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Magnesium-based Treatment for the Degradation of Octachlorodibenzofuran and Trinitrotoluene

Amal Mogharbel
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MAGNESIUM-BASED TREATMENT FOR THE DEGRADATION OF
OCTACHLORODIBENZOFURAN AND TRINITROTOLUENE

by

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A dissertation submitted in partial fulfillment of the requirements
for the degree of the Doctor of Philosophy
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ABSTRACT

The aim of the present research is to investigate the efficacy of using ball-milled zero-valent magnesium (ZVMg) with and without activated carbon (AC) for the dechlorination of polychlorinated dibenzofurans. Three different solvent systems are presented here which are ethanol, ethanol/ethyl lactate (90:10), and 2-butoxyethanol. These solvents in combination with ZVMg with and without activated carbon were tested towards the degradation of octachlorodibenzofuran (OCDF, the most highly chlorinated PCDF congener). All the tested systems were very powerful and reductively dechlorinated OCDF to less chlorinated congeners. However, the system of ball-milled ZVMg and ethanol was the only system which converted OCDF and all byproducts to dibenzofuran, the chlorine- free compound. Kinetic results for all the studied systems fit a pseudo-first-order decay model with respect to OCDF degradation. A detailed study of the formed byproducts during the dechlorination process and a proposed degradation pathway for OCDF are present in this research. The systems consisting of ZVMg and ZVMg/AC in acidified ethanol and acidified 2-butoxyethanol were examined towards the degradation of the low-chlorinated congener 2,8-dichlorodibenzofuran. This compound was degraded efficiently in all systems. The addition of activated carbon enhanced the degradation kinetics of 2,8-dichlorodibenzofuran degradation. Another study using ZVMg and ZVMg/AC in acidified ethanol was conducted to evaluate the efficiency of the system towards the remediation of the explosive contaminant trinitrotoluene (TNT). Both systems were effective in the degradation of TNT and the reactions were found to follow pseudo-first-order kinetics. A plausible degradation pathway is proposed in this study based on the identified degradation products.

To my parents,
Without your help my success would not have been possible. I love you!

To my siblings,
For always providing me a lending hand.
For always being close, even when we were all the way across the globe.
Thank you from the bottom of my heart.

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LIST OF ACRONYMS/ABBREVIATIONS

AC	Activated carbon
DLCs	Dioxin-like compounds
DFT	Density functional theory
EL	Ethyl lactate
EtOH	Ethanol
GC	Gas chromatogram
HTTS	Hybrid Thermal Treatment System
IARC	International agency for research on cancer
MS	Mass spectrometry
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzo- <i>p</i> -dioxin
PCDF	Polychlorinated dibenzofuran
PCM	Polarizable Continuum Model
POP	Persistent organic pollutant
SEM	Scanning electron microscopy
TAT	2,4,6-Triaminotoluene
TEF	Toxicity equivalent factor
TNT	2,4,6-Trinitrotoluene
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
ZVI	Zero-valent iron

ZVM	Zero-valent metal
ZVMg	Zero-valent magnesium
ZVZ	Zero-valent zinc

CHAPTER ONE: GENERAL INTRODUCTION

Overview of Polychlorinated Dibenzofurans

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and the ‘dioxin-like’ poly chlorinated biphenyls (PCBs) are a group of persistent organic pollutants (POPs) called dioxins¹. Dioxins are polyhalogenated aromatic hydrocarbons and they are related in both structure and chemical properties. The focus of this dissertation is the family of polychlorinated dibenzofurans, which have been less thoroughly studied than other dioxins due to their high price and/or the unavailability of the individual congeners. PCDFs can have up to eight chlorine atoms attached to the carbon backbone which, based on number and placement, result in the formation of 135 individual congeners. The general molecular structure of PCDFs with the traditional numbering of the chlorine atoms is represented in Figure 1. The replacement of even a single hydrogen with chlorine makes the resultant PCDF more toxic than its parent compound. Even though PCDFs have never been produced intentionally, they exist in the environment. PCDFs are released to the environment through natural processes and as a result of high-temperatures associated with industrial activities. Mainly, the source of PCDFs in the modern society is the burning of wastes from various households, and from metallurgical industries such as those that produce steel². The reduction of PCDF emissions in the past decade has been of help in the reduction of human exposure, however, recent activities carried out by industries, which led to the increase of PCDFs in the environment, are the reason behind the presence of PCDFs in all compartments of the ecosystem. The presence of PCDFs in the environment also leads to the contamination of the food chain to some levels. Therefore, certain foods intended for human

consumption, such as milk, fish, and meat, can be sources of PCDFs². The existence of PCDFs in the environment means that most people interact with these toxic compounds in their everyday activities, which is a cause for alarm considering its health impacts.

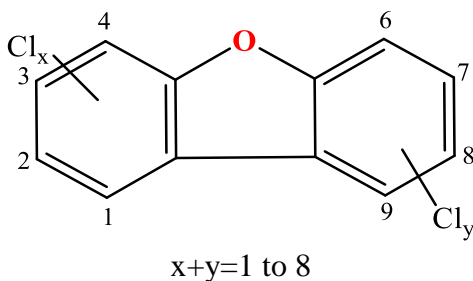


Figure 1: General molecular structure for polychlorinated dibenzofurans.

Environmental and Health Effects

The World Health Organization (WHO) notes that small exposure to dioxins such as PCDFs can lead to skin lesions that may include irregular darkening of the skin and chloracne. Further, short-term exposure to PCDFs can also lead to altered liver functions, causing significant discomfort to an individual³. In regard to long-term exposure to PCDFs, the WHO underlines that one of the major resultant health effects is the impairment of the immune system, making individuals more prone to opportunistic diseases. Another long-term health effect of exposure to PCDFs is that it may lead to impairment of the nervous system, which can cause nervous system breakdown and the development of issues related to nervous system effects such as full-body or partial paralysis. This is especially dangerous for children whose nervous system is still in the developing stage³. WHO has also noted that, in humans, long-term exposure to PCDFs can be the cause of severe issues in the reproductive and endocrine systems.

According to previous research, constant exposure to dioxins can lead to the development of cancer. Between 1997 and 2012, WHO's International Agency for Research on Cancer (IARC) conducted a study on the effect of dioxins on the health of individuals, and on the basis of both animal data and data on human epidemiology, IARC classified some dioxins as 'known carcinogens'³. However, there is no result suggesting that dioxins can alter human genetics and interfere with the genetic makeup of an individual. Therefore, considering that elements classified as carcinogens are products that are seriously harmful to the health of people, it is clear that dioxins such as PCDFs are detrimental to human health.

The WHO also noted that the ubiquitous nature of dioxins means that every individual faces a certain minimum background exposure to these toxins, which contributes towards overall body burden³. However, it is noteworthy that the currently known average levels of regular background exposure do not have any known effect on the health of humans. Because of this lack of conclusive data, there is an even greater need for reducing the current background exposure considering the high toxicity potential of dioxins.

Toxicity of PCDFs

When PCDFs were first being evaluated, risk assessments were focused only on 2,3,7,8-Cl₄DD which was considered the most toxic congener. Soon, it was recognized that all PCDF and PCDD congeners with chlorine substituents in positions 2,3,7, and 8 of the aromatic rings are highly toxic. These congeners contribute to the overall toxicity of PCDF/PCDD mixtures as they tend to persist in the environment and accumulate in food-chains. Therefore, Toxicity Equivalency Factors (TEFs) have been established for risk assessment of complex mixtures of PCDF/PCDD

for regulatory purposes. The TEFs were developed based on acute toxicity values obtained from *in vivo* and *in vitro* studies. The TEF approach has been implemented by many agencies as an administrative tool in order to convert quantitative analytical data for individual congeners of PCDF and PCDD into a single Toxic Equivalent. The most commonly used TEFs today are the International Toxicity Equivalency Factors (I-TEFs) established by a NATO/CCMS Working Group on Dioxins and Related Compounds, and WHO-TEFs. Since the focus of this study is the family of PCDFs, Table 1 summarizes the I-TEFs and WHO-TEFs that have been established for the 2,3,7,8-substituted members. However, no TEFs have been assigned for all congeners which do not contain 2,3,7,8-substituents⁴.

Table 1: I-TEFs and WHO-TEFs for 2,3,7,8-substituted PCDF congeners.

Congener	I-TEF	WHO-TEF
2,3,7,8-Cl ₄ DF	0.1	0.1
1,2,3,7,8-Cl ₅ DF	0.05	0.05
2,3,4,7,8-Cl ₅ DF	0.5	0.5
1,2,3,4,7,8-Cl ₆ DF	0.1	0.1
1,2,3,7,8,9-Cl ₆ DF	0.1	0.1
1,2,3,6,7,8-Cl ₆ DF	0.1	0.1
2,3,4,6,7,8-Cl ₆ DF	0.1	0.1
1,2,3,4,6,7,8-Cl ₇ DF	0.01	0.01
1,2,3,4,7,8,9-Cl ₇ DF	0.01	0.01
1,2,3,4,6,7,8,9- Cl ₈ DF	0.001	0.0001

Regulatory History

The recognition of the toxic effects of dioxins made many countries, including the US, implement specific regulations that would control exposure to such toxic substances. The primary focus of these rules, since their inception, has been the reduction of the release of dioxin-like compounds such as PCDFs into the environment, mainly through controlling stack emissions from waste combustors. The efforts outlined by the regulations have been helpful in yielding positive results since the '70s⁵. There are also regulations in place that focus on the reduction of uptake by food consumption rather than source, which further limits the total body burden experienced by humans. Recent research found that food was a primary route for human exposure to PCDFs, and for that reason there have been new regulations developed with the purpose of reducing PCDF contamination of food. In the US, the complex regulation responsibilities fall across various federal and state agencies and departments that handle such problems as the environment, agriculture, food safety, and public health.

