°C, respectively. Figure 5.7 also shows that the there was a quick removal of DMP when the temperature was raised to 35°C. This is a clear indication that temperature plays a significant role in completing the chemical reaction between H_2O_2 and Fe^{2+} and thus more OH^o radicals are produced.

Similar results have been reached when applying Fenton system on other organic compounds. Mohanty and Wei (69) found a good improvement of the TOC removal when the temperature of the solution containing the contaminant was raised from 21 to 40°C. In another study by Basu and Wei (145), it was found that the rate of reaction in Fenton system increased significantly with the increase of temperature within the range of 15 to 35°C.

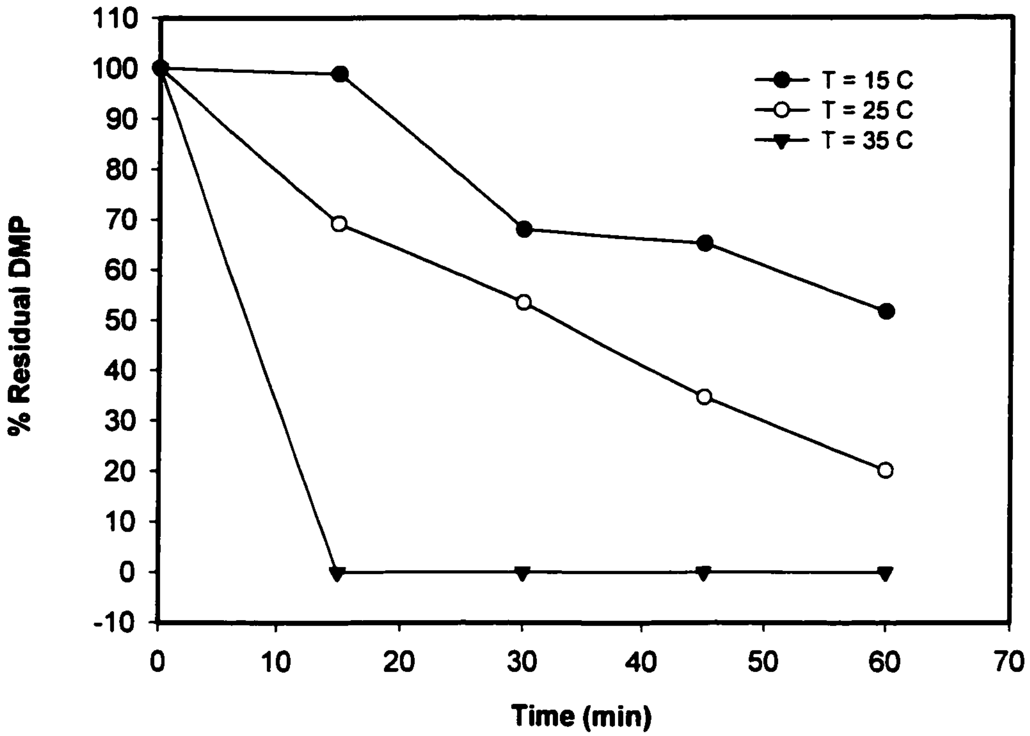


Figure 5.7: Removal of DMP by Fenton Process at Various Temperatures (DMP_i = 0.1 mM, H_2O_2 = 1.0 mM, Fe^{2+} = 0.2 mM, pH= 3)

Obviously, the effect of temperature on the kinetics of Fenton system depends on the type of substrate considered. For instance, in their investigation about degradation of Amines by Fenton system, Casero et al (78) indicated that there was no effect of temperature on the removal of o-dianisidine. A temperature range of 10-45°C was used in their study. Similar results were reported by Watts et. al. (128) when they examined the removal of dioxine by Fenton process. They found that both elevated temperatures as well as higher H_2O_2 concentrations improved dioxin removal. They indicated that a removal of dioxine at 80°C was 85% compared to 15% removal at 20°C using 35% H_2O_2 and that there was almost no removal using 3.5% H_2O_2 at 20°C.

5.1.2.6 Effect of DMP_i

The initial concentration of the organic pollutant (DMP_i) has been kept constant so far at 0.1 mM while investigating the effect of other parameters. A common practice in similar studies is to keep the initial concentration of the target compound constant while changing the concentration of H_2O_2 and Fe^{2+}. In Fenton system, it is more desirable to report the concentration of H_2O_2 and Fe^{2+} as a ratio with respect to the initial concentration of the pollutant (i.e. $DMP_i : H_2O_2 : Fe^{2+}$) since its efficiency is highly dependent on the chemical balance between these parameters.

Two experiments were conducted to examine the effect of DMP_i on its removal efficiency by the Fenton process. In one experiment, the initial concentration of DMP

(DMP_i) used was 0.1 mM (≈ 20 ppm) while in the other one the initial concentration of DMP (DMP_i) used was 0.2 mM (≈ 40 ppm). Other parameters such as Fe^{2+}, H_2O_2, pH and temperature were kept constant. The results of these tests are shown in Table A.1.8 and Figure 5.8. Figure a 5.8 show that about 80% of DMP was removed after 60 minutes of reaction time when the initial concentration of DMP was 0.1 mM (≈ 20 ppm) while no considerable removal was observed when the initial concentration was 0.2 mM (≈ 40 ppm). Notice that the ratio of DMP with respect to both Fe^{2+} and H_2O_2 was changed in the second experiment. In fact, the ratios of DMP_i : $Fe^{2+}$and DMP : H_2O_2 in the first experiment were 0.1 : 0.2 (i.e. 1 : 2) and 0.1 : 1 (i.e. 1 : 10) respectively. However in the second experiment, the ratios of DMP:$Fe^{2+}$and DMP:H_2O_2 were 0.2 : 0.2 (i.e. 1 : 1) and 0.2 : 1 (i.e. 1 : 5) respectively. Thus it seems that, under the conditions of the second experiment, the OH^{o} radicals produced from $Fe^{2+}$and H_2O_2 could be insufficient to decompose the relatively high concentration of DMP.

The effect of DMP_i on the removal efficiency by Fenton process was further investigated by conducting several experiments at various values of H_2O_2 / DMP_i and Fe^{2+}/ DMP_i The water samples were spiked with 0.2 mM of DMP. The results are listed in Table A.1.9 and plotted in Figure 5.9, which show the DMP removal efficiencies at different H_2O_2 /DMP_i and Fe^{2+}/ DMP_i ratios. For example, the efficiency of Fenton system was improved slightly when H_2O_2 / DMP_i was doubled from 10 to 20 at a constant Fe^{2+}/DMP_i of 2.

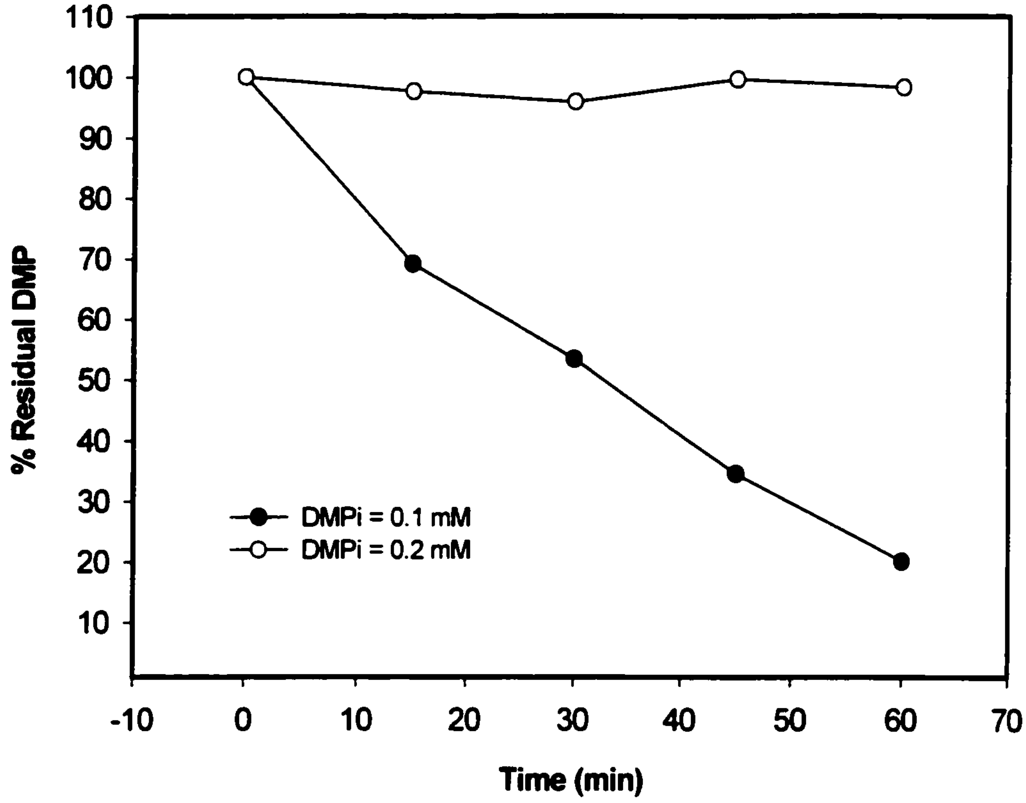


Figure 5.8: Removal of DMP by Fenton Process at Two DMP_i levels (H_2O_2 = 1.0 mM, Fe^{2+} = 0.2 mM, pH= 3, Temp. = 25°C)

However, the efficiency was improved dramatically when Fe^{2+}/DMP_i ratio was doubled from 2 to 4 at a constant H_2O_2 / DMP_i ratio of 10. This means that Fe^{2+} concentration is the limiting factor in determining the efficiency of Fenton system as long as there is a reasonable enough amount of H_2O_2 available. Comparing Figure 5.2 and 5.9 shows that the removal pattern of DMP is similar when the ratio of DMP : Fe^{2+} : H_2O_2 is kept constant. For example, at Fe^{2+} : DMP_i and H_2O_2 : DMP_i of 2 : 1 and 20 : 1, respectively, more than 60% of DMP was removed when DMP_i of 0.2 mM was used compared to about 50% removal when DMP_i of 0.1 mM was used.

5.1.2.7 <u>Effect of UV Radiation</u>

As shown in equation 2.9, light irradiation accelerates the Fenton reaction and the photolysis of Fe^{3+} complexes yielding oxidative radicals and regenerating Fe^{2+} through the photolysis of the Fe^{3+}-organic complexes or its intermediates in solution especially organic acids (68). UV light is expected to enhance the generation of OH^{o} radicals and therefore higher removal of DMP is expected (37, 43, 72,).

To study the effect of UV light on the efficiency of Fenton system in removing DMP, the spiked water samples were subjected to UV source after the reactants were added and Fenton reaction started. A UV lamp of 0.1 mWatt was used to supply the radiation. In this experiment, an initial concentration of 0.1 mM of DMP_i was used. 1.0 mM of H_2O_2 and 0.2 mM of Fe^{2+} was applied. Temperature and pH were kept constant at

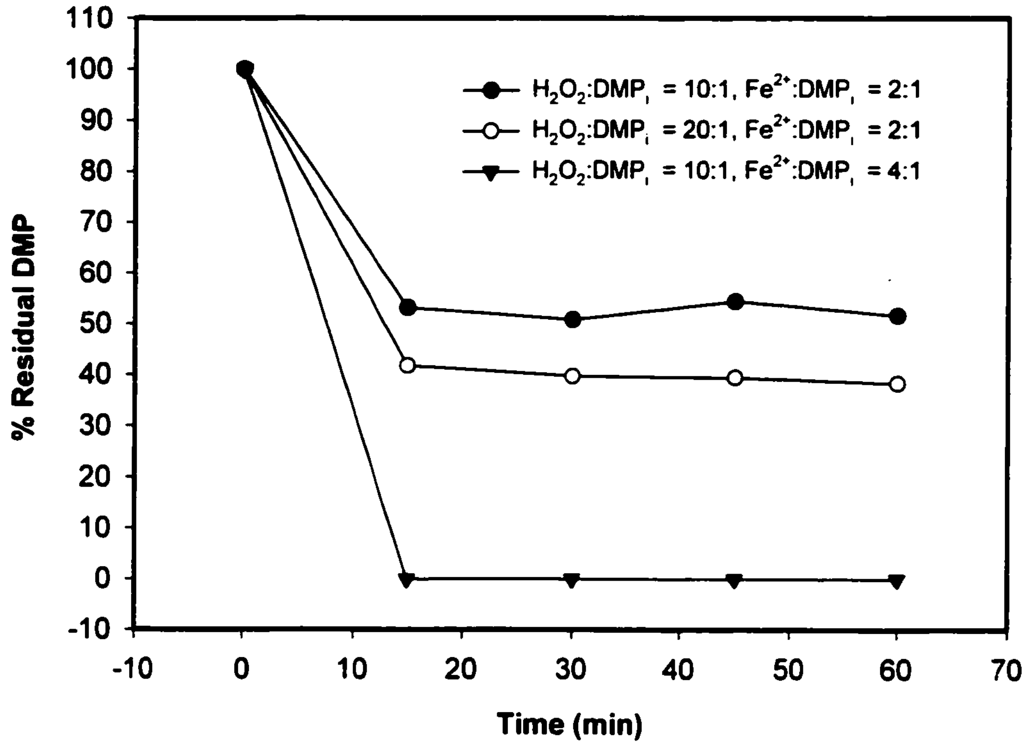


Figure 5.9: Removal of DMP by Fenton Process at Various H_2O_2: DMP_i :Fe^{2+} Ratios (DMP_i = 0.2 mM, pH= 3, Temp. = 25°C)

25°C and 3 respectively. The results of these tests are shown in Table A.1.10 and Figure 5.10. Figure 5.10 shows that when UV light was introduced along with the Fenton process, a significant enhancement of DMP removal was achieved. After 15 minutes of reaction time, only 30% of DMP was removed by Fenton system, while more than 95% removal was achieved when the solution was irradiated by a UV light.

It can be also observed from Figure 5.10 that the pattern of DMP removal in Fenton is different from photo-Fenton system. A quick and high removal rate of DMP was observed in the case of Photo-Fenton process, while the removal rate by Fenton was gradual. This can be attributed to the UV light, which promotes the production of (OH^{o}) radicals by the mechanism depicted in equation 2.9. The effect of UV light is discussed in details when discussing the UV/H_2O_2 process.

5.1.2.8 Removal of DMP from Groundwater

Even though the main objective of this study is to evaluate the efficiency of advanced oxidation processes (AOPs) in removing DMP from water, an attempt was made to explore the efficiency of Fenton process in removing DMP from a contaminated groundwater rather than pure water. A sample of groundwater was collected from water well located in Dhahran, Saudi Arabia. The groundwater sample was chemically analyzed to determine its inorganic constituents.

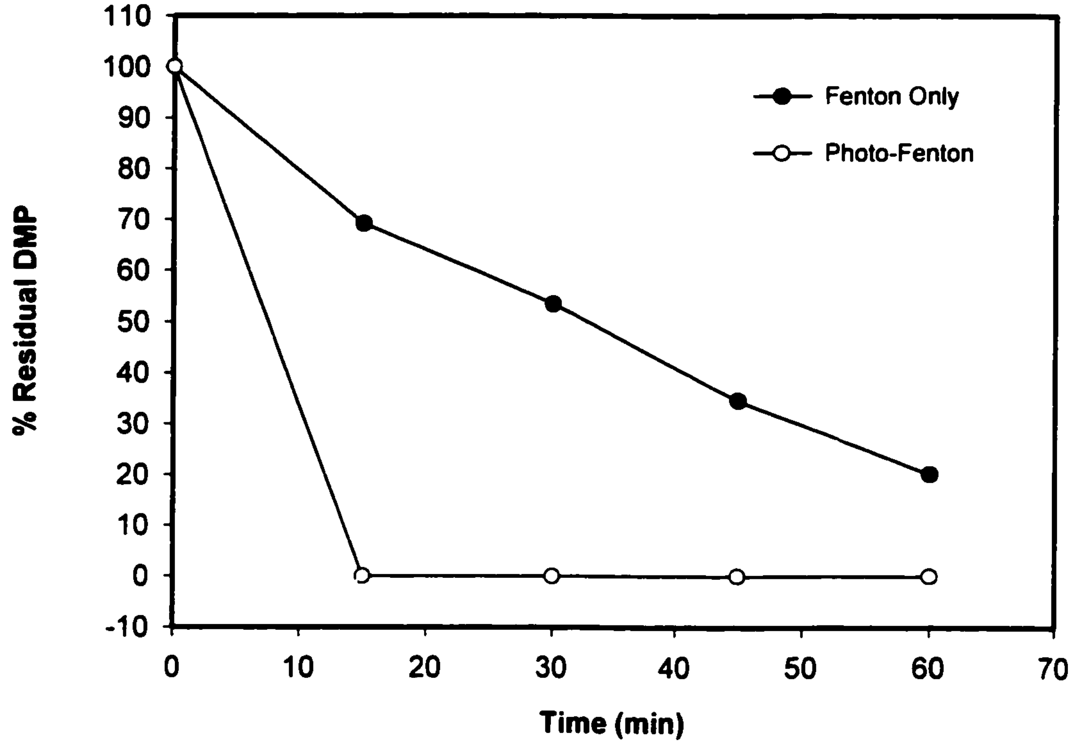


Figure 5.10: Removal of DMP by Fenton and Photo-Fenton Process (DMP_i = 0.1 mM, H_2O_2 = 1.0 mM, Fe^{2+} = 0.2 mM, pH= 3, Temp. = 25°C)

The results of the groundwater sample analysis are listed in Table A.1.11. The groundwater sample was spiked with 0.1 mM of DMP and transferred to the photo-reactor. Initial concentrations of Fe^{2+} and H_2O_2 were set at 0.2 and 1.0 mM, respectively. Other parameters including pH and temperature were set at 3 and 25°C, respectively. Results of this experiment are shown in Table A.1.12 and Figure 5.11. Figure 5.11 also shows the removal pattern of DMP from pure water conducted earlier under the same conditions for the sake of comparison. It can be noticed that Fenton system was completely inefficient in removing DMP from groundwater in contrary to the case of pure water. Basically, there was no removal of DMP from groundwater after a reaction time of 60 minutes. However, under the same conditions, more than 80% of DMP spiked in pure water was removed after 60 minutes of reaction time. It is true that OH^o radicals oxidize dissolved target compounds at high reaction rates on the order of 10^9 $M^{-1}S^{-1}$, however, the efficiency of oxidation can be reduced by scavengers of hydroxyl radicals (207). Scavengers, or inhibitors, of hydroxyl radicals are these compounds (other than the target compound) that have a reasonably high rate of reaction with OH^o radicals.

These compounds will be involved in reactions with the OH^o radicals and deplete a certain amount of it. This will negatively affect the reactivity of OH^o radicals with the target compounds. For example, carbonate and bicarbonate ions have reaction rates of 1.5×10^7 $M^{-1}S^{-1}$ and 4.2×10^8 $M^{-1}S^{-1}$, respectively, with OH^o radicals (208).