In regards to environmental regulations of dioxin-like compounds (DLCs) such as PCDFs, the related laws in the US cover significant areas, including air and water emissions. EPA has the power of creating statutes governing the release and interactions of DLCs with the environment as per the various environmental Acts established in the country. Some of the laws that help EPA in minimizing DLCs in the environment include the Safe Drinking Water Act, the Clean Water Act, and the Clean Air Act. The Safe Drinking Water Act regulates the emissions of DLCs into the water, with the legally enforceable limit being $3 \times 10^{-8} \text{ mg/L}^5$. The Act also has a maximum contamination goal of zero. However, this is not enforceable as law considering the difficulties that can occur in regards to achieving the goal.

Apart from the federal regulations discussed, some states have established additional guidelines and rules that govern the release of DLCs to the environment. The states of Wisconsin, Missouri, and California are examples of jurisdictions that have taken a step further in response to DLCs and to minimize their effects in the environment⁵. Many of the laws established by the states concerning DLCs are up to date, with some not coming into force for several more years. Since waste combustors have been the primary source of DLCs such as PCDFs, they have been the primary focus of many laws established by the states, with the particular goal being to minimize the emissions made by such incinerators⁵.

Past and Current Remediation Options for PCDFs

There are several technologies available for the remediation of PCDF contamination. Some focus on cleaning up PCDFs from contaminated soil and ash. These methods may utilize extraction of contaminated materials followed by specific treatment, while others use decomposition reactions of the contaminants at the point of contamination. These remediation options are generally grouped into three categories: biological, chemical, and thermal procedures.

Biological Remediation

Biological remediation, or bioremediation, utilizes microorganisms such as fungi and bacteria for decomposition of the contaminants. The process works by allowing the microorganisms to grow in the areas contaminated by the toxins while utilizing the pollutants as a food source. For many years, bioremediation through the use of microorganisms has been successful in the remediation of sludge, soils, and groundwater that have contaminants such as PCDFs. However, some microorganisms are still in the experimental stage concerning their ability to perform the task of remediation. Bioremediation technologies can include a further categorization as one of two processes such as bioaugmentation and biostimulation⁶. In biostimulation processes, the primary activity involves the stimulation of the growth and metabolic activity of microorganisms that aim at degrading and transforming the contaminants. Bioaugmentation, on the other hand, entails the process of introducing alien microorganisms into the soil present at the site, or in bioreactors, with the aim of achieving decomposition. Concerning fungal remediation, white-rot fungi are among those popularly used, as they help in the decomposition of lignin.

The advantages of bioremediation include the fact that it is a relatively low-costs process under favorable conditions, does not produce any waste, and can be applied both *in-situ* and *ex-situ*⁶. The limitations, on the other hand, are that it is only able to degrade a limited number of contaminants, has a lot of factors to be controlled, has a longer degradation time, and it is difficult to monitor the degradation process.

Chemical Remediation

Chemical remediation, or rather a physical remediation, involves the extraction of the contaminated soil and ash, followed by chemical reaction with the PCDFs. While some utilize the separation mechanism as the primary remediation method, others engage in the direct decomposition of PCDFs and other dioxin-like compounds via chemical reactions that might include supercritical water oxidation and decomposition by base catalysts⁶. Supercritical water oxidation involves the application of oxidizers in supercritical water with the aim of oxidizing the organic compounds. The type of oxidizers used in the procedure include gases such as hydrogen peroxide and pure oxygen typically, with hydrogen peroxide being responsible for ensuring maximum decomposition⁶. On the other hand, base-catalyzed decompositions also involve the decomposition and degradation of PCDFs in the soils. The presence of oxygen donors promotes the reactions and enhances the decomposition.

The advantages of chemical remediation include the fact that it produces a relatively low amount of harmful waste and leads to more than 99% contaminant reduction⁶. The disadvantages include that it has relatively higher costs, has limitations in contaminants removed, has problems in scaling up, and the fact that the equipment is prone to corrosion.

Thermal Remediation

Thermal remediation, as its name suggests, uses heat for the enhancement of vaporization of the contaminating elements and their decomposition. Thermal blanket and microwave energy technology, which are two standard techniques under thermal remediation, use vaporization of the PCDFs to get rid of the contaminants. At relatively high temperature, PCDFs decompose to a more acceptable form. Hybrid Thermal Treatment Systems (HTTS) are thermal remediation methods used for treating waste. A thermal blanket system is another type of thermal remediation, which is useful in controlling the top surface of soil contaminated by PCDFs and other dioxin-like compounds⁷. The technique involves heating the soil at temperatures ranging from 815 to 925 degrees Celsius. However, the rate of decomposition depends on the depth of the soil and the temperature that penetrates the soil.

Application of microwave energy is a third thermal remediation technique. However, its use is not as frequent as the other two methods highlighted. The principle of the technique works by emitting microwave energy at a wavelength ranging between 100MHz and 300GHz, which further penetrates the soils and functions by evaporating the water in the soil and along with the contaminants present⁷. Another type of thermal remediation is melting treatment, which is another efficient method for the degeneration of PCDFs, especially from municipal waste combustors. The furnaces are equipped with control systems that minimize further formation of PCDFs in the post-combustion zone.

The advantages of thermal remediation include the fact that it has a larger capacity of feed, has high waste removal efficiency, and is available for portable *in situ* processes⁷. Some of the

potential issues associated with this treatment are that it leads to a larger volume of waste gas to be treated, requires pre-treatment of feed, and involves the treatment of light heavy metals.

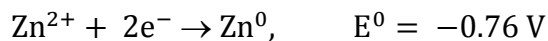
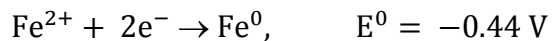
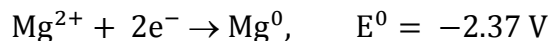
Zero Valent Metals for Reductive Dechlorination

The use of zero-valent metals (ZVM) such as zero valent iron (ZVI), zero valent zinc (ZVZ), and zero valent magnesium (ZVMg) has been found to be an effective remediation technology for the degradation of aromatic halogenated compounds via reductive dechlorination. This method has been studied extensively over the past decades. Little attention has been paid to the use of ZVZ for the reductive dechlorination of organic contaminants since toxic Zn species can be formed and released from the zinc particles during the reaction, which raises a great environmental concern⁸. Further, when ZVZ was used for the degradation of OCDD under basic and neutral conditions, OCDD was dechlorinated to hexa- and penta-chlorodibenzodioxin and no further degradation was observed⁷. In the case of using ZVI, anaerobic conditions are required to prevent the metal corrosion. This corrosion occurs due to the formation of insoluble oxide layers on the metal surface, reducing the metal activity and affecting the reaction rate, thus limiting the capabilities of ZVI for reductive dechlorination. Since reaction kinetics of ZVI are very slow under ambient conditions, high temperature, high pressure, or an inert atmosphere are required to get the best results⁹. Several studies have shown that organic contaminants such as OCDD, PCBs, and chlorophenols can be degraded to less chlorinated compounds in the presence of ZVI at elevated temperatures. To overcome this limitation, catalysts such as silver, copper, platinum, and palladium can be added to form a bimetal. By using bimetallic systems, better performance for the degradation of aromatic compounds was achieved. However, concerns have been raised when using bimetallic systems because of possible formation of toxic byproducts and the high cost of

treatment. A study done on the degradation of octachlorodibenzodioxin using Mg/Pd has resulted in 69% removal after 30 minutes. The solvent used in the study was 10% methanol/water; however, the degradation byproducts were not observed in the study¹⁰. This is of great concern since more toxic products could be formed. The unidentified byproducts as well as the high cost associated with the use of Pd are the major limitations of this treatment. Therefore, there is still a huge need to develop an efficient and cost-effective technology for PCDF degradation. One area that has gained great attention and showed satisfactory results in the degradation of a variety of POPs is the use of ZVMg and acidified ethanol for reductive dehalogenation. This method was developed and optimized by *Maloney, et al.*, at the Industrial and Environmental Laboratory at University of Central Florida (UCF)¹¹.

Zero-valent magnesium

Among the ZVM used for the reductive dehalogenation of OCs, ZVMg has been shown to be a very powerful and effective reductant even at ambient conditions. Magnesium particles are known to be resistant to aerobic conditions and have a longer life time due to the formation of a self-limiting oxide layer on the Mg surface upon exposure to oxygen. Moreover, magnesium has a high negative reductive potential compared to other zero valent metals, such as iron and zinc, according to the following equations¹².



A new treatment system consisting of ZVMg and acidified ethanol has been developed by researchers at the Industrial and Environmental Laboratory at UCF for the hydrodehalogenation of a variety of halogenated POPs. For instance, successful degradation of multiple PCB congeners was achieved using this remediation technology.

Overview of 2,4,6-Trinitrotoluene

Nitroaromatics are a class of toxic compounds that pose great environmental concerns¹³. One nitroaromatic which is of particular concern is the explosive compound 2,4,6-trinitrotoluene, which was developed in the 1900s¹⁴. The molecular structure of TNT is presented in Figure 2. TNT is a yellow, odorless, nitroaromatic compound that does not form naturally in the environment. TNT is stable both chemically and thermally¹⁴. It is widely used for military applications and for mining and industrial applications¹⁵. The low water solubility of TNT (30 mg/L)¹⁶ causes TNT particles to be dissolved slowly and release into the environment continuously over time. TNT contaminants have been found in the marine ecosphere, surface water, ground water, as well as in sediments and soils¹⁶. Furthermore, it has been found that TNT is toxic to humans, animals, aquatic flora, and other organisms. Its toxicity was observed even at low concentrations¹⁷. TNT is also classified as a poisonous, carcinogenic, and mutagenic compound¹⁸. The primary route of human exposure to TNT occurs through ingestion of contaminated food or drinking contaminated water¹⁹. Exposure to TNT can lead to serious health problems, such as aplastic anemia, abnormal liver functions and liver cancer, toxic hepatitis, skin irritation, skin and hair discoloration, and cataracts^{18, 20, 21}. In September 2001, the US EPA declared TNT a pollutant whose removal is a priority²². TNT was also listed by the US EPA in 2004 as a pollutant of great concern²³. The US EPA declared that the concentration of TNT should not exceed 17.2 g/kg of soil or 0.01 mg/L of water²⁴. However, TNT concentrations have reached 200 g/kg of soil and 100 ppm of water at certain ammunition production and processing locations^{17, 25}. TNT migrates through surface water and subsurface soil to ground water²⁶. TNT in surface water can be broken down by sunlight into other compounds, including 1,3,5-trinitrobenzene²³. In sediments and

groundwater, TNT is broken down by microorganisms very slowly. The symmetric position of the nitro groups on TNT makes the molecule more recalcitrant than either dinitrotoluene or mononitrotoluene. Moreover, this arrangement of the nitro groups makes it less susceptible to attack by dioxygenase enzymes involved in the microbial metabolism of aromatic compounds²².

Various remediation technologies have been developed for the removal of nitro aromatic compounds from the environment. Traditional methods such as landfilling, incineration, and thermal desorption have been used for TNT remediation. However, these processes are expensive and they may result in the emission of waste gas or new toxic byproducts^{17, 19, 27}. Bioremediation technologies including microbial remediation and phytoremediation utilize cost-effective and environmentally-friendly processes for TNT remediation²⁸. TNT can undergo mineralization microbial mineralization, however, this process is very limited due to the resistance of TNT towards oxidation. Thus, restricted conditions should be provided to enhance the microbial reduction of TNT. Furthermore, the transformation of TNT by gram-positive bacteria is not effective and is inhibited at low TNT concentrations (approximately 10 ppm)²⁹.

Other remediation technologies that have been used in recent years for TNT remediation include photocatalysis, oxidation processes, alkaline hydrolysis, and complexed and zero-valent iron (ZVI) treatment^{24, 30}. Even though these technologies have the potential to reduce the toxicity of TNT contamination, the reaction conditions required for these processes make them less useful for *in situ* remediations of explosives contamination. ZVI has been extensively applied for the reduction of a variety of organic pollutants, including TNT. Unfortunately, ZVI treatment is limited to anaerobic conditions to prevent metal corrosion that forms upon exposure to air. To enhance the reactivity of ZVI, controlled atmospheric conditions such as high temperature, high

pressure, or an inert atmosphere are required³¹. ZVMg is a powerful ZVM that can be used as an alternative reductive metal to ZVI. The formation of a self-limiting layer on the surface of ZVMg upon exposure to air (in contrast to ZVI) is a great advantage. This enables ZVMg to work even under ambient conditions. This advantage, as well as the higher reduction potential of ZVMg compared to ZVI (-2.37 V vs -0.44 V)³², leads researchers to explore ZVMg as an effective and low-cost process for contaminant remediation. This remediation technology combines the use of ball-milled ZVMg with acidified solvents such as ethanol to reductively degrade a variety of persistent organic pollutants^{11, 32, 33}. Since this system shows great results on the reductive dehalogenation of chlorinated compounds, it seems to be a promising process for the remediation of nitroaromatic compounds.

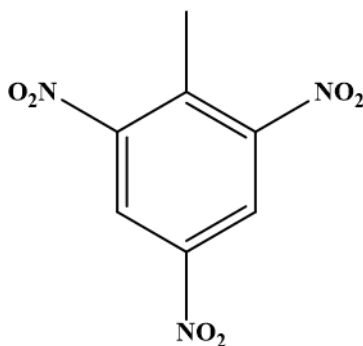


Figure 2: Molecular structure of 2,4,6-trinitrotoluene.

Research Objectives

The use of zero-valent magnesium (ZVMg) with ethanol as a solvent and a proton donor has shown numerous advantages in the dechlorination process of many polychlorinated aromatic compounds. Furthermore, the ball-milling procedure has enhanced the degradation kinetics and the efficiency of the treatment especially, when activated carbon was ball-milled with ZVMg. The overall objective of this research is to evaluate the efficiency of ball-milled ZVMg with and without activated carbon, on the dechlorination of selected polychlorinated dibenzofuran (PCDF) congeners under different solvents. Octachlorodibenzofuran (OCDF), the fully chlorinated congener, was selected as a model compound for high chlorinated congeners and 2,8-dichlorodibenzofuran was selected as a model for low chlorinated congeners.

In chapter two, two systems of ball-milled ZVMg and ZVMg/AC in acidified ethanol are studied. The primary goal of this chapter is to examine the efficiency of the systems to reductively dechlorinate the fully-chlorinated congener OCDF and the low-chlorinated congener 2,8-dichlorodibenzofuran. Complete kinetic studies for the two congeners were conducted. Furthermore, the stability of dibenzofuran, the chlorine-free congener, in these two systems was investigated.

A dual system of ethanol/ethyl lactate (90:10) was the second solvent system used in this research. Studying the efficiency of this solvent on the degradation of OCDF over ball-milled ZVMg in the presence and absence of activated carbon is the main objective of the third chapter. Minor goals include investigating the effect of the addition of ethyl lactate on the degradation kinetics and studying the change in pH of ethanol and ethanol/ethyl lactate (90:10) solvent systems.

In chapter four, a new benign and green solvent, 2-butoxyethanol, was introduced to the systems of ball-milled ZVMg and ZVMg/AC in an effort to enhance the degradation process of OCDF. The objectives of this chapter include investigation of the influence of the new solvent on the degradation kinetics of OCDF and 2,8-dichlorodibenzofuran. Additional goals in this chapter involve the identification of the degradation products and proposing degradation pathways for the selected congeners.

Due to the effectiveness of ball-milled ZVMg with and without activated carbon, on the degradation of the selected PCDF congeners, this approach was used to investigate the efficiency of the systems towards the degradation of the explosive nitroaromatic compound 2,4,6-trinitrotoluene. In this study ethanol was used as a solvent and proton donor for the reductive degradation of TNT. This chapter includes kinetic studies for TNT degradation and proposes a pathway based on the identified byproducts.

CHAPTER TWO: REDUCTION DECHLORINATION OF OCTACHLORODIBENZOFURAN USING ZVMG AND ZVMG/AC IN ACIDIFIED ETHANOL

Introduction

Polychlorinated dibenzofurans (PCDFs) are a class of toxic organic compounds comprising 135 individual congeners¹. PCDFs are produced unintentionally as byproducts from different routes including incineration, industrial activities and combustion processes. Even though regulations have been implemented since 1970 in order to control or reduce the emission of PCDFs, industrial activities have led to the increased presence of PCDFs in the environment¹. Consequently, PCDFs have been detected in all compartments of the ecosystem. PCDF exposure can cause many health problems including endocrine system damage, skin pathology (e.g. chloracne), elevated blood lipids, heart attacks, and immune deficiency^{34, 35}.

Due to the persistence, toxicity, and bioaccumulative properties of PCDFs, it is important to develop an efficient, inexpensive, and environmentally friendly method for PCDF degradation. Given the widespread nature of PCDF contamination and the many forms of material contaminated, several remediation techniques are currently used for PCDF treatment such as incineration, bioremediation, and photo remediation. *Chen, et. al.* have studied the bioremediation of highly-chlorinated-dibenzofuran and dibenzodioxin contaminated soil. Their results have demonstrated that 99.9% of octachlorodibenzofuran (OCDF) and 95.8-99.7% of heptachlorodibenzofuran (HpCDF) were reduced to lower chlorinated congeners after 6 weeks. This reduction in OCDF and HpCDF concentrations was accompanied by the formation of hexachlorodibenzofuran (HxCDF) and pentachlorodibenzofuran (PCDF), which increased the

toxicity of the soil³⁶. Many other studies have been conducted on the dechlorination of OCDF via photolysis. For instance, a study done by *Wagenaar, et. al.* on the photodegradation of OCDF using different solvents has resulted in 35 to 50% loss of OCDF via reductive photodechlorination. In this study, HxCDF, PCDF, and tetrachlorodibenzofuran (TCDF) were observed after 136 min irradiation of the system containing methanol as a solvent. In the same study, they have found that OCDF photolysis in methanol solvent system was about 5 and 1.5 times more efficient compared with the other two solvent systems used in the same study (hexane and 1,4-dioxane, respectively)³⁷.