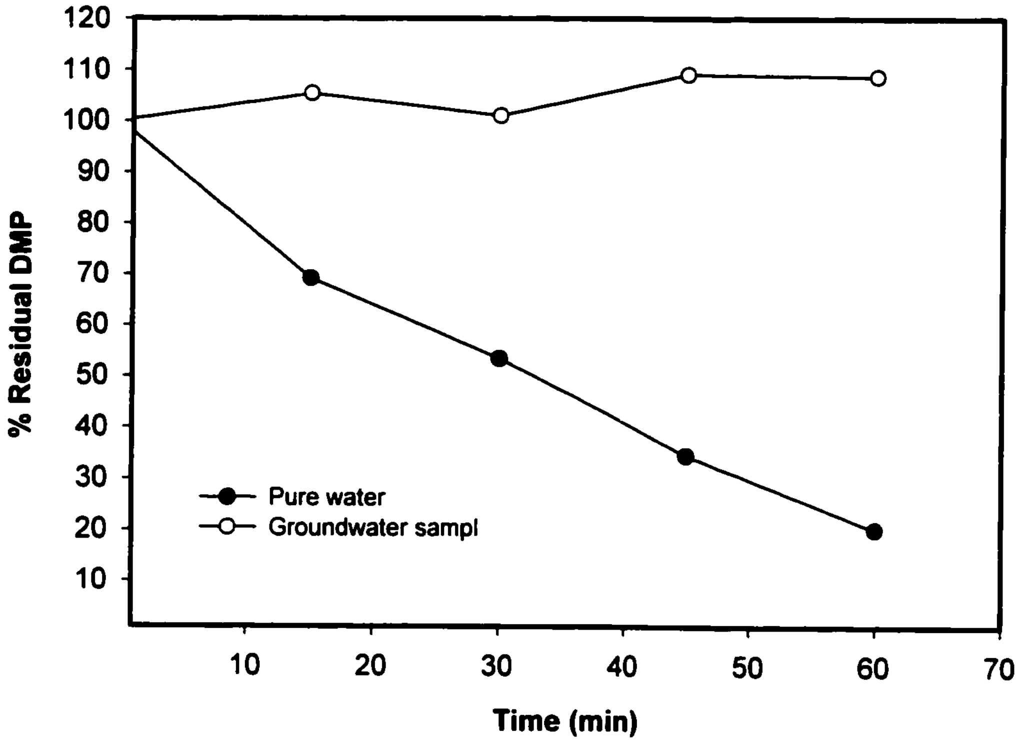


Figure 5.11: Removal of DMP by Fenton Process from Pure and Groundwater (H_2O_2 = 1.0 mM, Fe^{2+} = 0.2 mM, pH = 3, Temp. =25°C)

The data shown in Table A.1.11 indicate that the groundwater sample used in this study is characterized by the presence of fairly high concentrations of inorganic chemicals. For example, the groundwater sample contains a high concentration of sulfate (i.e. 752 ppm) and bicarbonate (i.e. 145 ppm). Many research studies (115, 116) have indicated that such inorganic contaminants react with OH^o radicals but with a rate usually slower than that of the target compound. However, the concentration of these compounds is higher. In this study, the sulfate and carbonate species in the ground water sample are much higher in concentration than DMP. Thus, it is expected that major portion of the OH^o radicals produced by the Fenton system, would be consumed by the inorganic compounds.

5.1.3 Removal of DMP by UV/H_2O_2 Process

In this method of treatment, hydrogen peroxide (H_2O_2) is added to the contaminated water and is then activated by the UV light to form hydroxyl radicals as depicted in equation 2.10. In this process, the mechanism of OH^o radicals production is different from that by Fenton process discussed earlier. In UV/H_2O_2 process, one molecule of H_2O_2 will split into two molecules of OH^o radicals by irradiation with UV light. Thus, in order to compare the two systems with respect to their efficiencies of DMP removal from water, the effects of the various factors that were discussed in the Fenton process were again tested in the UV/H_2O_2 process. In this regard, several experiments were conducted to investigate the effect of initial concentration of H_2O_2 and the dosage of

UV light on the removal of DMP from water. The effects of temperature and pH levels were also investigated.

5.1.3.1 Removal of DMP by Direct Photolysis

To examine the extent of DMP removal by direct photolysis (UV only), an experiment was conducted in which, a water sample spiked with 0.1 mM of DMP was irradiated by UV light for 60 minutes. The removal pattern of DMP by UV action only was monitored every 15 minutes. The results are shown in Table A.1.13 and plotted in Figure 5.12. The results show that a good portion of DMP was removed by the action of UV light only. Approximately 60% of DMP was removed after exposure of 60 minutes for UV light. This means that DMP can be decomposed to a certain extent by direct photolysis action only.

As stated in the previous chapter, compounds that absorb UV light and have high quantum yields of photolysis are good candidates for photodegradation. Since DMP was removed partially by direct photolysis, then it is expected that this compound can absorb some of the UV light at the designated wavelength. The absorption of UV light by DMP was examined using an hp 8451A diode array UV/VIS spectrophotometer. The absorption of a pure water sample spiked with 0.1 mM DMP was scanned from a wavelength of 200 nm to 300 nm. A spectrum is shown in Figure 5.13, which shows that a good absorption occurred at a wavelength range of 230 - 250 nm. This wavelength range represents the same range emitted by the low-pressure mercury (Hg) UV lamp used in this study. Thus, partial removal of DMP by UV light is expected. According to the direct photolysis theory, it seems that the partial decomposition of DMP occurred when it absorbs energy from a beam of a UV light and gained far more energy than it ever could by other method such as the ordinary heating. This energy can either be directly used to degrade the DMP molecules by breaking the chemical bonds or to initiate a photochemical process. The photo-decomposition process always involves excitation of one electron from a state of low energy to a state of higher energy. If the excited molecule does react, it may undergo photo-ionization or photo-dissociation.

To determine the DMP removal rate by direct exposure to UV irradiation, experiments were conducted at certain initial concentration of DMP. The results listed in Table A.1.14 and Figure 5.14. Figure 5.14 represents a plot of the ratio of C_o/C_t versus time on a semi-logarithmic scale. The slope of the curve shown in Figure 5.14 represents the laboratory photolysis rate constant of DMP (i.e. k), which is determined from the following equation:

$$\text{Ln}\ (C_o/C_t) = -k\ t \qquad (5.2)$$

Where:

C_o = initial concentration of DMP

C_t = concentration of DMP at time t

k = the first-order rate constant

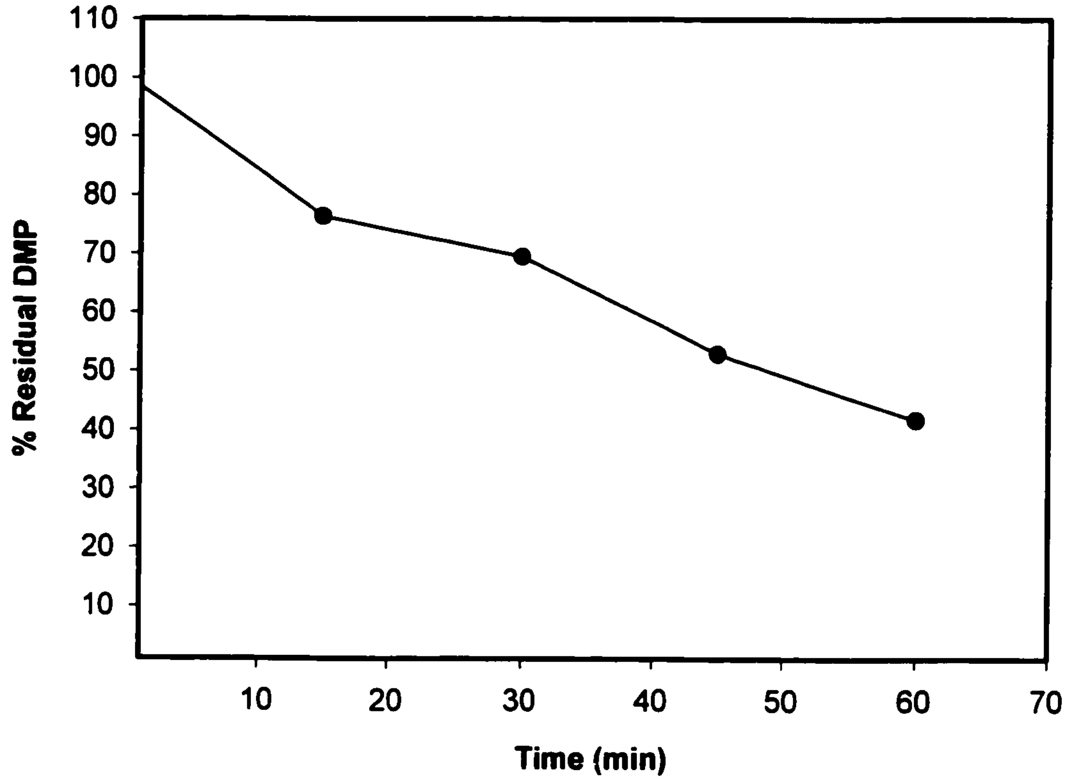


Figure 5.12: Removal of DMP by Direct Photolysis (DMP_i = 0.1 mM, H_2O_2 = 0 mM, pH= 3, Temp. = 25°C)

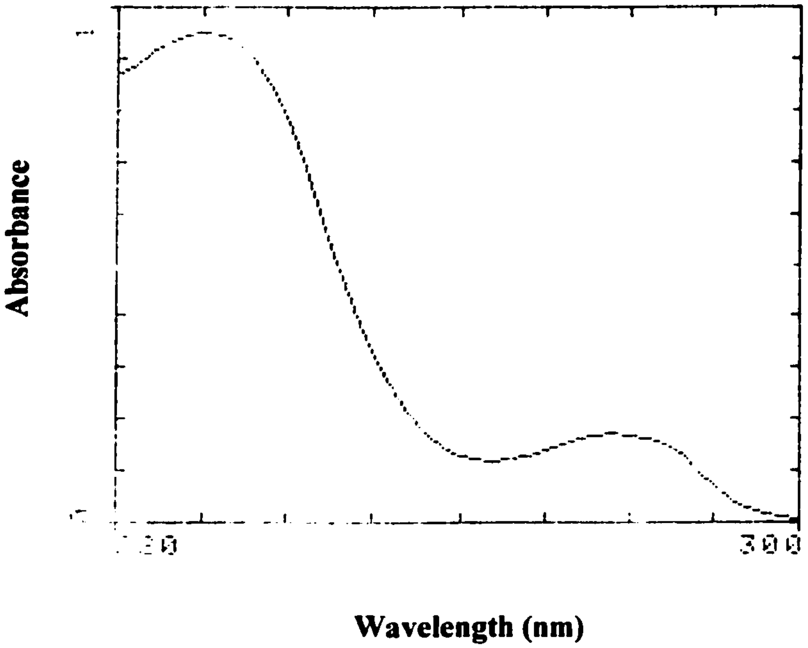


Figure 5.13: Absorption of UV Light by DMP in Water

From Figure 5.14, the curve was best fitted by the following linear relationship:

$$\mathrm{Ln}\,(C_o/C_t) = -0.0142 * t \qquad (5.3)$$

$$r^2 = 0.9835$$

Therefore, the rate (k) is found to be approximately 0.0142/min. It can be concluded that the rate of DMP removal by direct photolysis using UV light is a quite significant. However, the rate of DMP removal by direct photolysis (i.e. 0.0142/min) is lower than the rate of removal by Fenton process when Fe^{2+} of 0.4 mM was used. (i.e. 0.0989/min). This shows that Fenton process is more efficient in removing DMP than direct photolysis alone.

Another parameter that is usually calculated in the direct photolysis method is the half-life. The photolysis half-life ($t_{1/2}$) of any compound is equivalent to:

$$(t_{1/2}) = 0.693 / k \qquad (5.4)$$

Using a value of 0.0142 for DMP removal rate (k), the photolysis half-life of DMP in water is found to be approximately 50 min. In other words, 50 minutes are needed to degrade the 0.04 mM of DMP to its half concentration (0.02 mM) by direct irradiation with UV light emitting at a wavelength of 254 nm with an intensity of 100mWatt. Degradation of organic compounds by direct photolysis has been investigated by many researchers (58, 60, 66, 107, 209). These studies have shown that compounds like toluene

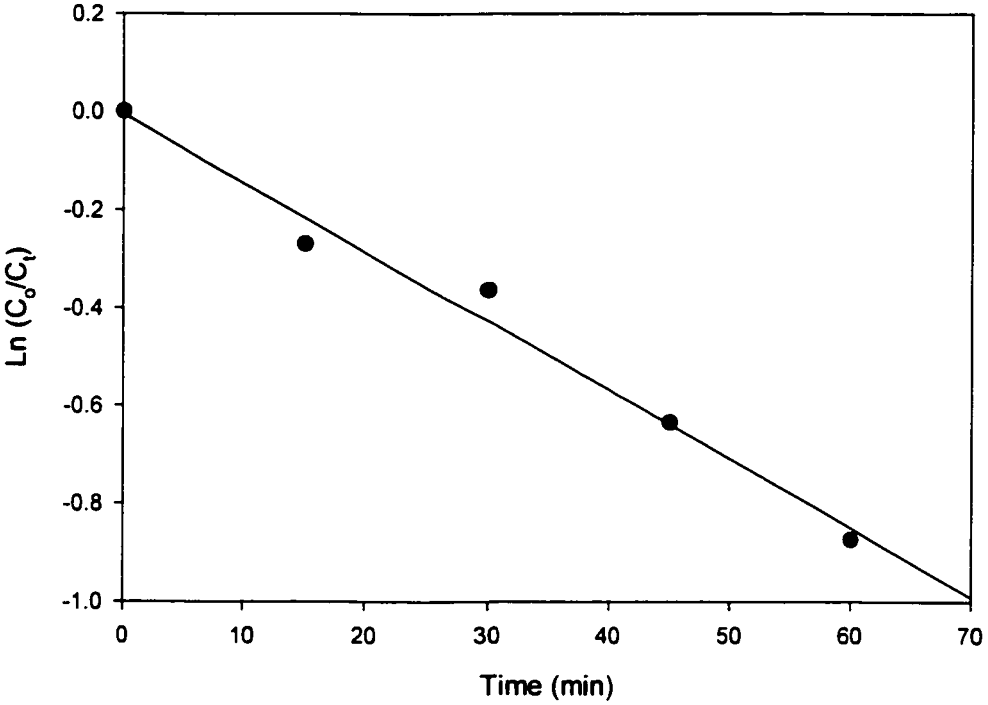


Figure 5.14: Plot of Ln (C_o/C_t) Versus Time by Direct photolysis

parathion, herbicides, phenols and benzene can be photo-oxidized to different degrees by UV light alone.

5.1.3.2 Effect of H_2O_2 Concentration

To study the effect of H_2O_2 concentration on the removal of DMP by UV/H_2O_2 process, experiments were conducted using initial concentrations of H_2O_2 of 1, 2 and 4 mM. The water spiked with 0.1 mM (20 ppm) of DMP was irradiated with UV light supplied by a 100 mWatt lamp irradiating at wavelength of 254 nm. The exposure to UV light was maintained for 60 minutes, which is the total reaction time used. Temperature and pH levels were set at 25°C and 3, respectively. The results are shown in Table A.1.15 and Figure 5.15. Figure 5.15 shows that the addition of H_2O_2 improves the removal of DMP from water. More than 70% of DMP was removed after 60 minutes of reaction time when 1 mM of H_2O_2 was added to the reactor, which contains water spiked with 0.1 mM of DMP. Approximately 80% of DMP was removed at an initial H_2O_2 dose of 2 mM, while the removal percentage increased to 98% when the initial dose was raised to 4mM of H_2O_2. It is clear that the combined action of H_2O_2 and UV light photooxidation has greatly improved the removal of DMP from water. Thus, in the UV/H_2O_2 system, as the concentration of H_2O_2 increases, the removal rate DMP also increases. This was not exactly the case when Fenton system was studied. In Fenton system, it was found that a drop in the removal efficiency occurred when excessive amount of H_2O_2 was used. This can be mainly due to the fact that the mechanisms of (OH^o) radicals production in the two

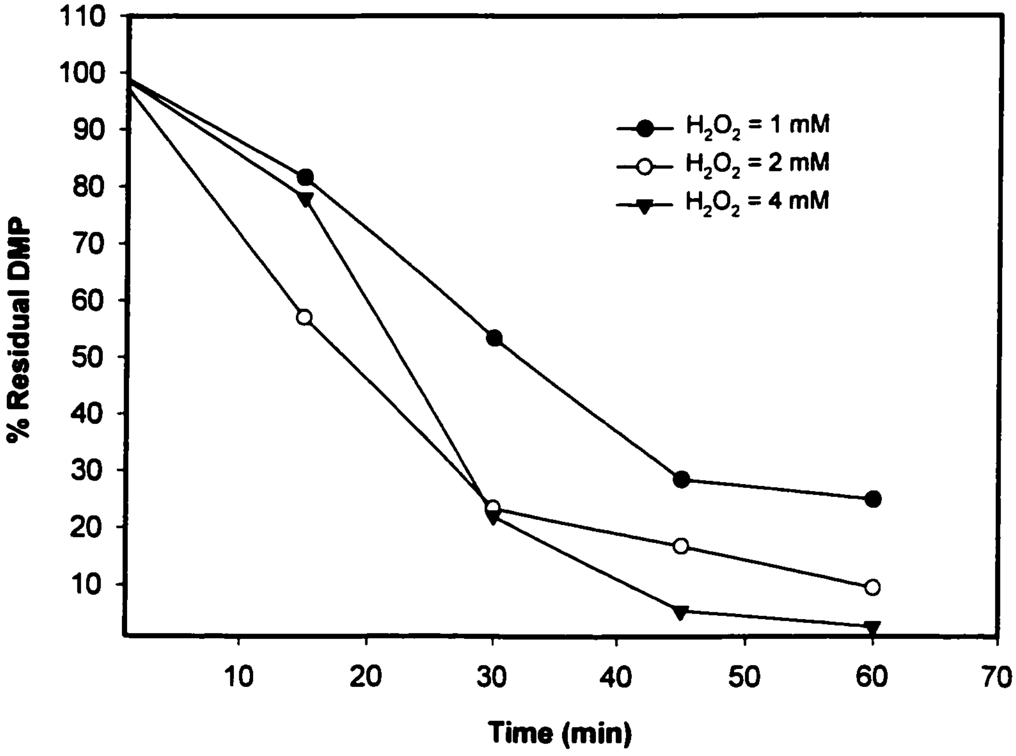


Figure 5.15: Removal of DMP by UV/H_2O_2 at Various H_2O_2 Concentrations (DMP$_i$ = 0.1 mM, pH= 3, Temp. = 25°C)

systems are different. It seems that in the UV/H_2O_2 system, the UV light continues to produce OH° radicals by splitting the H_2O_2 molecule according to equation 2.10. Furthermore, the other reactions that might occur during UV/oxidation process (i.e. 2.11 to 2.17) could have an important effect on the efficiency of the process in degrading DMP.

By comparing Figures 5.12 and 5.15, it can be noticed that the removal pattern of DMP by UV alone is different than the removal pattern by UV/H_2O_2 system. Figure 5.12 shows that DMP was removed in a fairly constant rate by UV alone; while the rate in the case of UV/H_2O_2 system was higher initially then it continued at a slower rate. This can be explained by the fact that the decomposition of DMP by UV alone may have occurred via photo-dissociation caused mainly by the intense energy of the UV light. However, in the UV/H_2O_2 system, additional factors including the H_2O_2 oxidant and OH° radicals were introduced to the reaction. Ultraviolet light in the UV/H_2O_2 system can also facilitate the reaction between DMP and OH° radicals formed from the dissociation of H_2O_2 molecules by initiating a series of reactions that involve various organic radicals (R°) as well as OH° radicals. The intermediates formed due to the decomposition of DMP can also affect the extent and removal pattern of DMP since these intermediates may have different reaction rates with OH° radicals. The overall conclusion is that the removal of DMP by UV/H_2O_2 system has been enhanced by the collective actions of UV light and OH° radicals.

In this study, the removal rate of DMP in water by UV/H_2O_2 process for an initial H_2O_2 concentration of 4 mM was also determined assuming a pseudo first order reaction. A semi-log plot of the ratio of DMP at time (t) (i.e. DMP_t) to the initial DMP concentration (i.e. DMP_i) versus time is shown in Figure 5.16. The rate coefficient was calculated to be 0.0611/min according to the following equation of the best fitted formula:

$$\text{Ln}\,[DMP/DMP_i] = -0.0611 * t \qquad (5.5)$$

$$r^2 = 0.95$$

Therefore, under the set conditions, the rate of removal of DMP by UV/H_2O_2 process is about 0.0611/min, which is much higher than the rate of removal by direct photolysis (i.e. 0.0142/min). Furthermore, the rate of removal by UV/H_2O_2 is slightly lower than that of Fenton (i.e. 0.09/min), which was determined earlier. However, the determination of the removal rate in the two cases was conducted under different conditions and the comparison in their efficiencies has to take into considerations other factors such as the cost. The advantages and disadvantages of both systems are discussed later.

5.1.3.3 Effect of UV dosage

As indicated above the UV light plays a significant role in the decomposition of DMP by UV/H_2O_2 process. In an attempt to study this effect closely, a set of three

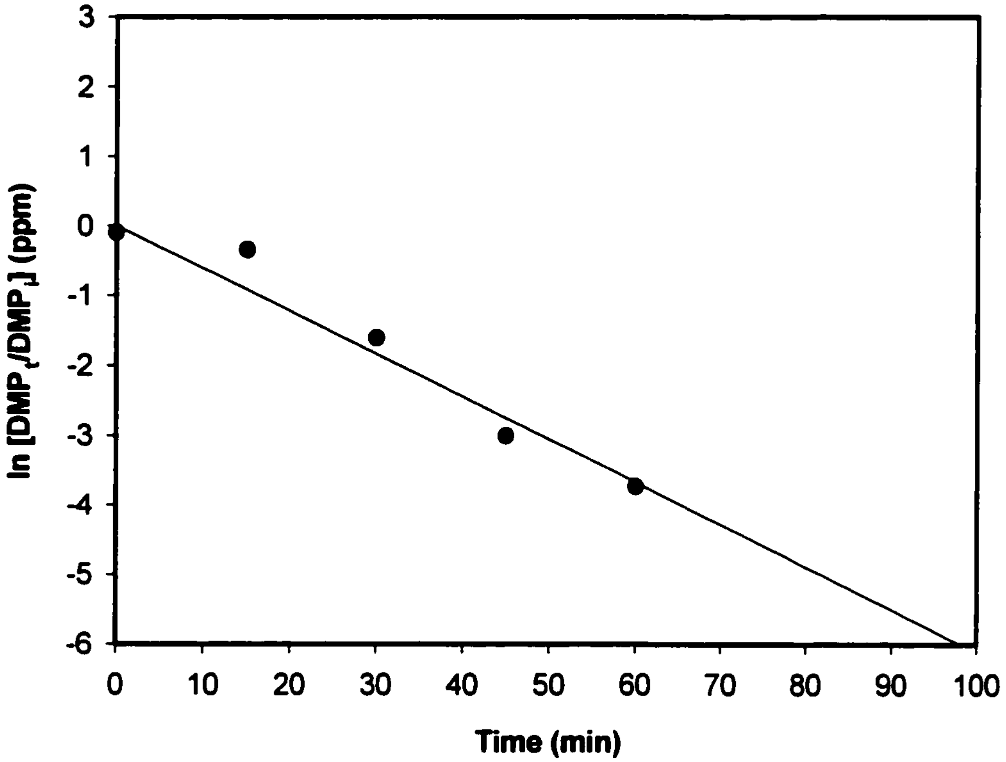


Figure 5.16: Plot of ln (DMP$_t$/DMP$_i$) versus Time in the UV/H_2O_2 Process. (DMP$_i$ = 0.1 mM, H_2O_2 = 4 mM, pH = 3, Temp. = 25°C)

experiments was conducted by which three (3) different UV dosages were used. The UV dosage is calculated as:

$$D = I \times t \tag{5.6}$$

Where:

D = UV Dose, $mW.s/cm^2$

I = Intensity, mW/cm^2

t = Exposure time, s

In this study, only one type of UV lamp (100 mW intensity and irradiation at a wavelength of 254 nm) was used in all experiments. Thus, the UV intensity (I) is constant in all experiments and the dosage of UV light source is a function of the exposure time (t) only. For this reason the experiments were conducting by changing the exposure time of the UV lamp from 0 to 60 minutes. The three exposure times selected for this part of the study were: 0, 30 and 60 minutes. Other factors such as H_2O_2, pH and temperature were kept constant. The results of these experiments were listed in Table A.1.16 and Figure 5.17.

The results show that UV radiation plays a significant role in the decomposition of DMP. It is clear that as the UV exposure time increases, and thus the UV dosage increases, removal efficiency of DMP by UV/H_2O_2 process also increases. It is also interesting to notice from Figure 5.17 that when the UV lamp was turned off at a certain

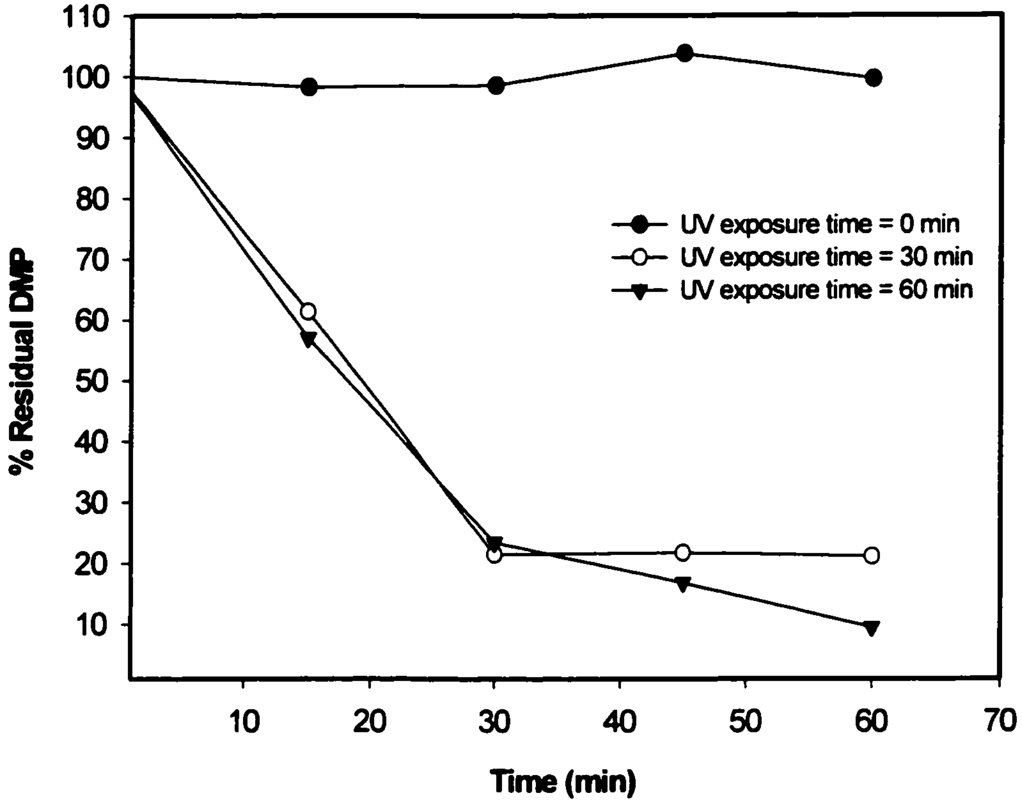


Figure 5.17: Removal of DMP by UV/H_2O_2 Process at Various UV Dosages (DMP_i = 0.1 mM, H_2O_2 = 4 mM, pH = 6, Temp. = 25°C)

time, no additional DMP removal was observed. By referring to the curve in Figure 5.17 when the UV exposure time of 30 minutes was used, removal of DMP remained at 80% even samples were taken 30 minutes after the UV light was cut off. This can be explained by the fact that when UV light is turned off, the reaction stops since no more production of OH^o radicals takes place as depicted in equation 10. The role of UV in this case is to produce OH^o radicals, which then attack the DMP molecules and degrade them. In addition to this, the photo-energy provided by the UV light as in the case of direct photolysis will not exist when the UV lamp is turned off.

5.1.3.4 Effect of pH

The effect of pH level on the removal efficiency of DMP by UV/H_2O_2 process was also studied. A set of experiments was conducted to observe the removal of 0.1 mM of DMP at various pH values. Initial concentration of H_2O_2 of 2 mM and the temperature was set at 25°C for all experiments. The initial pH levels of the aqueous solution spiked with the DMP compound were set at several levels before the addition of the H_2O_2. The pH levels used were: 3, 6 and 9. The results are listed in Table A.1.17 and plotted in Figure 5.18. The results clearly show that UV/H_2O_2 works better under acidic conditions in the range of pH = 3 to 6. On the other hand, when the pH was increased to 9, the removal efficiency of DMP dropped down. However, it seems that, the UV/H_2O_2 system is not very sensitive to the pH when compared by Fenton system. For instance, even at a high pH of 9 for example, 50% of DMP was removed after 60 minutes of reaction time,

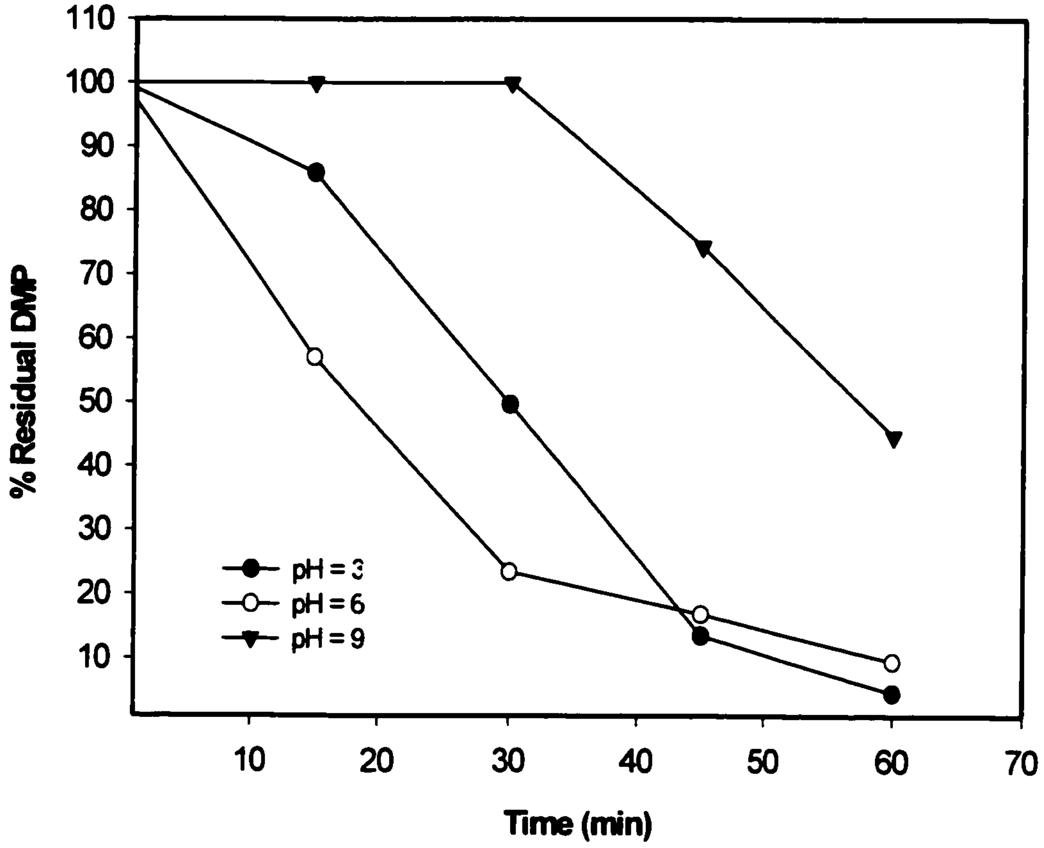


Figure 5.18: Removal of DMP by UV/H_2O_2 Process at Various pH values (DMP$_i$ = 0.1 mM, H_2O_2 = 2 mM, Temp. = 25°C)

while in Fenton system there was no appreciable removal of DMP at high pH values as was depicted in Figure 5.6. This can be attributed to the fact that pH plays a fundamental role on the equilibrium between ferrous and ferric ions which are not used in the UV/H_2O_2 system.

Therefore, it can be concluded from this part of the study that the effect of pH on the removal efficiency of DMP by UV/H_2O_2 process is not as significant as in Fenton process. In Fenton the pH must be adjusted to range of 2.5 to 3.5 in order for the process to be effective, while in UV/H_2O_2 process, as long as pH of the water to be treated is in the normal to acidic range, the process works efficiently. A drop in the efficiency of UV/H_2O_2 process can be experienced only if pH is above 7.

The adjustment of pH in any treatment process involves the usage of chemicals such as buffers, which impose an additional cost and effort. For this reason, it can be said that UV/H_2O_2 process has the advantage over Fenton system, which require a pretreatment step of pH adjustment to reach an acidic range of 3 to 4 since, in most cases, it does not require pH adjustment.

5.1.3.5 Effect of Temperature

The effect of temperature on the removal efficiency of DMP by UV/H_2O_2 process was investigated by carrying out several experiments in which the temperature of the water spiked with 0.1 mM DMP was raised from 15°C to 35°C. Other parameters such as initial concentration of H_2O_2 and pH were kept constant at 2.0 mM and 6, respectively. The water was treated in the photo-reactor by illuminating it with UV light. Samples were taken after 0, 15, 30, 45 and 60 minutes. The results of these tests are shown in Table A.1.18 and Figure 5.19. The results clearly show that temperature plays a significant role in enhancing the reaction rate between OH^o radicals and DMP, consequently the removal rate of DMP increases. Complete removal of DMP was achieved in less than 30 minutes when the temperature of the solution was raised to 35°C. On the other hand, when the temperature was only 15°C, it took nearly 30 minutes for the DMP to start to be degraded. In fact, the usual practice when dealing with irradiation by UV lamp, a warming up period of few minutes is needed to obtain the desired radiation intensity. It seems that the temperature of the spiked water increases few degrees due to the heat coming from the UV lamp, even-though the water jacket was used. However, the water jacket would keep the temperature with a range of ± 3°C. It is obvious from Figure 5.19 that the temperature improves the removal of DMP by UV/H_2O_2 process.

The heat energy introduced by the external heat source or by the internal heat energy coming from the UV source can enhance the decomposition of DMP by weakening and eventually breaking the bonds within the organic compound. This will facilitate the oxidation reaction between the OH^o radicals and DMP. It can be concluded that the removal of DMP either by Fenton or UV/H_2O_2 process is directly proportional to the temperature. However, temperature effect in the UV/H_2O_2 process is more pronounced.

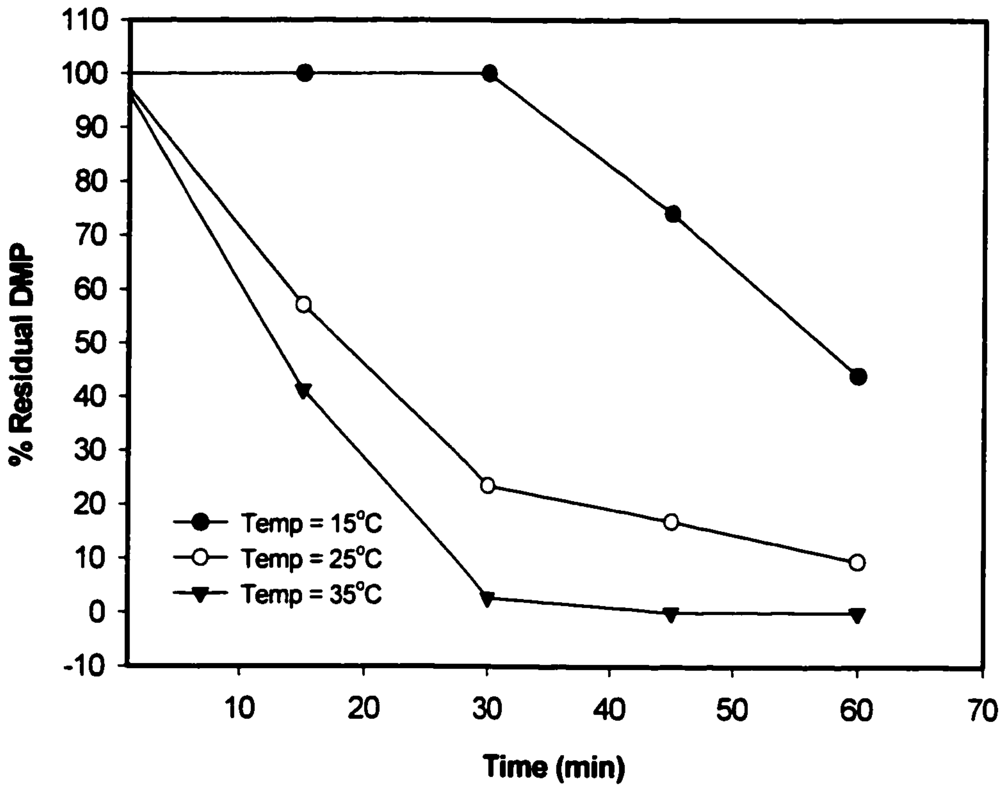


Figure 5.19: Removal of DMP by UV/H_2O_2 Process at Various Temperatures (DMP_i = 0.1 mM, H_2O_2 = 2 mM, pH= 6)

5.1.3.6 Effect of DMP_i

Similar to the discussion of Fenton process on the removal of DMP when its initial concentration was doubled, a set of experiments were carried out to the study the behavior under UV/H_2O_2 process. Two experiments were conducted in this study, in which the initial concentration of DMP (DMP_i) used was 0.1 mM (≈ 20 ppm) while in the other one the initial concentration of DMP (DMP_i) used was 0.2 mM (≈ 40 ppm). Other parameters such as H_2O_2, pH and temperature were kept constant at 1 mM, 6 and 25°C, respectively. The results of these tests are shown in Table A.1.19 and Figure 5.20. Figure 5.20 shows that more than 90% of DMP was removed after 60 minutes of reaction time when the initial concentration of DMP was 0.1 mM (≈ 20 ppm), while only 35% removal was observed at the initial concentration of 0.2 mM (≈ 40 ppm). It is clear that both the UV light intensity and the ratio between the substrate (DMP_i) and amount of H_2O_2 added have an influence of the extent of removal of DMP. Figure 5.1.20 also shows that at lower DMP_i (i.e. 0.1 mM), the removal was at higher rate initially followed by a lower rate afterwards. However, at higher DMP_i (i.e. 0.2 mM), the removal rate was low at all times. This can be attributed again to the ratio between DMP_i and H_2O_2 concentration. At DMP_i of 0.1 mM, the ratio of H_2O_2 / DMP_i is 10. This probably explains the higher removal rate in the first 30 minutes, since more H_2O_2 species were available, and hence more OH^o radicals were generated, with respect to DMP_i molecules. On the contrary, the H_2O_2/DMP_i ratio dropped to only 5 in the case of 0.2 mM of DMP_i and less H_2O_2 species were available and probably less OH^o radicals were generated to promote the oxidation process.

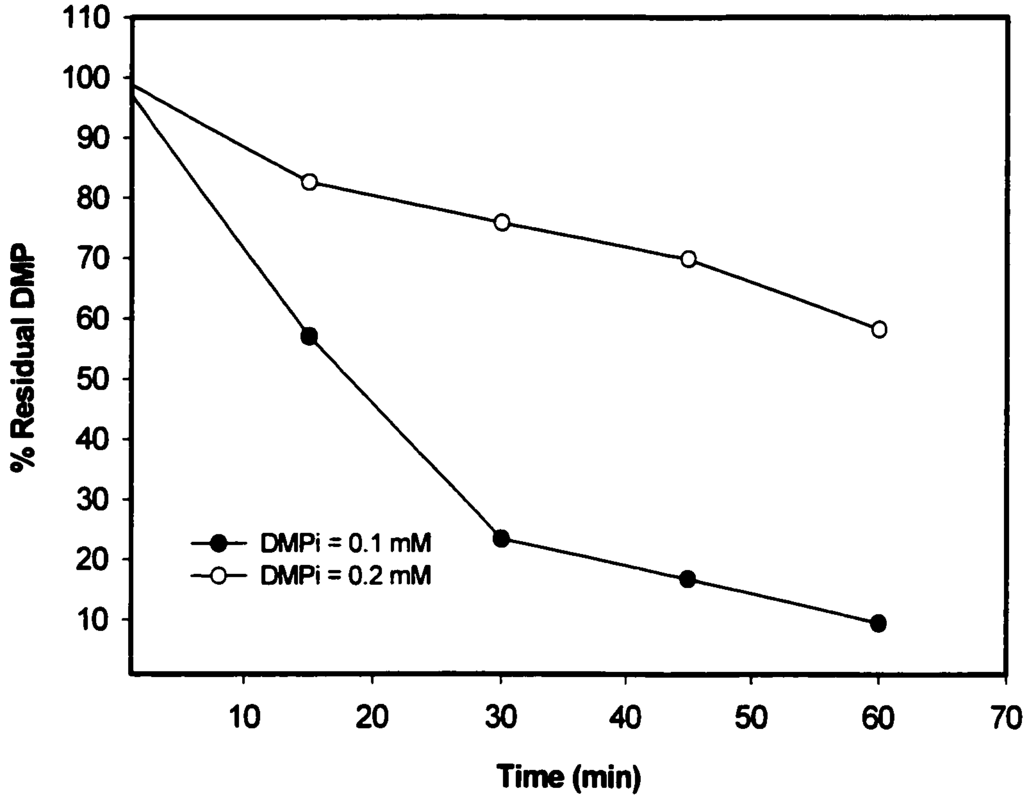


Figure 5.20: Removal of DMP by UV/H_2O_2 Process at Various DMP_i Levels (H_2O_2 = 1 mM, pH= 6)

5.1.3.7 Removal of DMP from Groundwater

In order to evaluate the efficiency of UV/H_2O_2 process in removing DMP if it exists in a groundwater sample rather than pure water sample an experiment was conducted in which, groundwater sample was spiked with 0.1 mM of DMP. The DMP-spiked groundwater sample was then transferred into the photo-reactor to be irradiated by UV light for 60 minutes.