Because of the limitations associated with the available treatment technologies such as the low removal efficiencies, low reaction rates, formation of undesirable byproducts, and high costs, there is a huge need to develop an efficient, environmentally friendly and cost-effective method for PCDF remediation. One of the most effective remediation techniques for chlorinated compounds is the use of zero-valent metals (ZVM) such as zinc, iron, and magnesium^{8, 9, 38}. This method has been successfully used for *in situ* remediation of a variety of chlorinated aromatic hydrocarbons such as PCBs. Even though studies have revealed that high removal efficiencies of organic contaminants were obtained using zero-valent zinc (ZVZ), limited work has been done using ZVZ due to the possible discharge of toxic Zn species to the environment⁹. The use of zero-valent iron (ZVI) is also unfavorable since it is restricted to anaerobic conditions to prevent the formation of passivating oxide layers on the iron surface upon exposure to air⁸. Indeed, zero-valent magnesium (ZVMg) has been shown to be a very powerful and effective reductant even at ambient conditions^{11, 33}. Magnesium particles are known to be resistant to aerobic conditions and have longer life time due to the formation of a self-limiting oxide layer on the Mg surface upon exposure to oxygen. Moreover, magnesium has a high negative reductive potential compared to other ZVM

such as iron and zinc (-2.37 V vs. -0.44 V and -0.76 V, respectively)³². Previous studies done by researchers in the Industrial and Environmental Laboratory at the University of Central Florida (UCF) have demonstrated that a system of ZVMg and acidified ethanol is capable to reductively dechlorinate a variety of organic contaminants at ambient conditions. This system has been successfully used for the degradation of Arochlors and different congeners of PCBs including PCB 151, PCB 153, PCB 28, and PCB 26^{12, 32, 39}.

Since the combination of ZVMg and ethanol as a solvent has been proven to be an effective treatment for organic contaminants such as PCBs, the present study was designed to further investigate the efficacy of the system for the dechlorination of polychlorinated dibenzofurans. For this study, OCDF, the fully chlorinated congener, was selected as a model compound of a high chlorinated congener and dichlorodibenzofuran (diCDF) was selected as a model low chlorinated congener.

Experimental Procedure

Chemicals and Materials

Neat octachlorodibenzofuran, 2,8-dichlorodibenzofuran, and dibenzofuran standards were purchased from Accustandard. 1,2,3,4,6,7,8-Heptachlorodibenzofuran, 2,3,4,7,8-pentachlorodibenzofuran, and 2,3,4,8-tetrachlorodibenzofuran standard solutions were also obtained from Accustandard. Absolute ethanol (USP grade) was obtained from Pharmco-AAPER. Toluene (Optima[®], 99.95%) was acquired from Fisher Scientific (Pittsburg, PA). Glacial acetic acid ($\geq 99.8\%$ purity) was obtained from Acros Organics, (Morris Plains, NJ). Micro-scale magnesium ($\sim 4 \mu\text{m}$) was acquired from Heart Metals (Tamaqua, PA). Activated carbon (charcoal

G-60) was obtained from Matheson Coleman & Bell (Gardena, CA). All chemicals were of high purity ($\geq 99\%$), ACS reagent, and analytical grade. Chemicals were used as received, unless otherwise specified. Helium gas for the gas chromatography-mass spectrometry analysis was purchased from Air Liquide (Orlando, FL).

For ball-milled ZVMg and ZVMg/AC loading measurements, a precision microscale analytical balance model AE 260-S (Mettler-Toledo AG, Greifensee, Switzerland) was used. Calibrated Eppendorf Research® pipettes (Eppendorf, Hamburg, Germany) were used to dispense the solutions. The filters used (0.45 μm pore size Nylon filters) were obtained from Fisher Scientific (Pittsburg, PA).

Ball-Milling Procedure for ZVMg and ZVMg/AC

The ball-milling process used in this study was based on a mechanical ball-milling procedure that was developed at the University of Central Florida. The aim of this process is to regenerate the metal surface in order to increase the activity of the metal. This process helps in cracking the passivating hydroxide/oxide layer on the magnesium surface which in turn creates more surface defects and changes the microstructure.

In this process, a galvanized steel canister containing sixteen stainless steel ball bearings (16 mm diameter) was used. Before the ball-milling procedure, the canisters and ball bearings were cleaned with ethanol for 15 minutes, then rinsed and dried with acetone.

For the ball-milled ZVMg preparation, 85.0 g of ZVMg was added to each canister. Whereas for ZVMg/AC preparation 76.5 g of ZVMg and 8.5 g of activated carbon were added to the canisters. Prior to closing, canisters were flushed with argon gas to prevent sparking. A twin arm paint shaker (Red Devil 5400) was used for milling and was equipped with custom wooden

plates that hold three canisters per arm. The milling was performed for 30 minutes. The metals were then removed and used.

Dechlorination Procedure

OCDF, 2,8-dichlorodibenzofuran, and dibenzofuran standard solutions were prepared by dissolving the neat standards in toluene, then diluting with absolute ethanol to the desired concentrations. Dechlorination experiments were conducted in clear glass screw-top vials (20 mL) with polytetrafluoroethylene (PTFE) lined caps containing 250 mg of ball-milled ZVMg or ZVMg/AC with 5 mL of 20 $\mu\text{g mL}^{-1}$ PCDF solution. To initiate the dechlorination, 50 μL of glacial acetic acid was added to each vial. Then, the vials were placed on a Lab Companion Reciprocating Shaker table (Series K-57013) at 200 rpm and 26 °C until the predesigned extraction time. All the experiments were done in duplicate. Control experiments were conducted without metal.

For the extraction of PCDFs from ethanol, equal volumes (5 mL) of toluene and water were added to the vials to induce the separation of toluene/ethanol layer. Then, the extract was centrifuged at 3140-3300 rpm for 10 minutes. A second water wash was performed and the top layer was collected, filtered with a Watman[®] 25-mm nylon syringe filter (0.45- μm pore size) attached to a disposable syringe, and stored for further analysis.

Analysis

An Agilent Technologies 6850 GC/MS system equipped with a Restek RTX[®]-5 column (30 m x 0.25 mm i.d., 0.25 μm film thickness) was used for the analysis of the samples. Helium was used as the carrier gas with a constant flow of 2 mL/min. The injector temperature was held at 250 °C and the ion source temperature was 280 °C. The instrument parameters were as follow:

the initial temperature was 140 °C, then the column was ramped at 3 °C /min to 300 °C. Injection volume was set at 1 µL and it was performed in a splitless mode. OCDF and lower chlorinated congeners were identified by comparison with the retention times of known standards.

Results and Discussion

Reductive Dechlorination of OCDF by Ball-milled ZVMg in Acidified Ethanol

The degradation of OCDF using ball-milled ZVMg and ethanol as a solvent and a hydrogen source was studied in this chapter. The fully chlorinated dibenzofuran OCDF was chosen in this study as a model compound in order to evaluate the efficiency of the system to remove the chlorine atoms and convert OCDF to less chlorinated congeners or a chlorine- free compound, dibenzofuran (DBF). The reaction between OCDF in acidified ethanol and ball-milled ZVMg or ZVMg/AC is characterized by the production of dibenzofuran, magnesium chloride, and magnesium ethoxide (Figure 3).

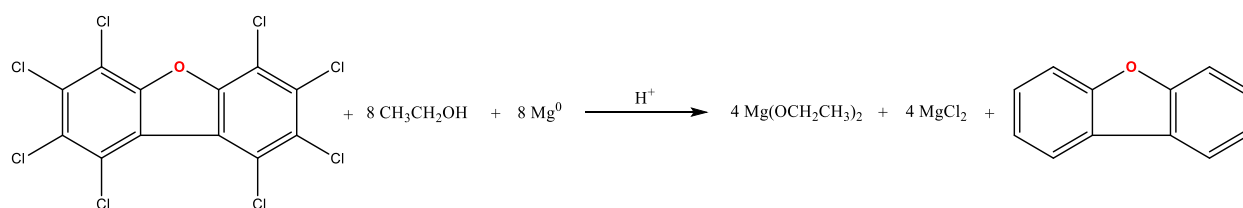


Figure 3: Dechlorination reaction of OCDF in acidified ethanol.

Data for the removal of OCDF over time in ethanol and ball-milled Mg is presented in Figure 4. As shown in this figure, OCDF degradation is time dependent. A reduction of 83.13% in OCDF concentration was achieved after 5 minutes of the treatment. By 6 hours of the reaction, only a trace amount of OCDF was detected (<1% of the initial concentration) and no OCDF was

detected after this time point. The results also indicate that OCDF was completely removed after 6 hours of the treatment and this was confirmed by the formation of lower chlorinated congeners over time which were detected by GS/MS.