Initial concentration of 1.0 mM of H_2O_2 was used for oxidation. Other parameters including pH and temperature were set at 3 and 25°C, respectively. The results of this experiment are listed in Table A.1.20 and plotted in Figure 5.21. In addition, the removal behavior of DMP spiked into pure water sample by UV/H_2O_2 process, under the same conditions, is also shown in Figure 5.21 for comparison purposes.

The data depicted in Figure 5.21 shows that the efficiency of UV/H_2O_2 process in removing DMP from pure water is slightly better than that from groundwater sample. For example, after 60 minutes, more than 65% of DMP was removed from the ground water sample and more than 70% of DMP was removed from pure water sample. The minor drop in efficiency of UV/H_2O_2 process in removing DMP from groundwater can be attributed to the presence of some inorganic chemical compounds, such as carbonates and sulfates that are known to react with OH^o radicals and tend to deplete some of the radicals formed by UV/H_2O_2 process. According to the conclusion reached above, the removal of

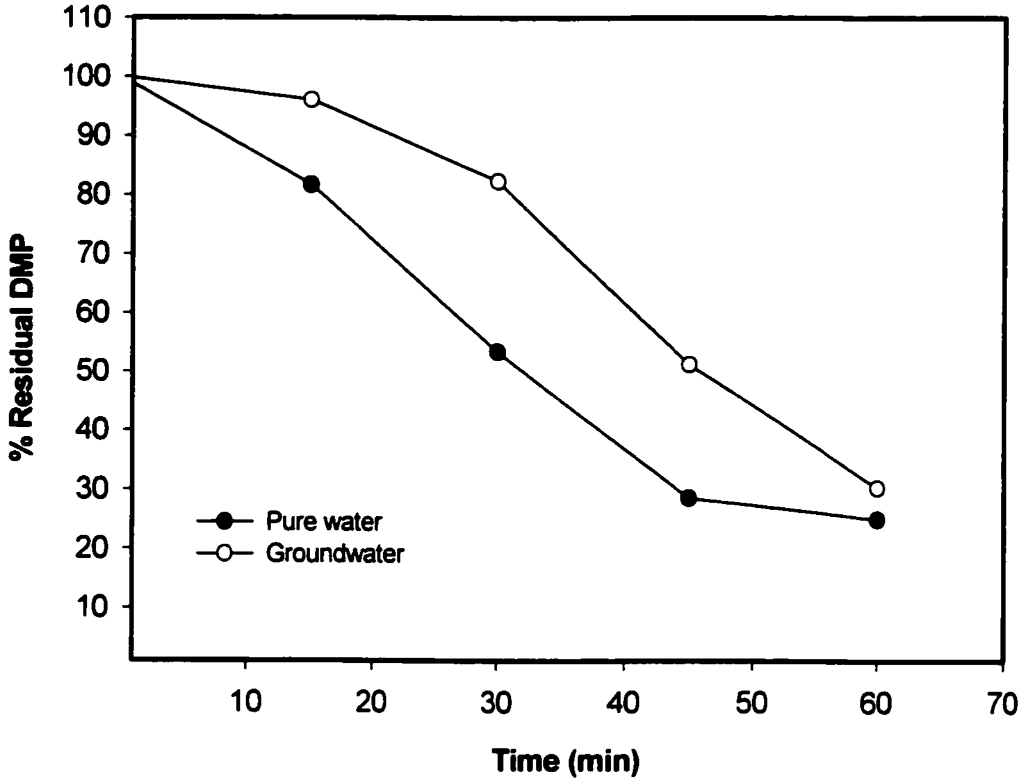


Figure 5.21: Removal of DMP by UV/H_2O_2 Process from Pure and Groundwater (H_2O_2 = 1.0 mM, pH = 3, Temp. =25°C)

DMP by UV/H_2O_2 process seems to be not solely due to the reaction with OH^o radicals and that other removal mechanisms such as direct photolysis by UV plays a significant role in the degradation of DMP. From here comes the efficiency of UV/H_2O_2 in degrading DMP in pure as well as groundwater samples. However, this was not the case with Fenton system, which failed to degrade DMP from groundwater samples as was shown in Figure 5.11. It seems that in Fenton process, the removal of DMP depends mainly on the reaction between the OH^o radicals and DMP molecules. This means that UV/H_2O_2 system has one more advantage over Fenton system since it was able to remove DMP from groundwater and not only pure water as the case in Fenton. It is obvious that one of the major drawbacks of Fenton system is that it usually requires a pretreatment step to reduce the concentration of the compounds that might inhibit the action of OH^o radicals such as chlorides, carbonates and sulfates. This step might not be necessary in the case of UV/H_2O_2 system.

5.2 Removal of DMP from "DMP/Methanol/Water" matrix

As stated before, the medium in which DMP exists could play a significant role on its removal efficiency using advanced oxidation process. This issue is of great interest to engineers since the pollutants to be treated are usually not found in the environment in pure systems. In the case of DMP treatment and since methanol (CH_3OH) is the type of alcohol usually used in the production of DMP; it is most likely that methanol will coexist with DMP in the water. This is mainly true if the contamination of water with DMP occurred during the production stage. If the contamination occurred after usage of products that contain DMP, methanol is not likely to exist. Thus, investigating the effect of methanol on the efficiency of AOP processes on DMP removal is very useful.

In the previous section, Fenton and UV/H_2O_2 processes were evaluated for their efficiencies in removing DMP from water only under various conditions of reactant concentrations, UV dosage, pH and temperature. In this section, more experiments were carried out with the exception that the water medium is spiked with methyl alcohol (methanol). In all experiments, certain amounts of methanol solvent were dissolved in distilled water to reach a concentration of 80 mM (2560 ppm). The concentration of methanol was arbitrary selected. This solution was used as the medium in which DMP is spiked into.

It is worth mentioning at this stage that this part of the study was not originally in the scope of work and only the removal of DMP from pure water was to be assessed. Evaluating the removal efficiency of methanol by AOPs requires a complete study by itself and which needs a very long time to carry out. However, it was decided to conduct extra tests on methanol-contaminated water since the results of these tests could be valuable from engineering point of view. The comparison between the efficiencies of Fenton and UV/H_2O_2 processes on the removal of DMP from this type of medium may help in selecting the best AOP treatment technology to be adopted and whether extra pretreatment steps are needed or not.

In this study, only the effect of the presence of methanol on the removal of DMP by Fenton and UV/H_2O_2 processes was evaluated under various conditions. The removal of methanol itself by these processes is beyond the scope of this study.

5.2.1 Removal of DMP by H_2O_2 alone

To evaluate the efficiency of H_2O_2 alone on the oxidation of DMP in water/methanol medium, several experiments were conducted at various concentration levels of H_2O_2. The initial concentration of DMP used was set at 0.1 mM (i.e. 20 ppm). The initial concentrations of H_2O_2 used were 1.0, 2.0 and 4.0 mM. In these experiments, pH, temperature and stirring rate were kept constant and the percentage of DMP removal was measured after 15, 30, 45 and 60 minutes. The results are shown in Table A.2.1 and Figure 5.22.

Similar to results obtained for DMP removal from water only, the results clearly indicate that H_2O_2 alone was not able to degrade DMP to any appreciable level within the experimental conditions used. Thus, irrespective of the presence of methanol, the hydrogen peroxide oxidant was not strong enough to decompose the DMP molecule for the same reasons stated in section 5.1. This result is expected since H_2O_2 alone was not able to degrade DMP and therefore it is only logical to find that H_2O_2 incapable to do so when additional organic compound such as methanol is present with water.

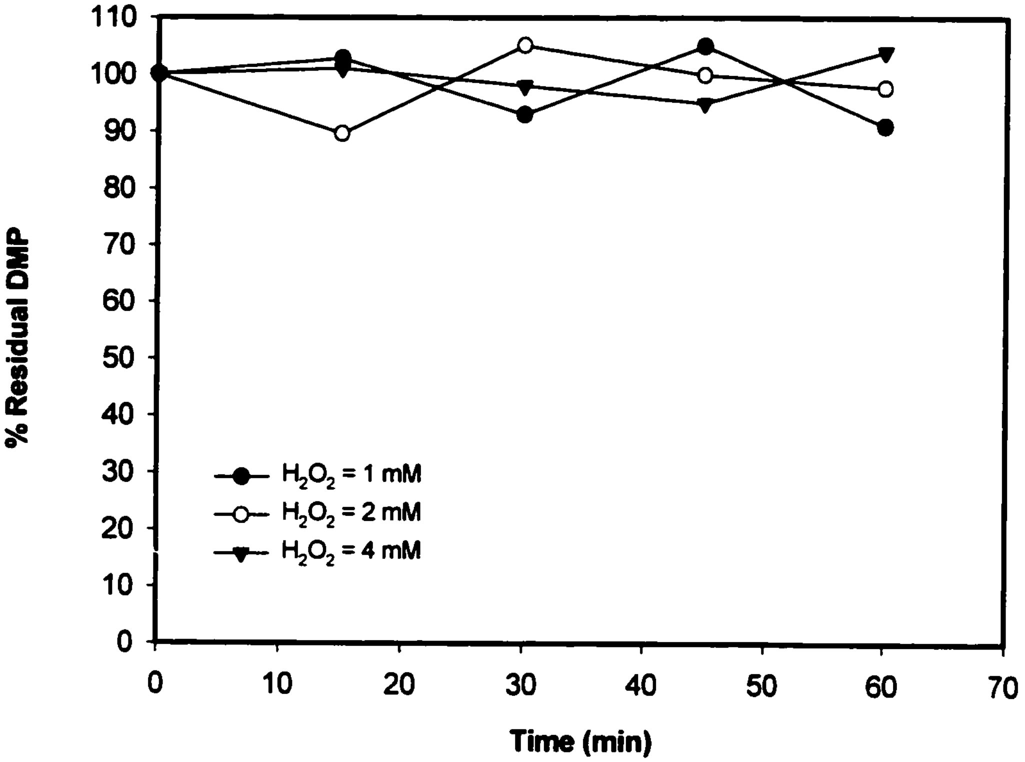


Figure 5.22: Removal of DMP H_2O_2 Alone. (DMP_i = 0.1 mM, CH_3OH = 80 mM, pH = 6, Temp. = 25°C)

5.2.2 Removal of DMP by Fenton Process

The Fenton process, which is based on a chemical reaction between H_2O_2 and Fe^{2+} to produce OH^o radicals is influenced by the reactants concentration levels in addition to the conditions of pH and temperature as was shown in section 5.1. In order to investigate the effect of methanol on the extent of DMP removal by Fenton process, a number of experiments were carried out similar to the experiments conducted in section 5.1.2 with the exception that DMP is spiked into water that is contaminated with methanol. The results of these experiments are discussed in the following paragraphs.

5.2.2.1 Effect of Fe^{2+} Concentration

Experiments were conducted to explore the effect of Fe^{2+} concentration on the removal of DMP from methanol-contaminated water samples by Fenton process. The tests were executed by varying the concentration of Fe^{2+} while keeping other parameters constant. The initial H_2O_2, pH and temperature were set at 2 mM (68 ppm), 3 and 25°C respectively. The results, listed in Table A.2.2 and plotted in Figure 5.23, show that no appreciable removal of DMP was observed even at Fe^{2+} concentration as high as 0.4 mM. This result was unlike the case of DMP spiked in water only, which showed a considerable removal of DMP from pure water. Methanol at this specific concentration, has negatively affected the performance of Fenton process in removing DMP.

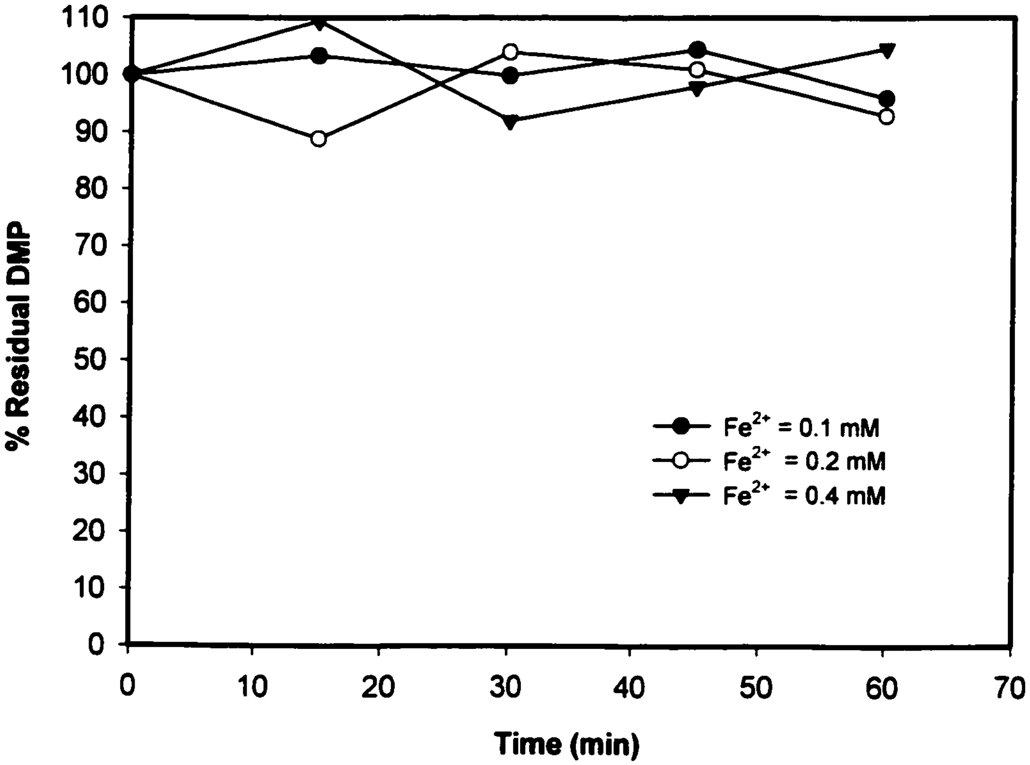


Figure 5.23: Removal of DMP by Fenton Process at Various Fe^{2+} Dosages. (DMP_i = 0.1 mM, CH_3OH = 80 mM, H_2O_2 = 2 mM, pH = 3, Temp. = 25°C)

The reason behind this behavior can be attributed to the fact that methanol, which exists at high concentration with respect to DMP (i.e. CH_3OH : DMP_i = 1 : 800) , can react with OH^o radicals and deplete them. In other words, methanol works here as an inhibitor to the DMP degradation by OH^o radicals. It is true that reaction rate of methanol with OH^o radicals could be slower than the reaction of DMP with these radicals, however, its concentration in the water matrix is much higher.

Thus, it can be concluded that if methanol exist in the water at high concentration with respect to DMP, Fenton process might be inefficient in removing DMP from water. This can be considered a major disadvantage of Fenton process if applied for the treatment of water contaminated with DMP in case inhibitors like methanol exist in large concentrations. If Fenton process is to be applied in any treatment unit in which the objective is to remove phthalate esters, a pre-treatment step has to be introduced to remove any compounds that might inhibit the reaction of phthalates with the hydroxyl radicals. Both organic (i.e. methanol) as well as inorganic compounds (sulfates and carbonates) can inhibit the reaction of OH^o radicals with the target compounds to oxidize them.

5.2.2.2 Effect of H_2O_2 Concentration

In this part of the study, few tests were carried out to study whether concentration of H_2O_2 could improve the efficiency of Fenton process in removing DMP from the methanol/water medium. It was decided to increase the concentration of H_2O_2 in order to increase the OH° radicals formed according to equation 2. The initial concentrations of H_2O_2 used were 0.5, 1.0, and 2.0 mM. Levels of pH and temperature were set at 3 and 25°C respectively. Initial concentration of Fe^{2+} was set at 0.2 mM. The results are shown in Table A.2.3 and Figure 5.24. The data depicted from Figure 5.24 show that no removal of DMP was noticed even at a high concentration of H_2O_2. This again proved that Fenton system did not show any efficiency in removing DMP in the presence of methanol.

It can be concluded here that, under the conditions used, increasing the concentration of H_2O_2 did not improve the performance of Fenton process in removing DMP from water contaminated with methanol. It is possible that very high concentration of both Fe^{2+} and H_2O_2 could result in the formation of high concentration of OH° radicals sufficient to degrade methanol and DMP. However, this is not very practical and involves a high cost. It is more realistic to search for more practical and cost-effective method for removing DMP from water in case it is contaminated with methanol.

5.2.2.3 Effect of UV Radiation

Many studies have shown that UV light enhances the generation of OH° radicals and therefore more removal of DMP could take place. Ultraviolet light has dual purpose of regenerating ferrous ions (Fe^{2+}) from ferric ions (Fe^{3+}) and producing more OH° radicals as described by equation 2.9.

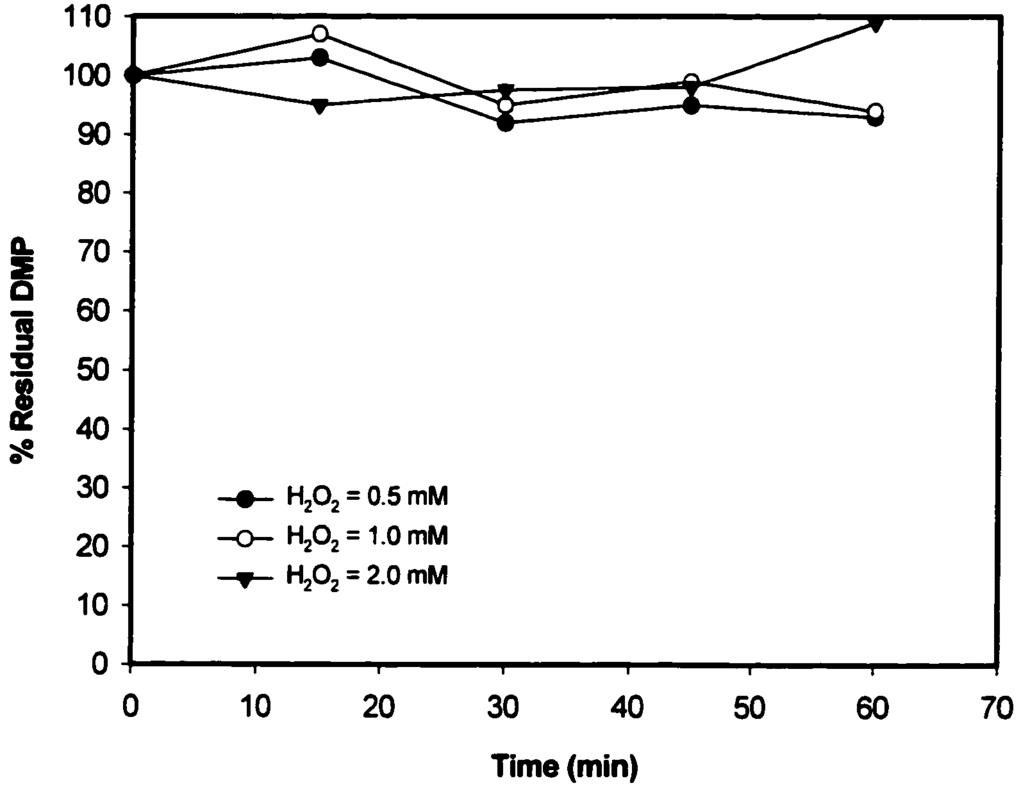


Figure 5.24: Removal of DMP by Fenton Process at Various H_2O_2 concentrations (DMP_i = 0.1 mM, CH_3OH = 80 mM, Fe^{2+} = 0.2 mM, pH = 3, Temp. = 25°C)

To study the effect of light on the efficiency of Fenton system on the removal of DMP, the spiked water samples, which contain methanol, were subjected to UV source following the addition of reactant and adjusting pH and temperature. In this experiment, an initial concentration of 0.1 mM of DMP_i was spiked in water containing 80 mM methanol. 1.0 mM of H_2O_2 and 0.2 mM of Fe^{2+} was applied. Temperature and pH were kept constant at 25°C and 3 respectively. The results of these tests are shown in Table A.2.4 and Figure 5.25. Comparing Figure 5.25 with Figures 5.22 through 5.24 shows that when UV light was introduced along with the Fenton process (i.e. photo-Fenton), a significant enhancement of DMP removal was achieved. For example, more than 90% of DMP was eliminated within 30 minutes, when the sample containing 0.05 mM of Fe^{2+} was exposed to UV light compared to less than 5% when no UV irradiation was used. However, when higher Fe^{2+} concentration was used (i.e. 0.2 mM), a drop in the removal efficiency was observed as shown in Figure 5.25. Thus the removal of DMP was tested under the same experimental condition, but without addition of Fe^{2+}. It was interesting to notice that more DMP was removed in this case. This decrease in removal of efficiency can be attributed to the decrease in the light intensity of the UV source due to the deposition of iron on the sleeve of the lamp. Thus it was concluded that the introduction of UV light enhanced the removal efficiency of DMP, while on the contrary, the addition of Fe^{2+} reduced that efficiency. It seems that OH^{o} radicals produced by Fenton process was insufficient to degrade DMP as was illustrated above, and that the removal of DMP was removed by another mechanism and most probably by direct photolysis and not by oxidation by OH^{o} radicals.

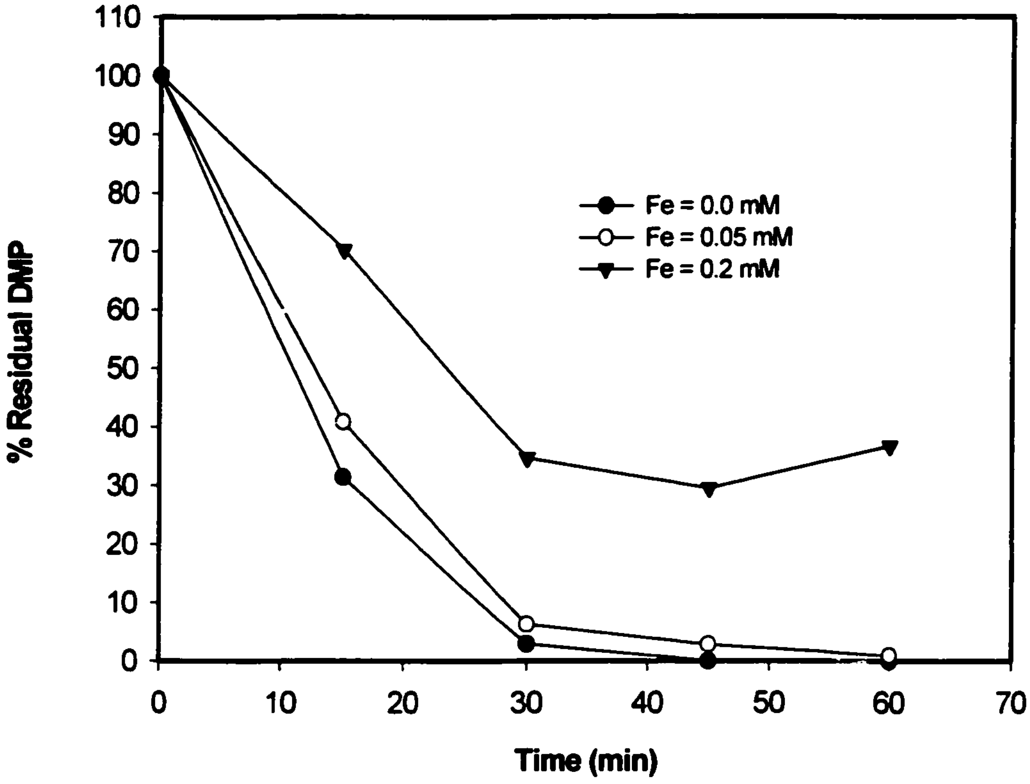


Figure 5.25: Removal of DMP by Photo-Fenton Process at Various Fe^{2+} Concentrations (DMP_i = 0.1 mM, CH_3OH = 80 mM, H_2O_2 = 1.0 mM, pH= 3, Temp. = 25°C)

Hence, it was decided to test the removal efficiency of DMP using UV/H_2O_2 process to study if its efficiency would affected in the presence of methanol. The effect of the main parameters (UV dosage, H_2O_2, pH and temperature) on the treatment efficiency of UV/H_2O_2 process was again tested and the results are discussed in the following section.

5.2.3 Removal of DMP by UV/H_2O_2 Process

Several experiments were conducted to investigate the effect of initial concentration of H_2O_2 and the dosage of UV light on the removal efficiency of DMP that exist along with methanol. The effects of temperature and pH levels were also investigated. The following paragraphs discuss the removal efficiency of DMP by UV/H_2O_2 process under various levels of hydrogen peroxide (H_2O_2), UV dosage, pH, and temperature. Reaction time of 60 minutes was used.

5.2.3.1 Removal of DMP by Direct Photolysis

The removal of DMP from methanol-contaminated water samples by direct photolysis was studied by conducting a set of experiments where the samples were exposed to UV light for 60 minutes. Temperature and pH levels were set at 25°C and 3, respectively. The results are shown in Table A.2.5 and Figure 5.26. From Figure 5.26, up to 40 % of DMP was removed due to the direct photolysis mechanism. However, the extent of DMP removal by direct photolysis in the absence of methanol was about 60%. Therefore, the removal efficiency of DMP by direct photolysis in the absence of methanol is higher than the efficiency in the presence of methanol. This can be clearly observed by comparing Figure 5.26 and Figure 5.12. It seems that the decomposition of DMP by photodegradation was affected slightly by the presence of methanol since some of the UV radiation was partly absorbed by the methanol itself. It is true that methanol has a weak absorption of UV light at wavelengths of 200 to 400 nm and that the maximum absorbance of UV light by methanol at wavelength of 250 nm is only 0.02. However, methanol concentration of 80 mM was much higher than the concentration of DMP, which was only 0.1 mM. This probably explains the effect that methanol impose on the removal of DMP by direct photolysis mechanism.

5.2.3.2 Effect of H_2O_2 Concentration

To test whether the efficiency of DMP removal from methanol-contaminated water can be improved by changing the initial concentration of H_2O_2, two experiments were carried out in which the H_2O_2 concentration was raised from 1 to 2 mM. The results, listed in Table A.2.6 and plotted in Figure 5.27, show that more than 50% of DMP was removed after 30 minutes of reaction time at H_2O_2 initial concentration of 1.0 mM. However, more than 95% of DMP was removed when the initial concentration of H_2O_2 of 2 mM was applied.

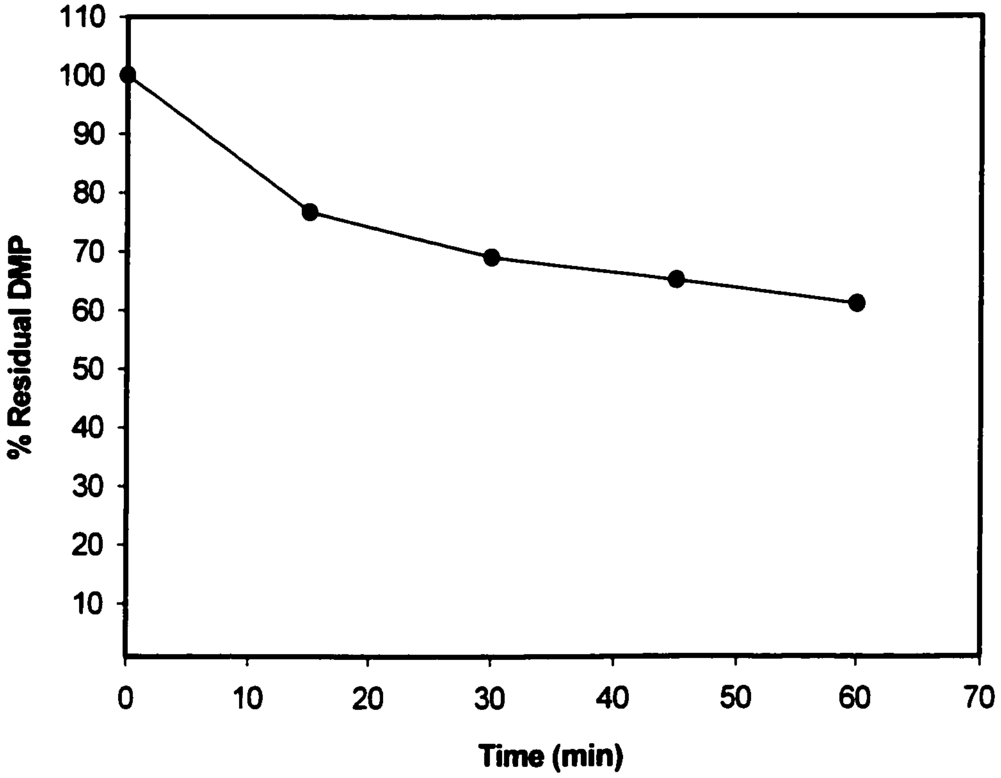


Figure 5.26: Removal of DMP by UV/H_2O_2 by Direct Photolysis (DMP$_i$ = 0.1 mM, CH_3OH = 80 mM, pH= 3, Temp. = 25°C)

Approximately, complete removal of DMP occurred after 60 minutes at both 1, and 2 mM of H_2O_2. This means that, under this range of H_2O_2 concentration, H_2O_2 concentration has a positive effect on the efficiency of DMP removal from water that contains methanol. This is somewhat similar to that concluded for the removal of DMP by UV/H_2O_2 process in the absence of methanol. This again can be considered as an advantage to the UV/H_2O_2 process over Fenton system, since the later process was significantly affected by the presence of methanol.

5.2.3.3 Effect of UV dosage

In an attempt to demonstrate the effect that UV dosage has on the removal of DMP in water which contains methanol, three (3) experiments were conducted in which UV exposure time was set at 30, 45 and 60 minutes. Other factors such as H_2O_2, pH and temperature were kept constant. The results of these experiments were listed in Table A.2.7 and Figure 5.28. The results show that UV radiation is essential in decomposing DMP compound. Figure 5.28 shows that when the UV lamp was turned off at a certain time, no additional DMP removal was observed. Similar results were found earlier when DMP was spiked into the methanol-free (i.e. pure) water. For example, when the UV lamp was turned off after 30 or 45 minutes, the percent DMP residual remained constant, while DMP continued to decrease when the light was left on for 60 minutes. This means that UV light is essential in initiating the oxidation reaction and production of OH^{o} radicals and the reaction stops completely.

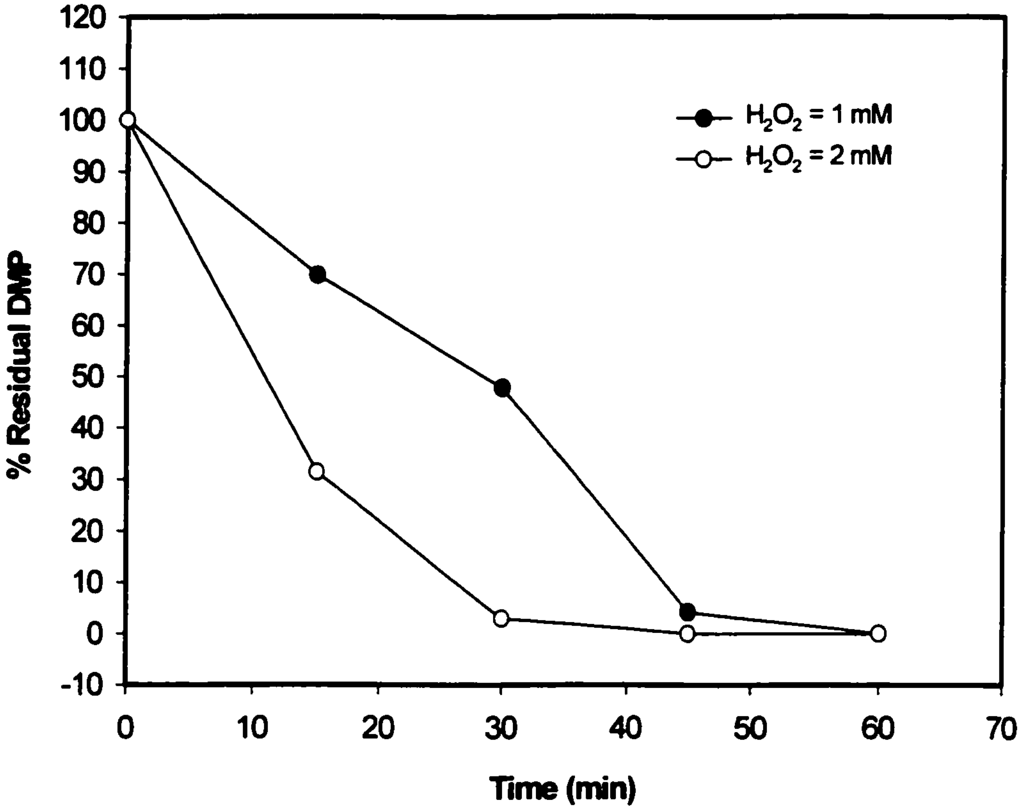


Figure 5.27: Removal of DMP by UV/H_2O_2 at Two H_2O_2 Concentrations (DMP$_i$ = 0.1 mM, CH_3OH = 80 mM, pH= 3, Temp. = 25°C)

5.2.3.4 Effect of pH

The effect of pH level on the removal efficiency of DMP by UV/H_2O_2 process was also studied. A set of experiments was conducted to observe the removal of 0.1 mM of DMP at various pH values. Initial concentration of H_2O_2 of 2 mM and the temperature was set at 25°C for all experiments. The initial pH levels of the aqueous solution spiked with DMP were set at several levels before the addition of the H_2O_2. The pH levels used were: 3, 6 and 9 respectively. The results are listed in Table A.2.8 and plotted in Figure 5.29. The results clearly show that UV/H_2O_2 works better under acidic conditions in the range of pH = 3 to 6. It can also be noticed that a slight drop in the removal efficiency resulted at pH = 9. This can be attributed to the formation of intermediates, which might have degradation mechanisms that are affected by the acidity or alkalinity of the solution. The same result was found when studying the removal efficiency of DMP from methanol-free water. It can be concluded that as long as the pH of the solution lies within the normal to acidic range, the efficiency of UV/H_2O_2 process on the removal of DMP from methanol-contaminated or methanol-free water is favorable, which can be easily visualized by comparing Figures 5.18 and Figure 5.29. This again can be considered as an advantage from an engineering point of view. That is to say that there will be usually no need for adding a step for adjusting pH in case the UV/H_2O_2 process was utilized for treating water contaminated with DMP irrespective of the presence of the alcohol.

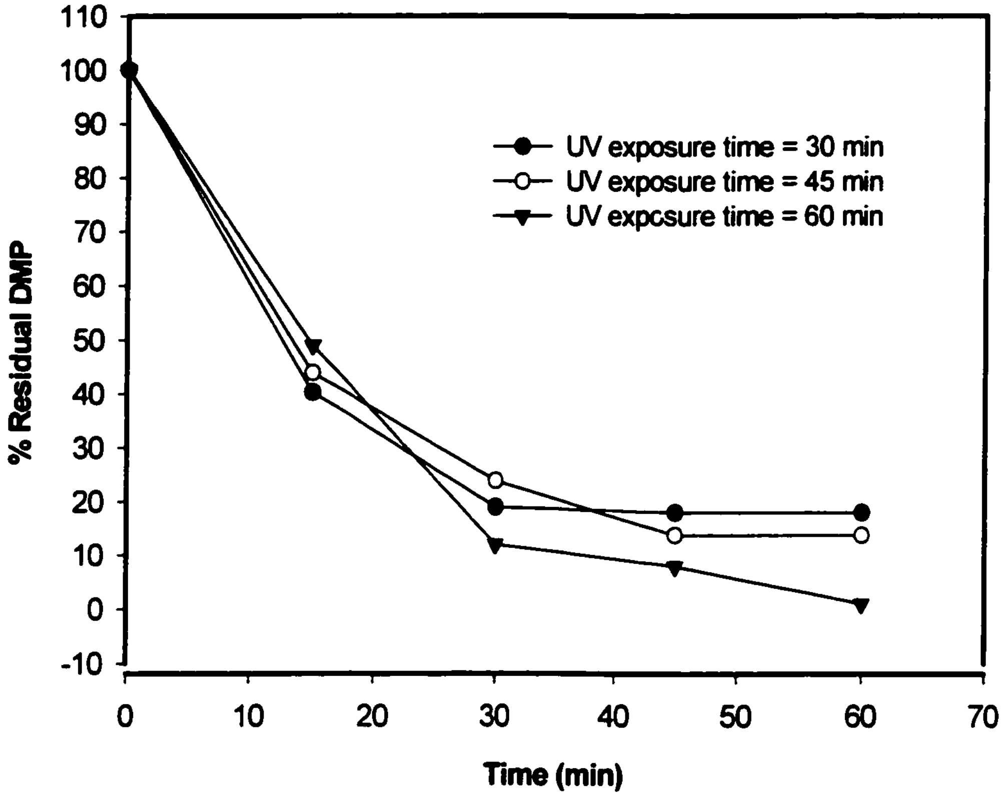


Figure 5.28: Removal of DMP by UV/H_2O_2 Process at Various UV Dosages (DMP_i = 0.1 mM, CH_3OH = 80 mM, H_2O_2 = 2 mM, pH = 6, Temp. = 25°C)

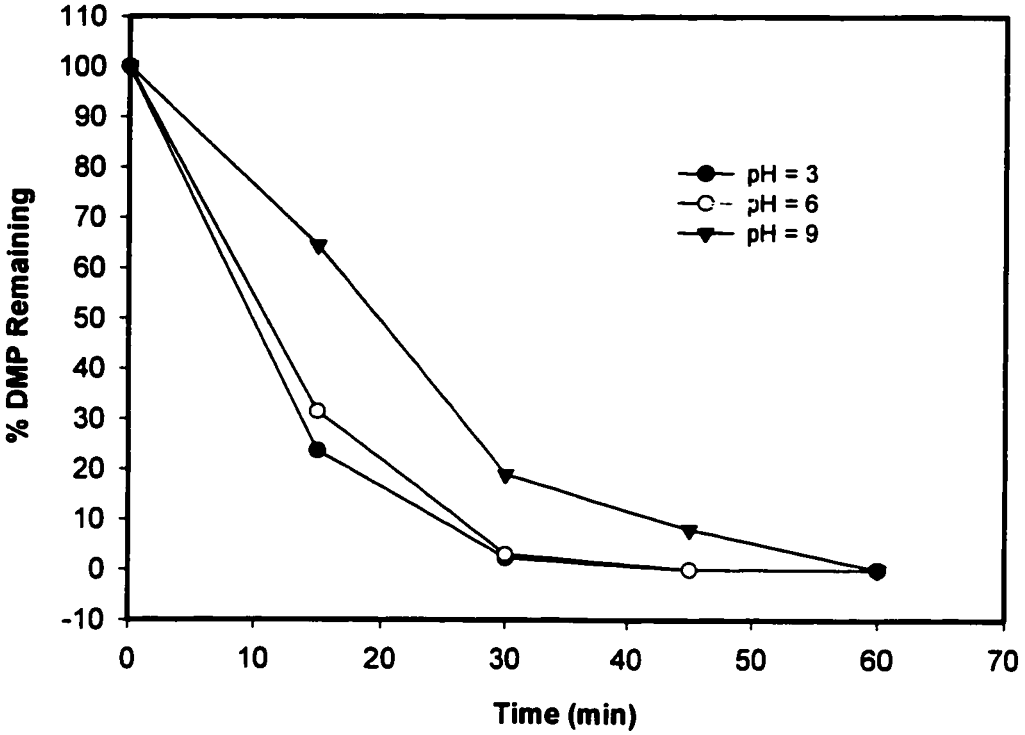


Figure 5.29: Removal of DMP by UV/H_2O_2 Process at Various pH Values (DMP$_i$ = 0.1 mM, CH_3OH = 80 mM, H_2O_2 = 2 mM, Temp. = 25°C)

5.2.3.5 Effect of Temperature

The effect of temperature on the removal efficiency of DMP from methanol-contaminated water by UV/H_2O_2 process was also investigated in this study. Several experiments were carried out in which the temperature of the water samples was set at 25 and 35°C, respectively. Initial concentration of H_2O_2 and pH were set at 2.0 mM and 6, respectively. The water was exposed to UV light and effluent samples were taken every 15 minutes for a period of one hour. The results of these tests are shown in Table A.2.9 and Figure 5.30.