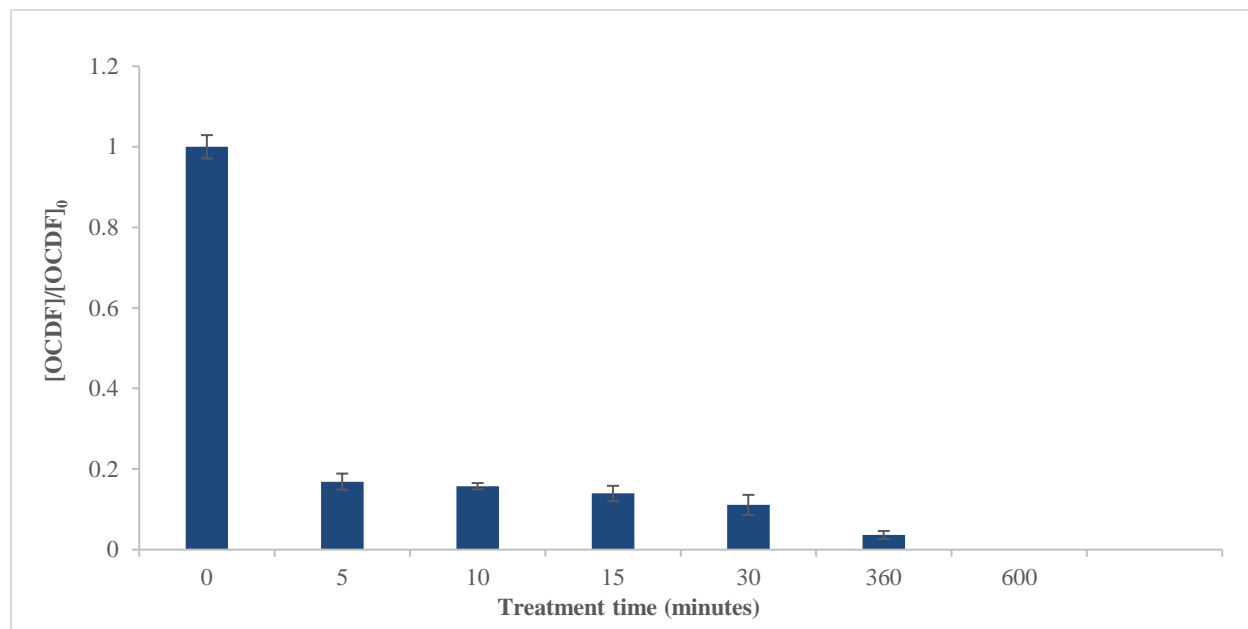


Figure 4: OCDF degradation using ZVMg in ethanol.

Figure 5 represents the distribution of the byproducts formed over 28 days of the treatment of OCDF using ball-milled ZVMg in ethanol. Some time points were not plotted in the figure to improve readability. However, complete time intervals can be found in the appendix as well as selected ion monitoring (SIM) parameters and example chromatograms, of the parent compound OCDF and the byproducts. As mentioned before, OCDF was degraded over time and this was accompanied with the observation of less chlorinated congeners in the reaction. After 2 hours, DBF started to form and after 10 days OCDF and all the formed by-products were converted to DBF. Different congeners were detected by the GC-MS including hepta-, hexa-, penta-, tetra-, tri-

, di-, mono-chlorodibenzofuran, and dibenzofuran. The results demonstrate that chlorine atoms were removed in a step wise process and the degradation of higher chlorinated congeners was faster than lower chlorinated congeners. To clarify, the results associated with the appearance and disappearance of high chlorinated congeners (octa- to tetra-chlorodibenzofuran) and low chlorinated congeners (tri- to mono-CDF and DBF) are presented in Figure 6 and Figure 7. Figure 6 shows that the formation of high chlorinated congeners started at the very beginning of the reaction (during the first 5 minutes). Even though the study was conducted over 28 days, no high chlorinated dibenzofuran congeners were detected after 6 hours of the study. Penta-CDF was the most stable congener among the high chlorinated congeners since it was formed in the first 5 minutes of the reaction and detected in the system up to 6 hours. For the low chlorinated congeners (Figure 7), tri- and di-CDF congeners started to form within the first 5 minutes of the treatment and increased in concentration until 2 days for the triCDF and 10 days for the diCDF congener. Then, their concentrations started to decrease until a complete degradation of these congeners was achieved where no further tri- and di-CDF congeners were detected in the system. DiCDF was the most stable congener of the low chlorinated congeners since it was observed for 10 days of the reaction; however, after this time point, no chlorinated congeners were observed in the system and all the formed byproducts were converted to the chlorine-free compound DBF.

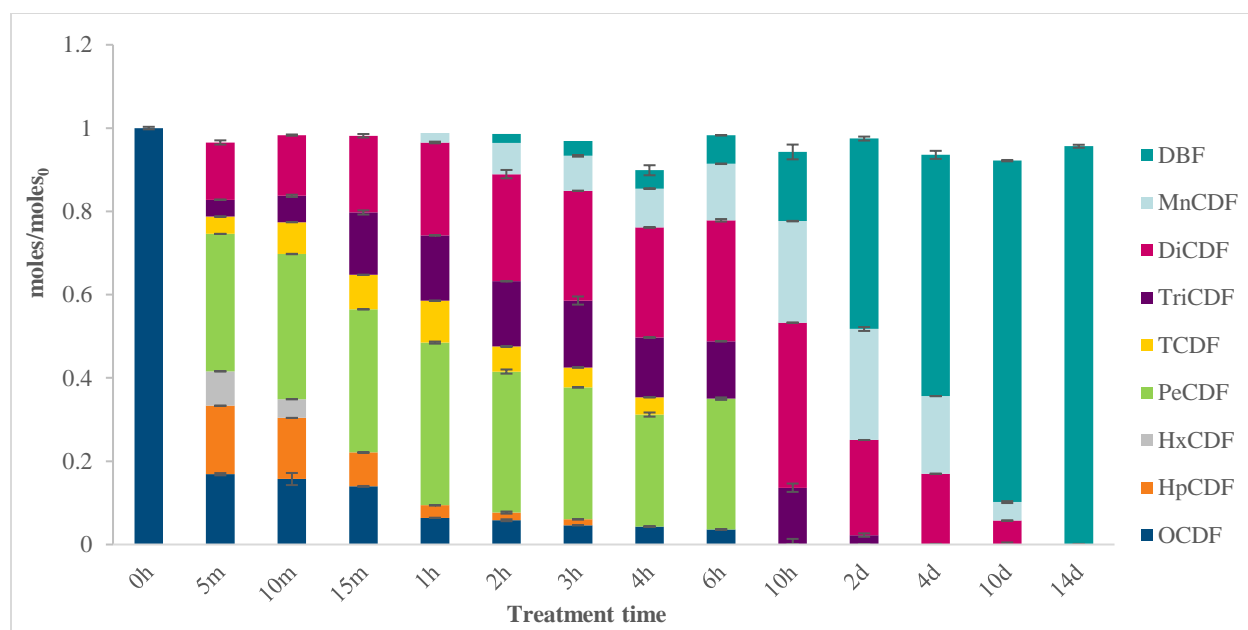


Figure 5: Distribution of dechlorination products resulting from OCDF reduction under ball-milled ZVMg and acidified ethanol.

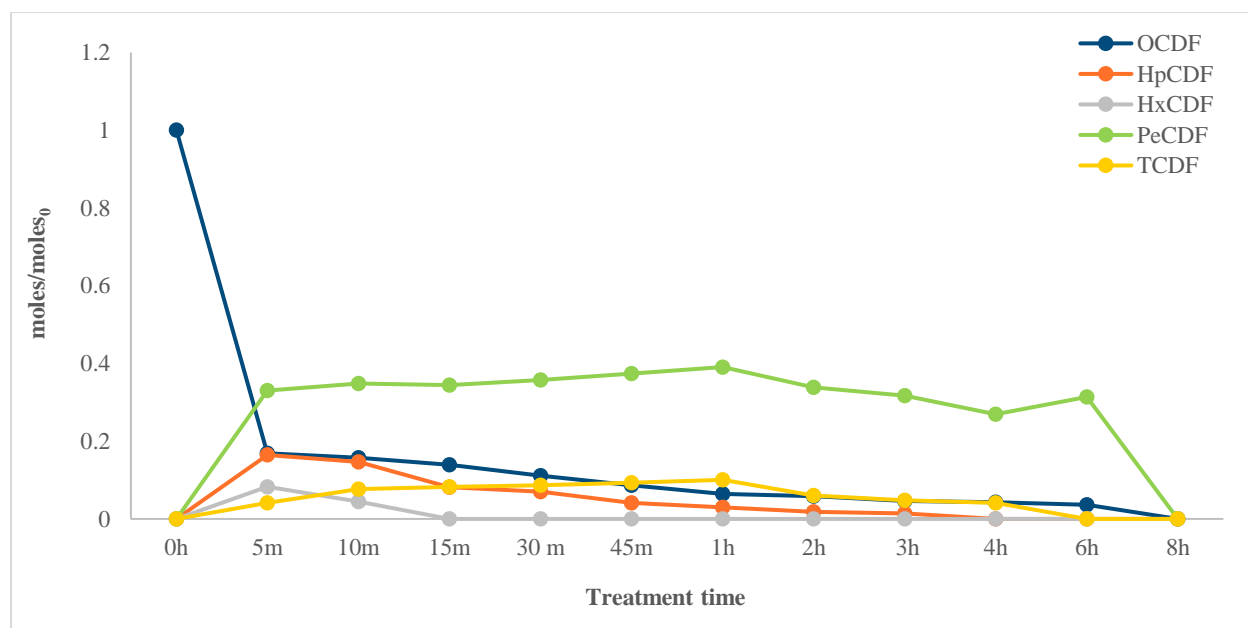


Figure 6: High-molecular weight products of OCDF dechlorination under ball-milled ZVMg and acidified ethanol.