The results suggest that temperature plays a significant role in enhancing the reaction rate between OH^o radicals and DMP, which increases the removal rate of DMP. Complete removal of DMP was achieved in less than 15 minutes when the temperature of the solution was raised to 35°C. More than 45 minutes was needed to achieve 95% removal of DMP. This result agrees with the result obtained earlier in section 5.1 and shown in Figure 5.19.

5.2.4.6 Effect of DMP_i

To evaluate the effect of initial concentration of DMP on its removal from the methanol-contaminated water by UV/H_2O_2 process, an experiment was conducted in which the initial concentration of DMP (DMP_i) used was 0.2 mM (≈ 40 ppm).

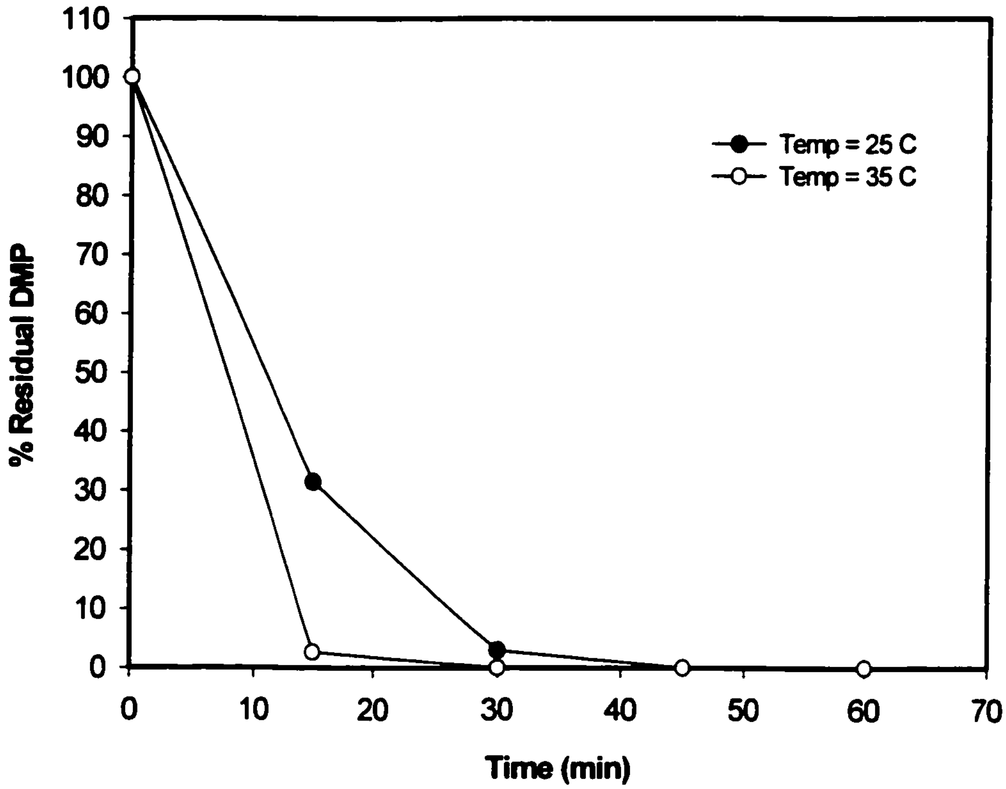


Figure 5.30: Removal of DMP by UV/H_2O_2 Process at Two Temperatures (DMP$_i$ = 0.1 mM, CH_3OH = 80 mM, H_2O_2 = 2 mM, pH= 6)

The results of this experiment were compared with results of a previous experiment in which DMP_i used was 0.1 mM (≈ 20 ppm). Other parameters such as H_2O_2, pH and temperature were kept constant at 1.0 mM, 6 and 25°C, respectively. The results of the test are shown in Table A.2.10 and Figure 5.30. Results show that more than 95% of DMP was removed after 30 minutes of reaction time when DMP_i was 0.1 mM (≈ 20 ppm) while only 65% removal was observed at DMP_i of 0.2 mM (≈ 40 ppm). It is obvious that both the UV light intensity and the ratio between the substrate (DMP_i) and amount of H_2O_2 added have an influence of the extent of removal of DMP. For this reason, it is necessary to consider the type and initial concentration of the target compound to be removed by UV/H_2O_2 process. The ratio between target compound concentration and H_2O_2 concentration is vital and has to be optimized prior to designing a treatment unit.

By comparing Figure 5.20 and Figure 5.31, it can be noticed that the presence of methanol did not affect the removal pattern of DMP by UV/H_2O_2 process. This can also be considered as an advantage of using UV/H_2O_2 over Fenton for the treatment of DMP. In other words, it does not seem very necessary to consider the concentration of methanol when designing a UV/H_2O_2 treatment unit for DMP in water that is contaminated with it.

In general, the results show that Fenton process was effective in removing DMP only in the absence of high concentration of methanol (CH_3OH) and inorganic salts that can exist in ground water, such as sulfates and which can also inhibit the action of (OH^o) radicals produced by Fenton system.

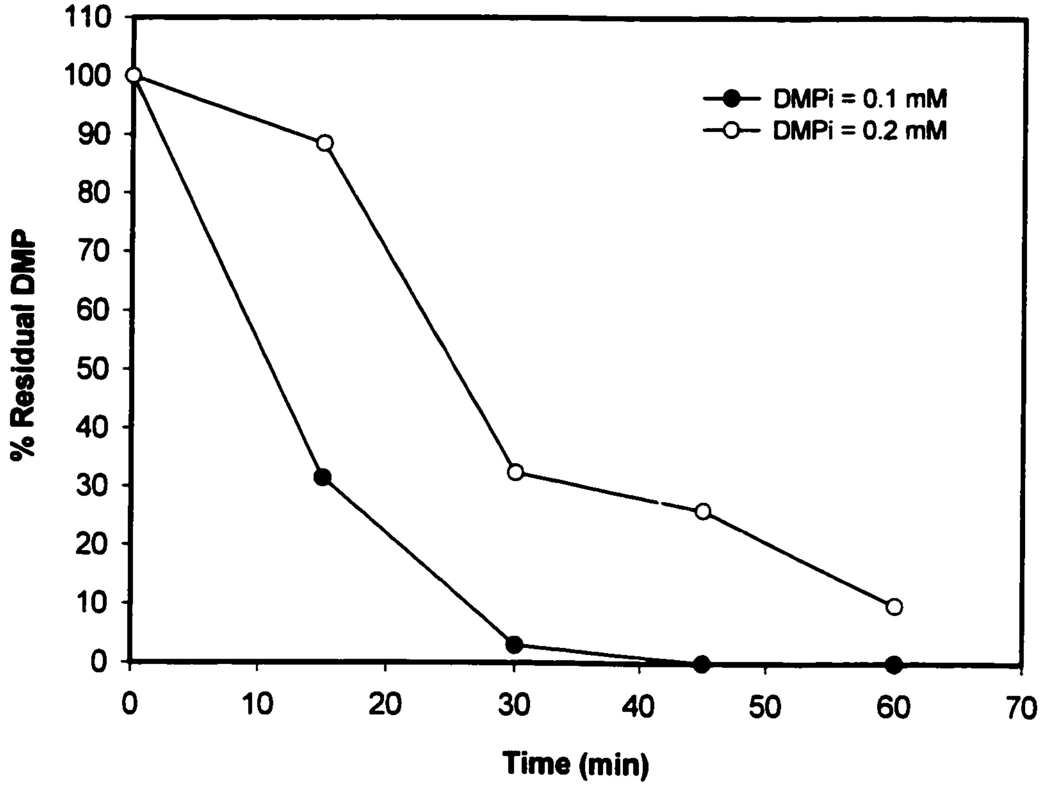


Figure 5.31: Removal of DMP by UV/H_2O_2 Process at Two DMP_i levels (H_2O_2 = 1 mM, CH_3OH = 80 mM, pH= 6, Temp. = 25°C)

Another disadvantage of Fenton's treatment is the production of iron sludge through the formation of iron hydroxides, which require proper disposal.

Finally, Fenton process was found to be very sensitive to the pH and adjusting the pH of the medium to be treated to around 3 to 4 seems to be necessary for the production of enough (OH^o) radicals capable of degrading the target compounds. On the other hand, the UV/H_2O_2 process showed a good efficiency in removing DMP despite the presence of methanol or other inorganic species. UV/H_2O_2 process also showed only a slight dependence on pH. These are considered as advantages of UV/H_2O_2 system over Fenton system.

Previous work on the efficiency of UV/H_2O_2 systems have also indicated that these systems have the ability to treat a wide variety of contaminants and have the advantage of being mobile and being able to be installed in a short time frame for the treatment of contaminated water at different sites. However, these systems are not applicable for the treatment of contaminated soils because UV light does not penetrate soil particles (16).

The main outcome of this study indicates that UV/H_2O_2 process is advantageous to Fenton system. Thus statistical analysis was performed on UV/H_2O_2 to optimize the various parameters affecting the efficiency of this treatment process.

5.3 Statistical Analysis

Based on the discussion above, factors such as H_2O_2, Fe^{2+}, UV dose, and temperature have shown to play a significant role in determining the efficiency of the advanced oxidation processes. However, the extent of effect that a factor plays could be different from other factors. In addition, the combined effect of two factors could be more significant in enhancing the performance of the treatment process than the individual effect of these factors alone. In order to determine the effect of the above factors individually and in combination, several tests were carried out randomly using the single-replicate $2^{\wedge k}$ factorial design analysis (210) which is presented in section 5.3.1. The estimated effects of the various factors were then used for the determination of their optimum levels using an optimization program called "Multisimplex" which will be discussed in section 5.3.2.

5.3.1 Experimental Design by the $2^{\wedge k}$ Factorial Analysis

Factorial designs are widely used in experiments involving several factors where it is necessary to study the joint effect of the factors on a response. By a factorial design, all possible combinations of the levels of the factors are investigated in each complete trial or replication of the experiment. The effect of a factor is defined to be the change in response produced by a change in the level of the factor and it is referred to as the main effect because it refers to the primary factors of interest in the experiment.

The $2^{\wedge k}$ factorial design is a special case of the general factorial design and is important because it is widely used in research work and forms the basis of other designs of considerable practical value. A complete replicate of such a design requires 2 x 2 x ...x 2 = $2^{\wedge k}$ observations. It provides the smallest number of runs with which k factors can be studied in a complete factorial design. Factorial designs allow the effect of a factor to be estimated at several levels of the other factors, yielding conclusions that are valid over a range of experimental conditions.

The first step in factorial analysis is to define the control (i.e. factors) and response variables in the experiment. In this study, the four main control variables considered were: initial concentration of H_2O_2; initial concentration of Fe^{2+}; UV dosage (represented by UV exposure time); and temperature. While the percent removal of DMP was considered as the response variable. Since pH of 3 was found to be efficient in both Fenton and UV/H_2O_2 processes, it was kept constant for all experiments.

The second step is to define the ranges (i.e. maximum and minimum) at which the above factors would be tested. In this study, the ranges used are shown in Table 5.1. These ranges were selected based on the results obtained and since they represent the practical ranges used in several research studies (16). According to the theory of factorial design theory, a total of sixteen (i.e. $2^{\wedge 4}$) experiments have to be performed, in which the removal of DMP from pure water was measured under a combination of various levels of the factors.

TABLE 5.1: Factors to be Studied by $2^{\wedge k}$ Factorial Analysis

Factor	Description	Range
A	H_2O_2	0 – 2 mM
B	Fe^{2+}	0 – 0.2 mM
C	UV_t	0 – 1 hr
D	Temperature	15 – 35 °C

In this study, the treatment combinations used are shown in Table 5.2. The levels of these control variables were set at their either minimum or maximum values. The results of the 16 experiments are shown in Table 5.3. The internationally used treatment combinations' notations shown in Table 5.3 are used for simplification purpose. For example the notation **(1)** represents the combined effect of all factors at minimum levels, while the notation **abcd** represents the combined effect of the 4 factors at maximum levels.

Once the response variable (i.e. % DMP removal) is determined, the effect of each factor or combination of factors can be estimated based on the definition of the average effect. The average effect of a factor is defined as the change in response produced by a change in the level of the factor averaged over the levels of the other factors. For example, the effect of factor A at the minimum level of B is equal to $[a - (1)]/n$, where n represents the number of replicates at which the factor is tested. At the same time, the effect of A at the maximum level of B is equal to $[ab - b]/n$. Therefore, averaging these two effects yields that:

$$\begin{aligned}\text{Average Effect of A} &= 1/2n\,\{[ab - b] + [a - (1)]\} \qquad (5.7)\\ &= 1/2n\,[ab + a - b - (1)]\end{aligned}$$

Similarly, the average effect of factor B is equal to

$$\text{Average Effect of B} = 1/2n\,[ab + b - a - (1)] \qquad (5.8)$$

Defining the interaction effect of AB as the average difference between the effect of A at the maximum level of B and the effect of A at the minimum level of B, yields:

$$\text{Effect of AB} = 1 / 2n\ [ab + (1) - a - b] \tag{5.9}$$

The term between parenthesis is usually referred to as the contrast of the factor. In general, the contrast of k factors in a $2^{\wedge k}$ factorial design can be calculated by expanding the right hand side of the following formula (210):

$$\text{Contrast}_{AB....K} = (a \pm 1)(b \pm 1).....(k \pm 1) \tag{5.10}$$

In expanding equation 5.10, ordinary algebra is used with "1" being replaced by (1) in the final expression. The sign in each set of parentheses is negative if the factor is included in the effect and positive if the factor is not included. The contrast constants used for the $2^{\wedge 4}$ design is shown in Table A.3.1.

From Table A.3.1, the contrast of the various factors can be determined. For example, in this study, and for a $2^{\wedge 4}$ factorial design, the contrast of A is equal to:

$$\begin{aligned}\text{Contrast}_A \quad &= -\ (1) + a - b + ab - c + ac - bc + abc - d + ad \\ &\quad - bd + abd - cd + acd - bcd + abcd \end{aligned} \tag{5.11}$$

TABLE 5.2: Various Levels of the Factors Used in Various Tests

Run #	H_2O_2 mM	Fe^{2+} mM	UV_t(hr)	Temp. °C
1	0	0	0	15
2	2	0	0	15
3	0	0.2	0	15
4	2	0.2	0	15
5	0	0	1	15
6	2	0	1	15
7	0	0.2	1	15
8	2	0.2	1	15
9	0	0	0	35
10	2	0	0	35
11	0	0.2	0	35
12	2	0.2	0	35
13	0	0	1	35
14	2	0	1	35
15	0	0.2	1	35
16	2	0.2	1	35

TABLE 5.3: Percent Removal of DMP at Various Treatment Combinations

Run #	Treatment Combibations	% DMP Removal
1	(1)	6.6
2	a	0.5
3	b	1.5
4	ab	43.0
5	c	61.0
6	ac	56.0
7	bc	44.3
8	abc	98.7
9	d	2.3
10	ad	3.9
11	bd	1.7
12	abd	84.2
13	cd	92.9
14	acd	100.0
15	bcd	91.4
16	abcd	100.0

The values in the right hand side of equation 5.11, can be obtained from Table 5.3.

Once the contrast for the effects have been computed, the estimates of the effects of the factors are computed according to the following formula:

$$\text{Effect of (AB....K)} = 2 * (\text{Contrast}_{AB....K})^2 * (n2^k)^{-1} \qquad (5.12)$$

In this study, the calculated the individual as well as the combined effects of the four factors are listed Table 5.4. The factors were then listed in descending order (j) from 15 to 1 as shown in Table 5.5.

The data in Table 5.5 clearly shows that, under the experimental conditions used, UV light is the most significant factor that affects the efficiency of DMP removal by the advanced oxidations processes applied in this study. The weight of the effect of UV light is approximately 62.59. Table 5.5 also shows that combined effect of H_2O_2 and Fe^{2+} is much lower than the effect of UV light alone, but higher than the individual effect of H_2O_2 and Fe^{2+}. Table 5.5 also shows that the effect of H_2O_2 is higher than the effect of Fe^{2+}. The effect of temperature on the performance of advanced oxidation processes is also positive with a weight of about 17.71.

TABLE 5.4: Estimated Effects of the Various Factors

Effect	Estimate
A	23.08
B	17.71
AB	23.68
C	62.59
AC	-6.80
BC	-11.59
ABC	-8.45
D	20.61
AD	1.88
BD	1.84
ABD	-3.08
CD	10.47
ACD	-10.30
BCD	-8.71
ABCD	-11.40

TABLE 5.5: Estimated effects of the Various Factors After Ordering

Effect	Estimate	Order (j)
C	62.59	15
AB	23.68	14
A	23.08	13
D	20.61	12
B	17.71	11
CD	10.47	10
AD	1.88	9
BD	1.84	8
ABD	-3.08	7
AC	-6.80	6
ABC	-8.45	5
BCD	-8.71	4
ACD	-10.30	3
ABCD	-11.40	2
BC	-11.59	1

The results of the $2^{\wedge 4}$ factorial analysis clearly indicate that irradiation the water contaminated with DMP is essential in removing this pollutant from water. This means that either photo-Fenton or UV/H_2O_2 process has to utilized to remove DMP from water. However, due to obviously the higher cost of photo-Fenton process, UV/H_2O_2 represent a more suitable process for the treatment.

5.3.2 Optimization of The Various Parameters in the UV/H_2O_2 Process

From engineering point of view, it is necessary to optimize the factors that affect the efficiency of the process which include UV dosage, H_2O_2 and temperature. The estimates of the effects of the various factors by $2^{\wedge 4}$ analysis were fed into an optimization software. The Window-based optimization software is called " Multisimplex ® Lite" and was developed by Grabitech Solutions AB, Sweden (211). This software is considered as a quick and easy way to optimize a technical system such as a process, an apparatus or an instrument. It is based on the modified simplex method, which was first introduced by Spendley et al. in 1962 (212). According to the software designer, Multisimplex ® Lite was developed as a true multivariate non-linear optimization tool that seeks the optimum level step-by-step with a minimum number of trials.

The optimization of a technical system is simply referred to as the process of adjusting the control variables to find the levels that achieve the best possible outcome (response). In this study, the control variables in the UV/H_2O_2 process were: concentration of H_2O_2, UV dosage, and temperature. The response factor was taken to be the extent of DMP removal (% DMP removed). Ultraviolet (UV) dosage is represented by UV exposure time since the intensity (I) of the lamp was constant. Since the reaction in the UV/H_2O_2 process stops when the UV lamp is turned off, the reaction time was replaced by the UV exposure time. In addition, pH value of the DMP-spiked water was kept at a constant level since its effect on the removal efficiency was minimal was shown earlier. Initial concentration of DMP was kept constant at 0.1 mM (20 ppm).

The basic Dantzig's simplex method was first conceived in the summer 1947 for solving linear programming (212) problem in the following format:

$$\begin{aligned} &\text{Minimize } CX \\ &\text{Subject to} \quad AX = b, \\ &\qquad\qquad\quad X \geq 0 \end{aligned} \tag{5.13}$$

Where, A represents an *m x n matrix* with rank (m) and (n) number of variables.

The simplex method is a clever procedure that moves from an extreme point to another extreme point, with a better objective. A simplex is a geometric figure having a number of vertices (corners) equals to one more than the number of dimensions in space; i.e. a simplex is defined by k+1 points in a k-dimensional space (212). When the simplex method is used for the optimization of experimental systems, each vertex corresponds to a set of experimental conditions.