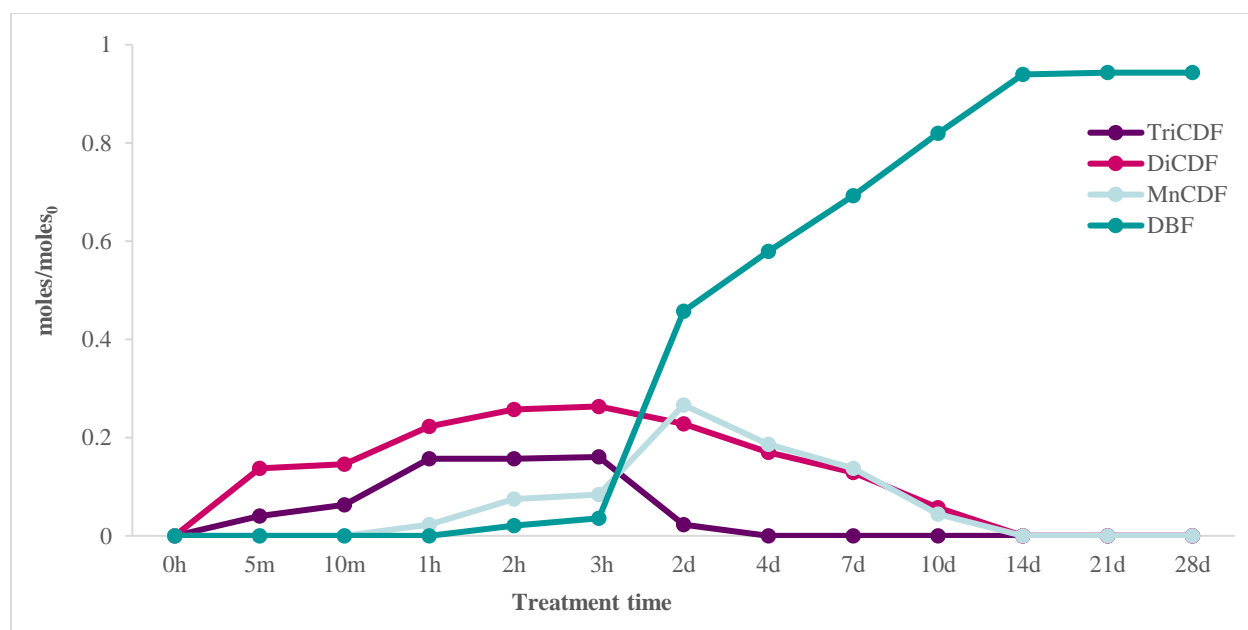


Figure 7: Low-molecular weight products of OCDF dechlorination under ball-milled ZVMg and acidified ethanol.

Reductive Dechlorination of OCDF by Ball-milled ZVMg with Activated Carbon in Acidified Ethanol

Activated carbon (AC) was added to the system in order to enhance the degradation kinetics of OCDF. The influence of the addition of activated carbon in the reduction of OCDF concentration over time is shown in Figure 8. OCDF degradation was confirmed by the characterization of the by-products formed in the system during the treatment time using GC-MS. Faster OCDF removal was observed in the presence of activated carbon. In this system, 90.8% reduction in OCDF concentration was achieved during the first 5 minutes of the reaction. A trace amount of OCDF was observed at 15 minutes of the reaction where a 95.2% reduction of its initial concentration occurred. Complete OCDF degradation was achieved after 15 minutes and no OCDF

was detected after that time point. This is in contrast to the ZVMg and ethanol system where complete OCDF degradation was achieved after 6 hours of reaction. This result indicates that the presence of activated carbon enhanced the reaction; however, no complete conversion to dibenzofuran was accomplished in this system. The percent reduction in OCDF concentration over time over ball-milled ZVMg and ZVMg/AC in ethanol are summarized in Table 2.

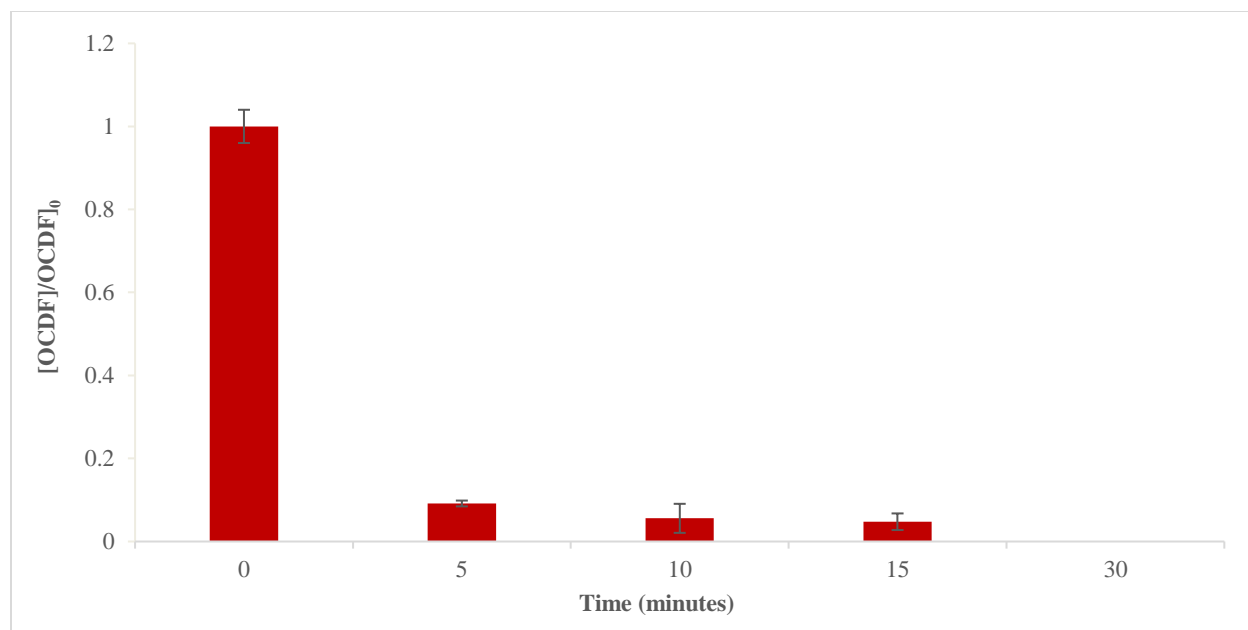


Figure 8: Total OCDF concentration in ball-milled ZVMg/AC and ethanol system.

Table 2: % Reduction in OCDF concentration under ball-milled ZVMg and ZVMg/AC in ethanol.

Time (minutes)	OCDF Reduction (%)	
	Ball-milled ZVMg in ethanol	ZVMg/AC in ethanol
5	83.1	90.8
10	84.3	94.4
15	86.4	95.2
30	88.9	100
360	96.4	100
600	100	100

Figure 9 illustrates the formation of the byproducts in the dechlorination of OCDF by ZVMg/AC and ethanol. Some data points were not plotted in the figure to improve readability. However, complete time intervals can be found in the appendix as well as selected ion monitoring (SIM) parameters and example chromatograms, of OCDF and byproducts. A rapid decrease in OCDF concentration was observed during the first 5 minutes of the reaction. This was accompanied by the appearance of different low chlorinated congeners including hepta-, hexa-, penta-, tetra-, tri-, and di-chlorodibenzofuran. Faster kinetics, in regards to the appearance and disappearance of the different congeners, were obtained by adding activated carbon to the system.

Table 3 summarizes the results associated with the appearance and disappearance of the different congeners obtained from the degradation of OCDF under ZVMg and ZVMg/AC in ethanol. Satisfactory dechlorination occurred in both treatment systems. As shown in Table 1,

hepta- and hexa-chlorodibenzofuran congeners started to form during the first 5 minutes of the reaction in both systems. In the presence of activated carbon, no hepta- and hexa-chlorodibenzofuran congeners were detected in the system after 10 minutes. The same congeners were completely degraded under ball-milled ZVMg after 3 hours or 10 minutes (for the hepta- and hexa-CDF, respectively). Tetrachlorodibenzofuran, the most toxic congener, was formed at 5 minutes in both systems and degraded within 15 minutes in ZVMg/AC compared to 4 hours in the ball-milled ZVMg system. For the ZVMg/AC system, penta- and tri-CDF congeners were more stable and they remained present in the system for long times compared to other congeners (6 and 10 hours for penta- and tri-chlorodibenzofuran, respectively). In this system, di- and mono-chlorodibenzofuran congeners were more resistant to the degradation as demonstrated by their presence in the system until the end of this study (4 weeks).

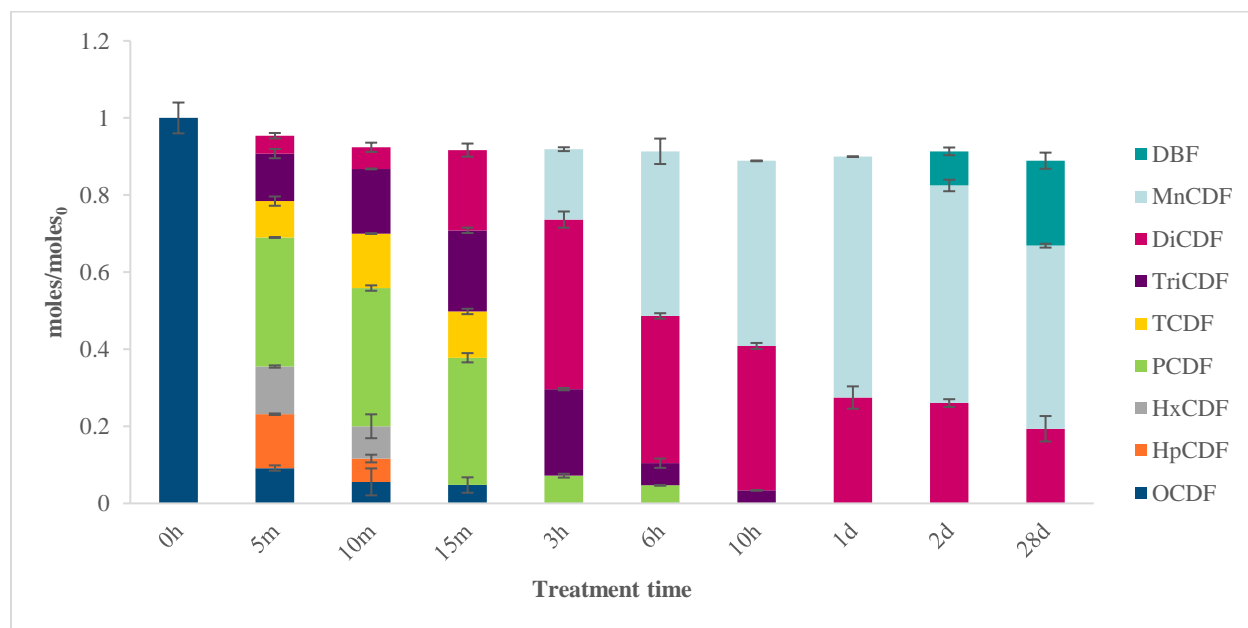


Figure 9: Distribution of dechlorination products resulting from OCDF reduction under ZVMg/AC and acidified ethanol.

Table 3: Appearance and disappearance time of the different congeners obtained from the degradation of OCDF under ball-milled ZVMg and ZVMg/AC in ethanol.

Congener	Ball-milled ZVMg + ethanol		ZVMg/AC + ethanol	
	Appearance	Disappearance	Appearance	Disappearance
OCDF	0h	6h	0h	15m
HpCDF	5m	3h	5m	10m
HxCDF	5m	10m	5m	10m
PCDF	5m	6h	5m	6h
TCDF	5m	4h	5m	15m
TriCDF	5m	2d	5m	10h
DiCDF	5m	10d	5m	-
MnCDF	1h	10d	3h	-
DBF	2h	-	2d	-

The role of activated carbon in the degradation process

Activated carbon has shown numerous advantages in past studies towards the degradation of recalcitrant organic pollutants via hydrogenation. This improvement can be attributed to the protection layers offered by graphite to the metal surface which prevent the formation of the oxide layers. Scanning Electron Microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX) was used to image the surface of ZVMg and ZVMg/AC before and 7 days after the degradation process for OCDF in acidified ethanol solution. The images presented in Figure 10 show an abundance of oxygen and carbon relative to magnesium due to the formation

of passivating oxide/ethoxide layers on the magnesium surface over time. The observed increased abundance of oxygen and carbon in ZVMg versus ZVMg/AC reveals that the addition of activated carbon to the system reduces the formation of the passivating layers on the magnesium surface³³.

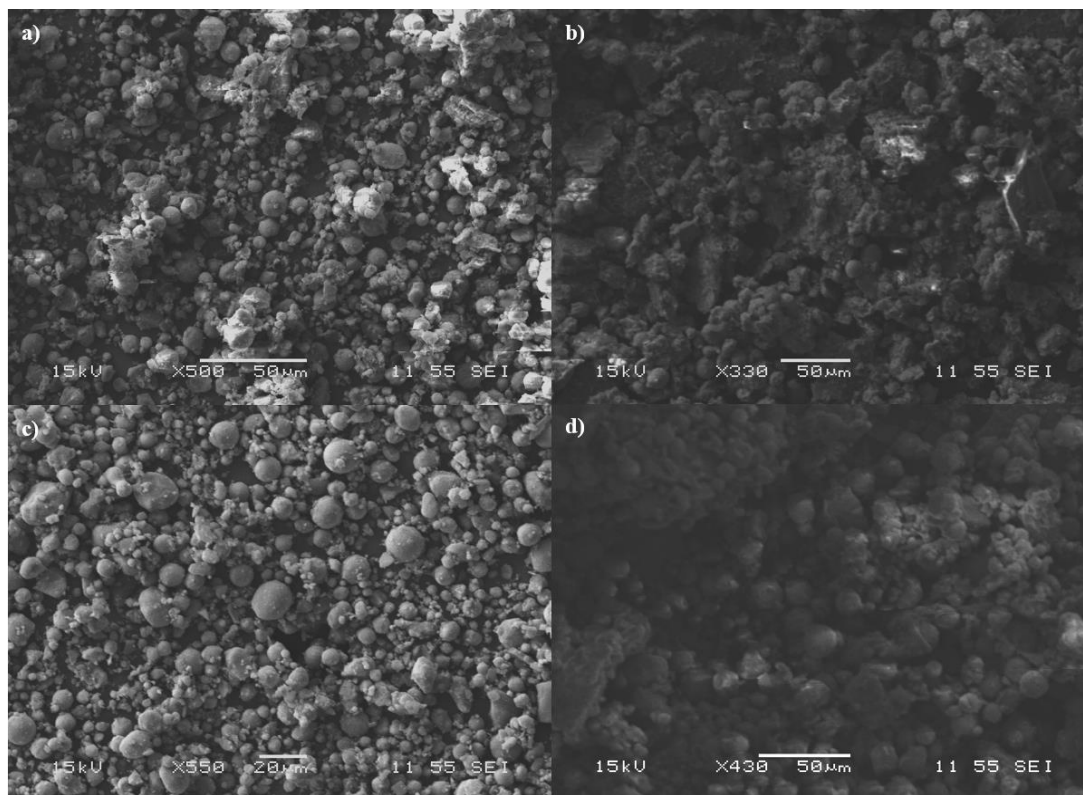


Figure 10: SEM images of a) ball-milled ZVMg prior to reaction, b) ball-milled ZVMg after 7 days exposure to OCDF in acidified ethanol, c) ZVMg/AC prior to reaction, and d) ZVMg/AC after 7 days exposure to OCDF in acidified ethanol.

Even though the use of activated carbon has enhanced the degradation kinetics, complete conversion to dibenzofuran was achieved without activated carbon. The presence of activated carbon inhibited the degradation of the low chlorinated congeners di- and mono-chlorodibenzofuran to the chlorine-free compound dibenzofuran. The same inhibitory effect was

observed in previous studies where the presence of activated carbon inhibited the degradation of low chlorinated PCBs and suppressed their conversion to biphenyl. This can be explained by the sorption effect of activated carbon which become stronger in case of the low chlorinated congeners. The sorption of PCDFs and other chlorinated compounds such as PCBs on the activated carbon surface has been documented in many studies^{1, 33}.

Degradation Kinetics and Mole Balance for the Degradation of OCDF by ZVMg and ZVMg/AC in Acidified Ethanol

Kinetic studies of OCDF degradation by ball-milled ZVMg with and without activated carbon in ethanol demonstrate that the reactions follow a pseudo-first-order kinetics model with respect to OCDF degradation. The normalized pseudo-first-order decay model with respect to OCDF disappearance under ball milled ZVMg and ZVMg/AC in ethanol are shown in Figure 11 and Figure 12. Previous studies done on the degradation of polychlorinated aromatic hydrocarbons such as PCBs using ZVMg in ethanol as a reducing system have obtained similar results^{32, 40}.

By comparing the kinetic results of the two systems (ball-milled ZVMg with and without activated carbon), it is clear that greater rate was achieved by using ball-milled ZVMg and AC. As mentioned before, this enhancement occurred due to protection layers added to the Mg surface by graphite, facilitating the activation process of the metal surface. The normalized pseudo-first-order rate constants yielded by these two systems were $k = 0.2414 \text{ h}^{-1}$ for the reaction without activated carbon and $k = 0.2558 \text{ min}^{-1}$ in the presence of activated carbon. The linear correlation coefficient values (R^2) were 0.9859 and 0.9730 for ball-milled ZVMg and ZVMg/AC, respectively.