With (x) variables, the first simplex design is based on (x+1) trials. This number of trials is also the minimum for defining a direction of improvement. After the initial trials, the simplex process is sequential, with the addition and evaluation of one new trial at a time. The simplex evaluates the response results of the trials that are introduced in the current simplex, and searches automatically for the best levels of the control variables for the next trial. The optimization process ends when the optimization objective is reached, or when the response cannot be improved further. The modified simplex method, which MultiSimplex software is based on, has much in common with the basic simplex method, but can adjust its shape and size depending on the response in each step (211). Using Multisimplex ® software requires empirical data from the system to be optimized. The first simplex trials are made around a reference point, usually the normal operating conditions. The designs suggested by Multisimplex ® provide initial trials that give unique information and cover a large volume of the control variables space, while fulfilling the step size (i.e. range of variation in a control variable) requirement. In this study, for optimizing UV/H_2O_2 process in removing 0.1 mM DMP from water at neutral pH, the maximum and minimum levels of the various parameters, listed in Table 5.1, were fed into the software, which in turn, suggested the following first trial (i.e. experimental set points) (i.e. H_2O_2 = 2.25 mM, UV exposure time = 35 minutes, and Temperature = 27.5°C)

An experiment at these conditions was conducted and the response variable (i.e. % DMP removal) was determined and fed into the software. The optimization process then continues searching for an optimum condition of these parameters. In this study, the optimization process was set to stop when a 100% removal is achieved with minimum levels of the parameters.

The outcome of the optimization process is shown in Table 5.6 and Figures 5.32 through 5.34. The results listed in Table 5.6 show that in order to reach a complete removal of 0.1 mM of DMP from water, a hydrogen peroxide of 2.4 mM should be applied along with raising the temperature to 40.9°C for 51.6 minutes of UV exposure time. These are considered as the optimum conditions in the UV/H_2O_2 process under the conditions used in this study. However, what could be an acceptable removal of 97.58% of DMP can be achieved by setting the levels of H_2O_2, temperature and UV exposure time at 2.0 mM, 33.6°C and 30.6 minutes, respectively.

At this stage, the cost of adjusting each factor to its optimum levels plays a decisive role in the design of the treatment unit for DMP based on UV/H_2O_2 process. The trade-off between these factors is essential in designing a treatment unit for DMP in water.

The optimum temperature of 33.6°C is only about 8°C above the room temperature (i.e. 25°C). Most probably the heat needed to reach this temperature can be supplied from the heat energy resulting from the UV lamp itself. This leaves the two primary design variables that must be optimized in sizing a UV/H_2O_2 system as UV power radiated per unit volume of water treated (i.e. UV dose) and the concentration of H_2O_2.

5.3.3 Sizing of UV/H_2O_2 System

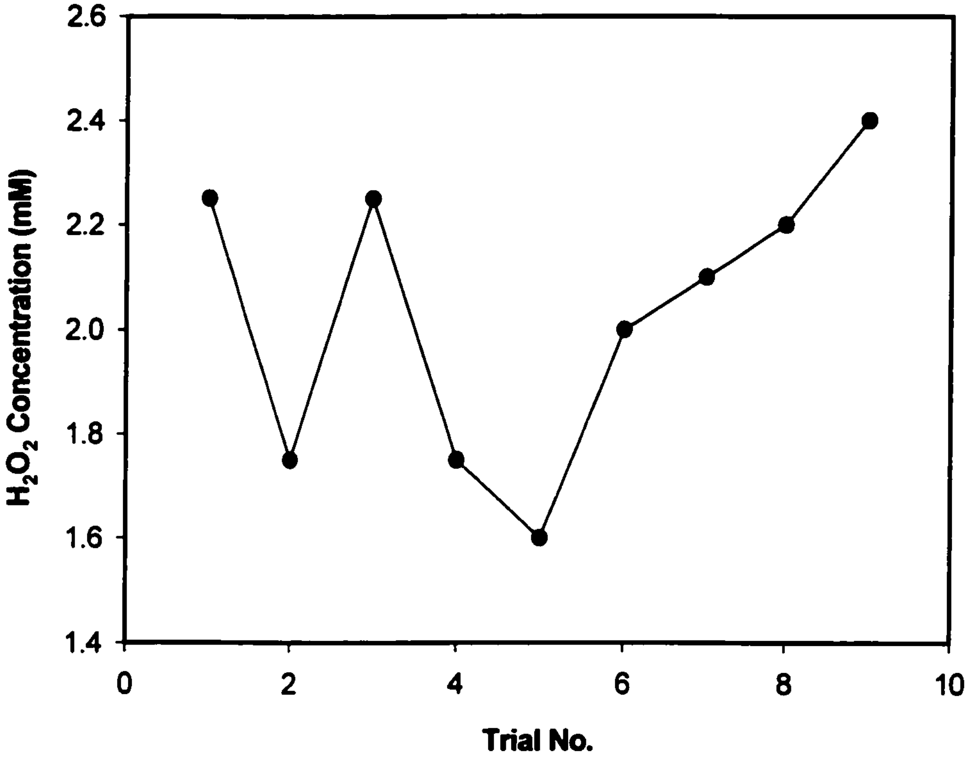
UV dose is considered as the total lamp electrical energy applied to a fixed volume of water. The units are usually measured in kWh/1000 US gallons. This parameter combines flow rate, residence time, and light intensity into a single term. The dose of light, peroxide, and/or proprietary catalysts required per unit volume of water treated varies from one type of contaminated stream to the other. However, UV dose can be calculated as follows (213):

$$\text{UV dose} = \frac{\text{lamp power (kW) x time (hrs) x 1000}}{\text{batch volume (gal.)}} \qquad (5.14)$$

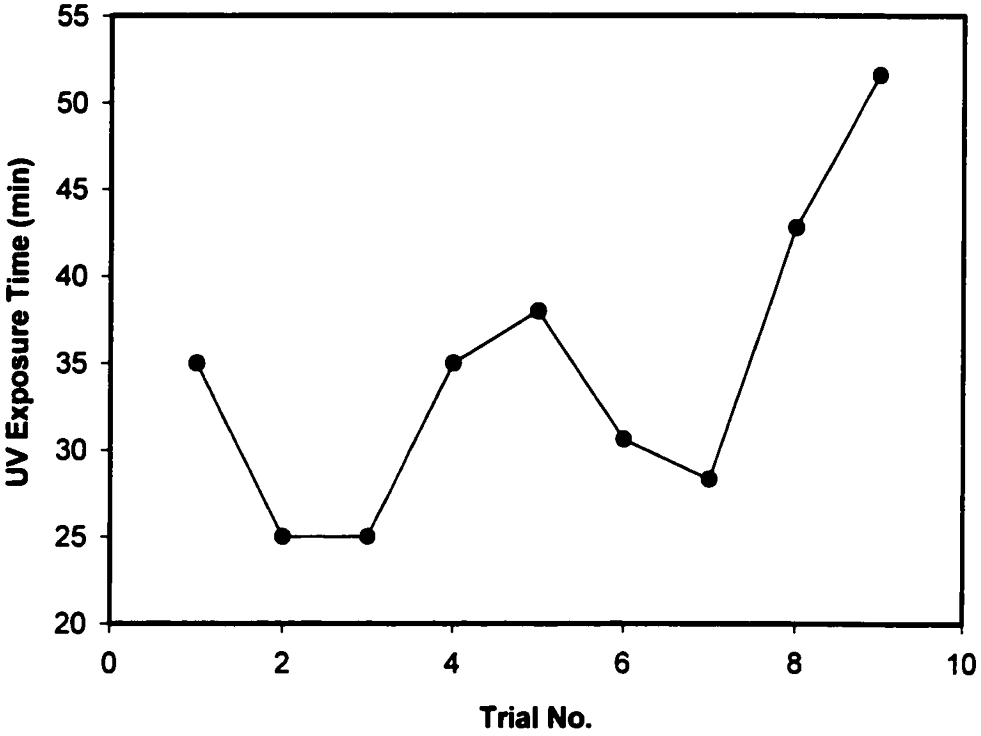
Design tests are performed to measure the UV dosage required to achieve the desired effluent concentration. The dosage to be applied to a particular stream is determined in an iterative manner by examining the effect of selected process variables such as pH, H_2O_2 level, and choice of catalyst. A plot of the contaminant concentration (on a log scale) as a function of UV dose represents a typical UV/H_2O_2 treatment curve resulting from a single test run. Although the reaction between the target compound and

TABLE 5.6: Results of the Optimization Process of UV/H_2O_2 System

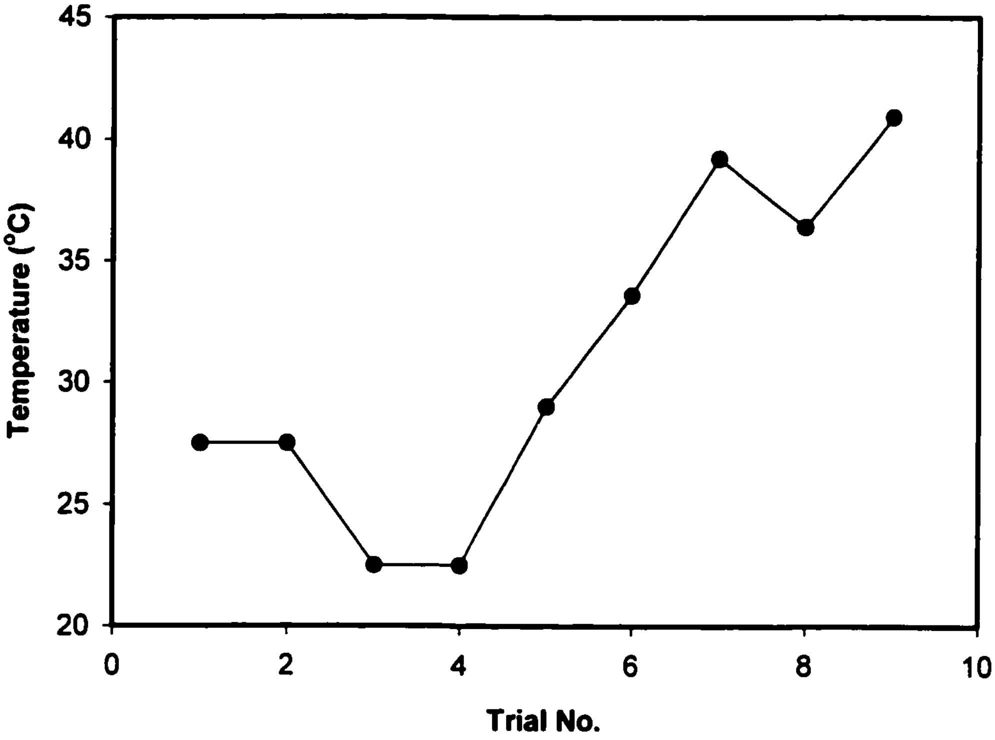
Trial No.	DMP_i (mM)	H_2O_2 (mM)	UV exposure Time (min)	Temp. (°C)	% DMP removal
1	0.1	2.25	35	27.5	96.06
2	0.1	1.75	25	27.5	88.05
3	0.1	2.25	25	22.5	68.63
4	0.1	1.75	35	22.5	86.21
5	0.1	1.6	38	29	94.31
6	**0.1**	**2**	**30.6**	**33.6**	**97.58**
7	0.1	2.1	28.3	39.2	99.41
8	0.1	2.2	42.8	36.4	99.59
9	0.1	2.4	51.6	40.9	100.00



Figures 5.32: H_2O_2 Concentration Vs Trial No.



Figures 5.33: UV Exposure Time Vs Trial No.



Figures 5.34 : Temperature Vs Trial No.

the OH^o radical is bimolecular, the latter is produced at a constant, steady state rate. Therefore, the contaminant concentration becomes the limiting reagent and hence pseudo-first-order reaction kinetics may apply.

In this study, the destruction curve of DMP in water by UV/H_2O_2 process is shown in Figure 5.37. The data was extracted from the original experiments. By measuring the inverse slope of this destruction curve, one has a very accurate and easily comparable measure of treatment performance. This measure is usually termed as the electrical energy per order (i.e. EE/O). The Electrical Energy per Order or EE/O is considered as a combination of the two key design variables, which include exposure to UV radiation and the number of orders of magnitude of contaminant concentration removed. The EE/O is a powerful scale-up parameter and is a measure of the treatment obtained in a fixed volume of water as a function of exposure to UV light.

The Electrical Energy per Order or EE/O is defined as the kilowatt hours of electricity required to reduce the concentration of a compound in 1000 gallons by one order of magnitude (or 90%). The steeper the slope, the smaller the EE/O value and the faster the treatment. In this study, using Figure 5.37, the EE/O value for the destruction of DMP by UV light is found to be about 16 according to the following best fitted formula:

$$\text{Log DMP} = -16.041 * \text{UV dose} + 26.289 \qquad (5.15)$$

$r^2 = 0.9733$

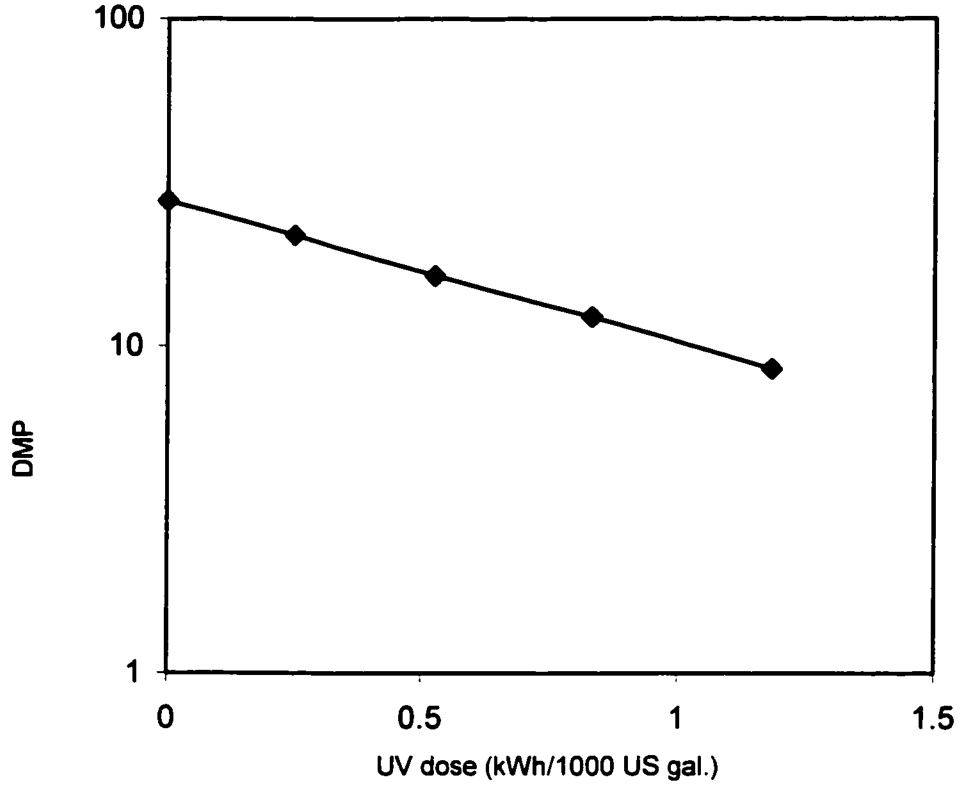


Figure 5.35: UV/H_2O_2 Removal Curve for DMP in water.

The linear relationship between UV dose and the log of contaminant concentration has important implications. First, a single number (EE/O) can completely describe the UV treatment characteristics of a contaminant. This makes the comparison of treatment performance as simple as comparing the EE/O values. Second, it takes the same amount of energy to treat the first 90% of the contaminant as it does to treat the subsequent 90% of the remaining contaminant. Thus, UV treatment is very efficient at reducing the mass loading of a contaminant and can be used as a very cost-effective pretreatment step. The EE/O measured in a design test is specific to the water tested and to the compound of interest, and it will vary for different applications. Typical EE/O for a range of organic contaminants are provided in Table 5.7 (213). Comparing the EE/O of 16 for the removal of DMP with other EE/Os listed in Table 5.7 shows that some organic compounds such as DCE, benzene, 1,4-Dioxane, TCE, toluene and xylene are removed better by UV than DMP. On the hand, compounds such as iron cynides, chloroform, DCA and atrazine have similar extent of removal by UV as DMP.

Once the EE/O for the contaminant is determined, the UV dose, which is defined as the amount of electrical energy required to treat 1000 gallons of water, can be calculated using the following equation:

$$\text{UV dose} = \text{EE/O} * \log (C_i/C_f) \tag{5.16}$$

Where:

C_i = the specified starting concentration (ppm)

C_f = the required discharge standard (ppm)

Table 5.7: Typical EE/O values for Contaminated Destruction

Compound	EE/O (kWh/1000 USgal./order)
1,4-Dioxane	2 - 6
Atrazine	10 - 30
Benzene	2 - 5
Chlorobenzene	5
Chloroform	15*
DCA	15*
DCE	2 – 5
Feron	10*
Iron Cynaide	10 – 40
NDMA	2 – 5
PCE	2 – 8
PCP	5 - 10
Phenol	5
TCE	2 – 4
Toluene	2 – 5
Xylene	2 – 5
TCA	15*
TNT	12
Vinyl Chloride	2 - 3

* Reduction catalyst required (Extracted from ref. 213)

In this study, assuming a starting concentration of 20 ppm of DMP (i.e. C_i) and that the required discharge standard is 1.0 ppm of DMP (i.e. C_f) and for a EE/O value of 16, the UV dose (kWh/1000 gal.) required is equal to:

UV dose = 16 x log (20/1) = 20.8 kWh/1000 gal.

This means that 20.8 kWh process unit is needed to treat 1000 gal of water contaminated with 0.1 mM of DMP. Based on this value of UV dose, one can estimate the initial capital cost of the treatment unit.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

1. The application of hydrogen peroxide oxidant (H_2O_2) alone was not sufficient to oxidize the DMP in water. A hydrogen peroxide concentration as high as 4.0 mM (i.e. 140 ppm), which represents a molar ratio of H_2O_2 to the initial DMP concentrations of 40:1, failed to decompose the target compound whether it existed in pure or methanol-spiked waters. This indicates that phthalates degradation requires a stronger oxidant such as (OH^o) radical.

2. Fenton process (i.e. Fe^{2+} + H_2O_2) was found to be effective in removing DMP from pure water, but it did not show any removal of DMP when the water was spiked with 80 mM methanol. The inefficiency of Fenton in the later case was attributed to the fact that most of the (OH^o) radicals formed via the Fenton process were depleted by the reaction with methanol rather than the target compound (i.e.

DMP). The higher molar concentration of methanol with respect to that of DMP (i.e. 800:1) is probably the main reason for the depletion of the (OH^o) radicals.

3. This study showed that the efficiency of Fenton process in removing DMP from pure water was affected by the initial concentrations of ferrous ions (Fe^{2+}). It was found that, at a certain level of H_2O_2, increasing the concentration of Fe^{2+} led to an increase in the removal of DMP. On the other hand, increasing the Fe^{2+} concentration did not improve the removal of DMP from methanol-spiked water by Fenton process.

4. The removal of DMP by Fenton process ssemed to follow a pseudo-first order reaction with a rate coefficient of 0.0989/min under the conditions used.

5. Increasing the initial concentration of hydrogen peroxide (H_2O_2), did not always led to an efficiency improvement of the Fenton process in removing DMP from pure water. Thus, the amount of H_2O_2 used in the Fenton process should be carefully selected for each case, since any excess amount might cause a drop in the efficiency of the process.

6. Both pH and temperature play a significant role in determining the efficiency of the Fenton process in removing DMP from pure water. A high temperature and a pH value of 3 to 4 were found to be best for achieving an efficient removal of

DMP. No major effect was observed for these two parameters when Fenton process was used to remove DMP from methanol-spiked water.

7. DMP could be partially degraded by direct photolysis (i.e. by UV light only). After irradiating with a 100 mWatt UV lamp for 60 minutes, 60% and 40% of DMP was approximately removed from pure and methanol-spiked water, respectively.

8. When the action of UV light is combined with action of Fenton's reagent (i.e. photo-Fenton), a more powerful oxidizing method was obtained. After 15 minutes of reaction time, only 30% of DMP was removed by Fenton system, while more than 95% removal was achieved by photo-Fenton method. This method was proven to be effective in removing DMP from pure as well as methanol-spiked water. However, in the later case, increasing the Fe^{2+} concentration caused a reduction in the removal efficiency of DMP due to blockage of the UV light passage by iron sludge. The cost of photo-Fenton process is expected to be too high compared to Fenton or UV/H_2O_2 processes.

9. The UV/H_2O_2 process was effective in removing DMP from both pure and methanol-spiked water. The addition of H_2O_2 in the UV/H_2O_2 process improved the removal of DMP.

10. The removal of DMP by UV/H_2O_2 process seem to follows a pseudo first-order reaction with a rate coefficient of 0.0611/min under the conditions used.

11. The solution pH effect on the efficiency of DMP removal by UV/H_2O_2 process was not significant as in the case of Fenton process, which can be an advantage of UV/H_2O_2 process over Fenton process. On the other hand, the temperature had a significant enhancement of the UV/H_2O_2 process efficiency of in DMP removal. The higher the temperature, the higher the removal efficiency of DMP by the UV/H_2O_2 process.

12. The initial concentration of the DMP had an effect on the performance of both Fenton and UV/H_2O_2 process. Lower removal rate of DMP was observed when the initial concentration of DMP (i.e. DMP_i) was increased. It was concluded that an optimum molar ratio between DMP_i, H_2O_2 and Fe^{2+} must be determined to obtain the best removal efficiency.

13. The efficiency of Fenton process dropped down drastically when DMP was spiked into local groundwater rather than pure water due to the existence of high inorganic salts such as sulfates and carbonates which inhibit the action of (OH^o) radicals. However, the efficiency of UV/H_2O_2 dropped only slightly under the same conditions, which can be considered as another advantage of UV/H_2O_2 system over Fenton system.

14. The 2^k factorial design conducted in this study showed that the effect of UV light was much higher than the effect of others factors.

15. Due to its many advantages, UV/H_2O_2 process was selected in this study to be the suitable oxidation process for the removal of DMP from water. The optimum conditions required to reach a considerable treatment efficiency of more than 97% of the 0.1 mM DMP at neutral pH value, determined by Multisimplex Software, were:

    H_2O_2 = 2.0 mM
    UV exposure time = 30.6 minutes
    Temperature = 33.6°C

6.2 Recommendations

1. The removal efficiency of phthalate esters, other than DMP compound, by Fenton and UV/H_2O_2 processes can be investigated.

2. The degradation mechanism of DMP can be studied to identify the intermediates formed during the oxidation process. It is anticipated that the degradation of DMP could take different pathways for different oxidation methods.

3. The effect of UV light on the performance of the UV/H_2O_2 process can be further investigated by changing the intensity as well as the wavelength of the UV light. This can be achieved by the using several UV lamps of different intensities irradiating at different wavelengths.

4. The inhibition effect of methanol and other inorganic compounds on the action of OH^o radicals can be further studied at different levels of these scavengers to determine the limits by which they can exist without sacrificing the efficiency of either the Fenton or the UV/H_2O_2 processes in removing DMP or other phthalate compounds.

Appendix A.1

Experiments Conducted on DMP in Water Only

TABLE A.1.1: Removal of DMP by H_2O_2 Only

	% DMP Residual At a Reaction Time (t)				
H_2O_2 (mM)	0 min	15 min	30 min	45 min	60 min
0.0	100.00	95.48	95.29	96.51	95.33
1.0	100.00	98.05	101.76	94.74	100.47
2.0	100.00	98.22	98.5100	103.72	99.54
4.0	100.00	99.79	100.16	100.18	100.07

DMP_i = 0.1 mM
Fe^{2+} = 0.0 mM
pH = 6
Temp. = 25°C

	% DMP Residual At a Reaction Time (t)				
Fe^{2+} (mM)	0 min	15 min	30 min	45 min	60 min
0.1	100.00	97.23	101.11	106.11	98.83
0.2	100.00	62.07	62.07	60.59	56.65
0.4	100.00	9.17	2.83	0.00	0.00

TABLE A.1.2: Removal of DMP by Fenton Process at Various Fe^{2+} Concentrations

DMP_i = 0.1 mM
H_2O_2 = 2.0 mM
pH = 3
Temp. = 25°C

TABLE A.1.3: Removal Rate of DMP by Fenton Process

Time (min)	DMP_i (ppm)	DMP_t (ppm)	DMP_t/DMP_i	Ln (DMP_t/DMP_i)
0.0000	20.0000	19.4500	0.9725	-0.0279
15.0000	20.0000	1.7700	0.0885	-2.4248
30.0000	20.0000	0.4800	0.0240	-3.7297
45.0000	20.0000	0.1600	0.008	-4.8283
60.0000	20.0000	0.1300	0.0065	-5.0360

Fe^{2+} = 0.2 mM
H_2O_2 = 1.0 mM
pH = 3
Temp. = 25°C

TABLE A.1.4: Removal of DMP by Fenton Process at Various H_2O_2 Concentrations

	% DMP Residual At a Reaction Time (t)				
H_2O_2 (mM)	0 min	15 min	30 min	45 min	60 min
0.5	100.00	99.96	87.13	78.70	80.19
1.0	100.00	69.18	53.46	34.59	20.13
2.0	100.00	62.07	62.07	60.59	56.65

DMP_i = 0.1 mM
Fe^{2+} = 0.2 mM
pH = 3
Temp. = 25°C

TABLE A.1.5: Removal of DMP by Fenton Process at Various H_2O_2 Application Modes

	% DMP Residual At a Reaction Time (t)				
H_2O_2 (mM)	0 min	15 min	30 min	45 min	60 min
1.0 AT ONCE	100.00	69.18	53.46	34.59	20.13
1.0 @ 5 intervals	100.00	101.70	73.30	73.30	77.84

DMP_i = 0.1 mM
Fe^{2+} = 0.2 mM
pH = 3
Temp. = 25°C

TABLE A.1.6: Removal of DMP by Fenton Process at Various pH Levels

pH	% DMP Residual Reaction Time (t)				
	0 min	15 min	30 min	45 min	60 min
3	100.00	69.18	53.46	34.59	20.13
5	100.00	89.90	82.32	66.67	58.08
7	100.00	98.18	103.70	96.34	96.95
9	100.00	100.58	102.65	97.81	98.74

DMP_i = 0.1 mM
Fe^{2+} = 0.2 mM
H_2O_2 = 1.0 mM
Temp. = 25°C

TABLE A.1.7: Removal of DMP by Fenton Process at Various Temperatures

Temp. (°C)	% DMP Residual At Reaction Time (t)				
	0 min	15 min	30 min	45 min	60 min
15	100.00	98.88	67.08	65.17	51.69
25	100.00	69.18	53.46	34.59	20.13
35	100.00	00.00	00.00	00.00	00.00

DMP_i = 0.1 mM
Fe^{2+} = 0.2 mM
H_2O_2 = 1.0 mM
pH = 3

TABLE A.1.8: Removal of DMP by Fenton Process at Various DMP_i

DMP_i (mM)	% DMP Residual At Reaction Time (t)				
	0 min	15 min	30 min	45 min	60 min
0.1	100.00	69.18	53.46	34.59	20.13
0.2	100.00	97.63	95.91	99.57	98.28

Fe^{2+} = 0.2 mM
H_2O_2 = 1.0 mM
pH = 3
Temp. = 25°C

TABLE A.1.9: Removal of DMP by Fenton Process at Various H_2O_2 / Fe^{2+}

H_2O_2 / Fe^{2+}	% DMP Residual At Reaction Time (t)				
	0 min	15 min	30 min	45 min	60 min
2.5	100.00	0.00	0.00	0.00	0.00
5.0	100.00	53.22	50.81	54.44	51.67
10.0	100.00	41.77	39.68	39.30	38.30

DMP_i = 0.2 mM
pH = 3
Temp. = 25°C

TABLE A.1.10: Removal of DMP by Fenton and Photo-Fenton Processes

	% DMP Residual At Reaction Time (t)				
DMP_i (ppm)	0 min	15 min	30 min	45 min	60 min
Fenton	100.00	69.18	53.46	34.59	20.13
Photo-Fenton	100.00	00.00	00.00	00.00	00.00

UV lamp intensity = 100 mW
DMP_i = 0.1 mM
Fe^{2+} = 0.2 mM
H_2O_2 = 1.0 mM
pH = 3
Temp. = 25°C

TABLE A.1.11: Characteristics of Local Groundwater

Analyte	Concentration (ppm)
Copper (Cu)	0.224
Iron (Fe)	0.23
Magnesium (Mg)	96.196
Manganese (Mn)	0.01
Calcium (Ca)	293.7
Potassium (K)	31.8
Sodium (Na)	1347.8
Silicon (Si)	7.318
Strontium (Sr)	8.13
Fluoride (F)	1.5
Chloride (Cl)	1498
Nitrite (NO_3)	6.6
Sulfate (SO_4)	752
Phosphate (PO_4)	126
Bicarbonate (HCO_3)	145
Total dissolved solids (TDS)	3640
pH	7.2

TABLE A.1.12: Removal of DMP From Pure and Groundwater by Fenton Process

Medium	% DMP Residual At Reaction Time (t)				
	0 min	15 min	30 min	45 min	60 min
Pure Water	100.00	69.18	53.46	34.59	20.13
Groundwater	100.00	105.38	101.08	109.10	108.71

DMP_i = 0.1 mM
Fe^{2+} = 0.2 mM
H_2O_2 = 1.0 mM
pH = 3
Temp. = 25°C

TABLE A.1.13: Removal of DMP by Direct Photolysis

	% DMP Residual At Reaction Time (t)				
	0 min	15 min	30 min	45 min	60 min
UV Only	100.00	78.57	59.18	44.39	30.70

UV lamp intensity = 100 mW

DMP_i = 0.1 mM

pH = 6

Temp. = 25°C

TABLE A.1.14: Photolysis Rate of DMP

Time (min)	DMP_i (ppm)	DMP_t (mM)	DMP_t/DMP_i	Ln (DMP_t/DMP_i)
0.0000	20.00	19.20	1.0	2.22E-16
15.0000	20.00	14.6688	0.764	-0.26919
30.0000	20.00	13.344	0.695	-0.36384
45.0000	20.00	10.176	0.530	-0.63488
60.0000	20.00	8.016	0.4175	-0.87347

pH = 3

Temp. = 25°C

TABLE A.1.15: Removal of DMP by UV/H_2O_2 Process at Various H_2O_2 Concentrations

	% DMP Residual At a Reaction Time (t)				
H_2O_2 (mM)	0 min	15 min	30 min	45 min	60 min
1.0	100.00	81.66	53.38	28.52	24.92
2.0	100.00	57.04	23.42	16.82	9.47
4.0	100.00	78.06	22.07	5.46	2.63

UV Lamp intensity = 100 mW
DMP_i = 0.1 mM
pH = 3
Temp. = 25°C

TABLE A.1.16: Removal of DMP by UV/H_2O_2 Process at Various UV Dosages

	% DMP Residual At a Reaction Time (t)				
UV Exposure Time (min)	0 min	15 min	30 min	45 min	60 min
0.0	100.00	98.22	98.51	103.71	99.54
30	100.00	61.34	21.41	21.71	21.11
60	100.00	57.04	23.42	16.82	9.47

UV Lamp intensity = 100 mW
DMP_i = 0.1 mM
pH = 6
Temp. = 25°C

TABLE A.1.17: Removal of DMP by UV/H_2O_2 Process at Various pH Levels

	% DMP Residual At a Reaction Time (t)				
pH Value	0 min	15 min	30 min	45 min	60 min
3	100.00	85.86	49.68	13.51	4.58
6	100.00	57.04	23.42	16.82	9.47
9	100.00	100.00	100.00	74.36	44.71

UV Lamp intensity = 100 mW
DMP_i = 0.1 mM
H_2O_2 = 2 mM
Temp. = 25°C

TABLE A.1.18: Removal of DMP by UV/H_2O_2 Process at Various Temperatures

Temp. (°C)	% DMP Residual At a Reaction Time (t)				
	0 min	15 min	30 min	45 min	60 min
15	100.00	100.00	100.00	74.05	44.03
25	100.00	57.04	23.42	16.82	9.47
35	100.00	41.29	2.72	0.00	0.00

UV Lamp intensity = 100 mW

DMP_i = 0.1 mM

H_2O_2 = 2 mM

pH = 6

TABLE A.1.19: Removal of DMP by UV/H_2O_2 Process at Various DMP_i

	% DMP Residual At Reaction Time (t)				
DMP_i (mM)	0 min	15 min	30 min	45 min	60 min
0.1	100.00	57.04	23.42	16.82	9.47
0.2	100.00	82.58	75.83	69.84	58.21

UV Lamp intensity = 100 mW

H_2O_2 = 2 mM

pH = 6

Temp. = 25°C

TABLE A.1.20: Removal of DMP From Pure and Groundwater by UV/H_2O_2 Process

Medium	% DMP Residual At Reaction Time (t)				
	0 min	15 min	30 min	45 min	60 min
Pure Water	100.00	81.66	53.38	28.52	24.92
Groundwater	100.00	95.97	82.26	51.21	30.24

UV lamp intensity = 100 mW
H_2O_2 = 1 mM
pH = 3
Temp. = 25°C

Appendix A.2

Experiments Conducted on DMP in Water & Methanol

TABLE A.2.1: Removal of DMP by H_2O_2 Only

	% DMP Residual At a Reaction Time (t)				
H_2O_2 (mM)	0 min	15 min	30 min	45 min	60 min
1.0	100.00	102.80	93.00	105.00	91.00
2.0	100.00	89.63	105.10	99.90	97.70
4.0	100.00	101.00	98.00	95.00	104.00

DMP_i = 0.1 mM
CH_3OH = 80 mM
pH = 6
Temp. = 25°C

TABLE A.2.2: Removal of DMP by Fenton Process at Various Fe^{2+} Concentrations

	% DMP Residual At a Reaction Time (t)				
Fe^{2+} (mM)	0 min	15 min	30 min	45 min	60 min
0.1	100.00	103.43	99.90	104.50	96.00
0.2	100.00	88.90	104.00	101.00	92.90
0.4	100.00	109.50	92.00	98.00	104.70

DMP_i = 0.1 mM
CH_3OH = 80 mM
H_2O_2 = 2.0 mM
pH = 3
Temp. = 25°C

TABLE A.2.3: Removal of DMP by Fenton Process at Various H_2O_2 Concentrations

	% DMP Residual At a Reaction Time (t)				
H_2O_2 (mM)	0 min	15 min	30 min	45 min	60 min
0.5	100.00	103.00	92.00	95.00	93.00
1.0	100.00	107.00	95.00	99.00	94.00
2.0	100.00	95.00	97.60	98.10	109.00

DMP_i = 0.1 mM
CH_3OH = 80 mM
Fe^{2+} = 0.2 mM
pH = 3
Temp. = 25°C

TABLE A.2.4: Removal of DMP by Photo-Fenton Process at Various Fe^{2+} Concentrations

Fe^{2+} (mM)	% DMP Residual At Reaction Time (t)				
	0 min	15 min	30 min	45 min	60 min
0.0	100.00	31.40	2.94	0.00	0.00
0.05	100.00	40.83	6.26	2.80	0.90
0.2	100.00	70.30	34.65	29.50	36.70

DMP_i = 0.1 mM
CH_3OH = 80 mM
Fe^{2+} = 0.2 mM
H_2O_2 = 1.0 mM
pH = 3

TABLE A.2.5· Removal of DMP by Direct Photolysis

	% DMP Residual At Reaction Time (t)				
	0 min	15 min	30 min	45 min	60 min
UV Only	100.00	76.60	69.00	65.00	61.00

UV lamp intensity = 100 mW

DMP_i = 0.1 mM

CH_3OH = 80 mM

pH = 6

Temp. = 25°C

TABLE A.2.6: Removal of DMP by UV/H_2O_2 Process at Various H_2O_2 Concentrations

	% DMP Residual At a Reaction Time (t)				
H_2O_2 (mM)	0 min	15 min	30 min	45 min	60 min
1.0	100.00	69.80	47.80	4.20	0.00
2.0	100.00	31.40	2.94	0.00	0.00

UV Lamp intensity = 100 mW
DMP_i = 0.1 mM
CH3OH = 80 mM
pH = 3
Temp. = 25°C

TABLE A.2.7: Removal of DMP by UV/H_2O_2 Process at Various UV Dosages

UV Exposure Time (min)	% DMP Residual At a Reaction Time (t)				
	0 min	15 min	30 min	45 min	60 min
15	100.00	40.30	19.00	18.00	18.00
30	100.00	43.90	23.86	13.77	13.77
60	100.00	49.00	12.00	8.00	1.00

UV Lamp intensity = 100 mW
DMP_i = 0.1 mM
CH_3OH = 80 mM
pH = 6
Temp. = 25°C

TABLE A.2.8: Removal of DMP by UV/H_2O_2 Process at Various pH Levels

	% DMP Residual At a Reaction Time (t)				
pH Value	0 min	15 min	30 min	45 min	60 min
3	100.00	23.60	2.30	0.00	0.00
6	100.00	31.40	2.94	0.00	0.00
9	100.00	64.36	18.90	8.00	0.00

UV Lamp intensity = 100 mW

DMP_i = 20 ppm

CH_3OH = 80 mM

H_2O_2 = 2 mM

Temp. = 25°C

TABLE A.2.9: Removal of DMP by UV/H_2O_2 Process at Various Temperatures

	% DMP Residual At a Reaction Time (t)				
Temperature (°C)	0 min	15 min	30 min	45 min	60 min
25	100.00	31.40	2.94	0.00	0.00
35	100.00	2.62	0.00	0.00	0.00

UV Lamp intensity = 100 mW
DMP_i = 20 ppm
CH_3OH = 80 mM
H_2O_2 = 2 mM
pH = 6

TABLE A.2.10: Removal of DMP by UV/H_2O_2 Process at Various DMP_i

DMP_i (ppm)	% DMP Residual At Reaction Time (t)				
	0 min	15 min	30 min	45 min	60 min
20	100.00	31.40	2.94	0.00	0.00
40	100.00	88.40	32.40	26.00	9.80

UV Lamp intensity = 100 mW
CH_3OH = 80 mM
H_2O_2 = 2 mM
pH = 6
Temp. = 25°C

Appendix A.3

Contrast Constants for 2^4 Factorial Design

TABLE A.3.1: Contrast Constants for $2^{\wedge 4}$ Factorial Design

	A	*B*	*AB*	*C*	*AC*	*BC*	*ABC*	*D*	*AD*	*BD*	*ABD*	*CD*	*ACD*	*BCD*	*ABCD*
(1)	−	−	+	−	+	+	−	−	+	+	−	+	−	−	+
a	+	−	−	−	−	+	+	−	−	+	+	+	+	−	−
b	−	+	−	−	+	−	+	−	+	−	+	+	−	+	−
ab	+	+	+	−	−	−	−	−	−	−	−	+	+	+	+
c	−	−	+	+	−	−	+	−	+	+	−	−	+	+	−
ac	+	−	−	+	+	−	−	−	−	+	+	−	−	+	+
bc	−	+	−	+	−	+	−	−	+	−	+	−	+	−	+
abc	+	+	+	+	+	+	+	−	−	−	−	−	−	−	−
d	−	−	+	−	+	+	−	+	−	−	+	−	+	+	−
ad	+	−	−	−	−	+	+	+	+	−	−	−	−	+	+
bd	−	+	−	−	+	−	+	+	−	+	−	−	+	−	+
abd	+	+	+	−	−	−	−	+	+	+	+	−	−	−	−
cd	−	−	+	+	−	−	+	+	−	−	+	+	−	−	+
acd	+	−	−	+	+	−	−	+	+	−	−	+	+	−	−
bcd	−	+	−	+	−	+	−	+	−	+	−	+	−	+	−
abcd	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

NOMENCLATURE

DMP	Dimethyl Phthalate
mg	milligrams (10^{-3} gm)
μg	micrograms (10^{-6} gm)
ng	nanograms (10^{-9} gm)
mL	milliliter (10^{-3} L)
ppm	parts per million
$[C]$	pollutant concentration (M)
$[OH^{o}]$	hydroxyl radical concentration (M)
$k_{OH}{}^{o}$	second-order rate constant for the reaction of OH^{o} with the pollutant
C_o	initial concentration of DMP
C_t	concentration of DMP at time t
k	the first-order rate constant
D	UV Dose, $mW.s/cm^2$
I	intensity, mW/cm^2
t	exposure time, s
m	rank of the matrix A
n	number of variables in matrix A.

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