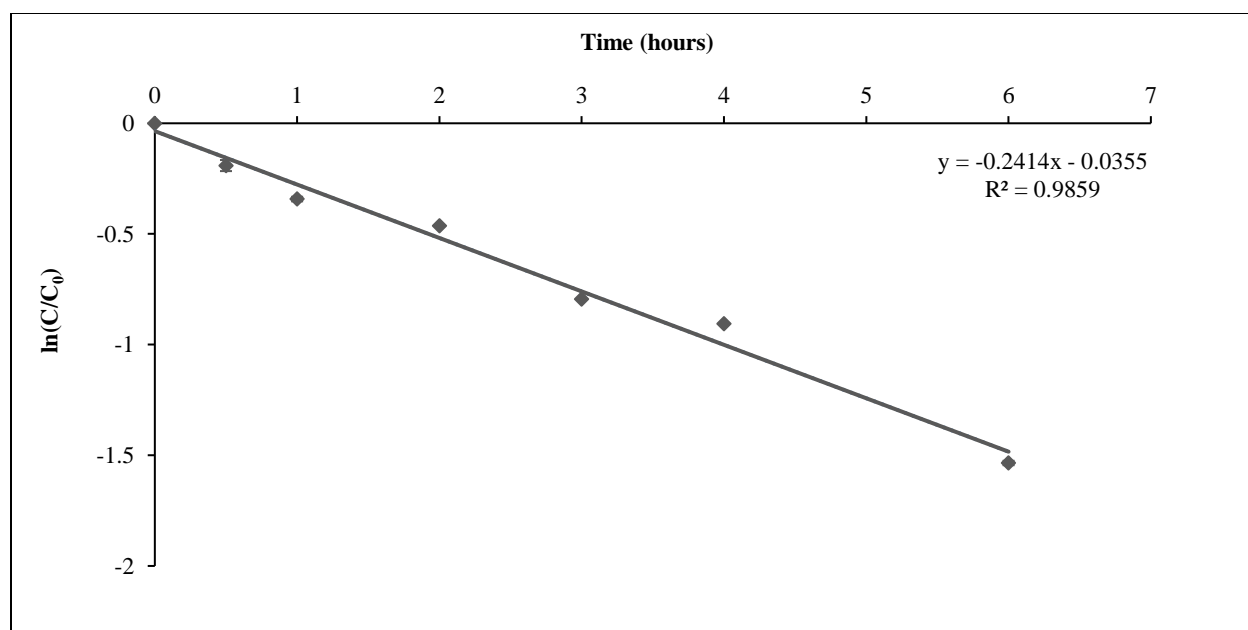


Figure 11: Pseudo-first-order degradation plot of OCDF by ZVMg in acidified ethanol.

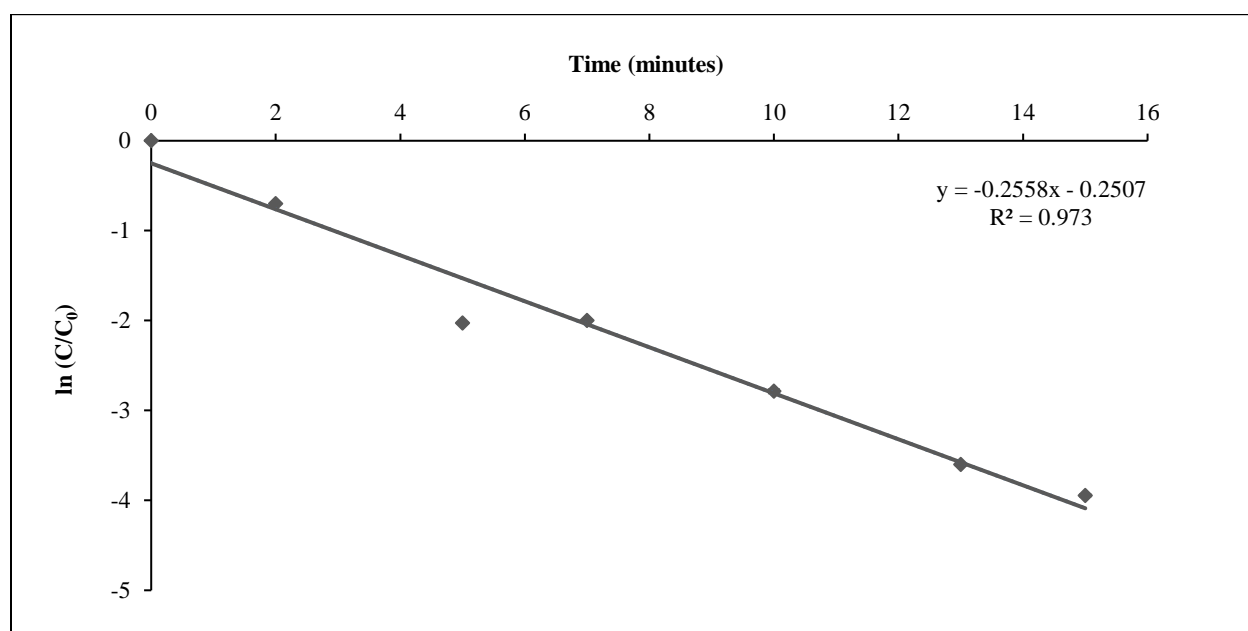


Figure 12: Pseudo-first-order degradation plot of OCDF by ZVMg/AC in acidified ethanol.

Figure 13 illustrates the mole balance for the dechlorination of OCDF using ball-milled ZVMg and ZVMg/AC in acidified ethanol after 4 weeks of the degradation. In the first system (ball-milled ZVMg in acidified ethanol), DBF formation increased over time in proportion to the disappearance of OCDF and the lower chlorinated congeners that were formed during the reaction, concluding with a 94.3% DBF formation after 4 weeks of the treatment. It can be concluded that in this system, OCDF and all by-products formed were converted to dibenzofuran, the chlorine-free compound. In contrast to the second system where activated carbon was added, di- and monochlorodibenzofuran were detected in the system as well as dibenzofuran until the end of this study. The overall mole balance of this system was 88.9%. The monochlorodibenzofuran congener was the most abundant by-product corresponding to 47.5% of the final products; whereas, dichlorodibenzofuran and dibenzofuran constitute 19.4% and 22.1% of the final products, respectively. A decrease in the mole balance was observed in this system due to the desorption effect of activated carbon which is noticed more significantly in the case of low chlorinated congeners as explained previously.

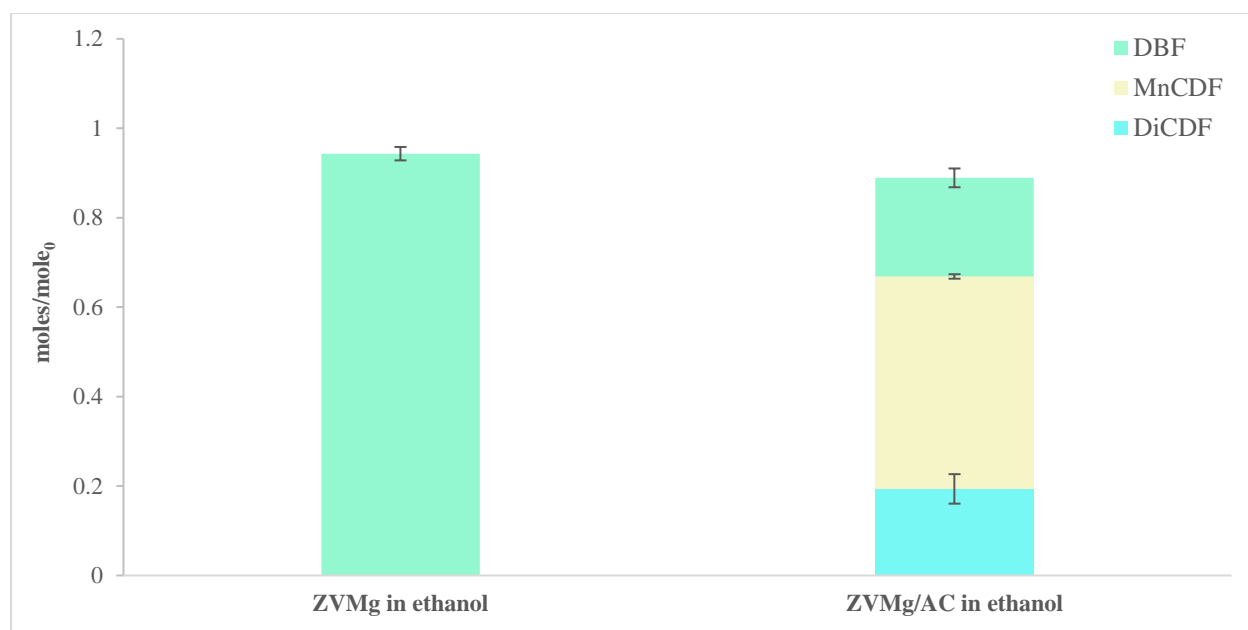


Figure 13: Mole balance for the dechlorination of OCDF using ball-milled ZVMg and ZVMg/AC in acidified ethanol after 4 weeks of the treatment.

Efficacy of the System to Dechlorinate the Low Chlorinated Congener 2,8-Dichlorodibenzofuran

2,8-Dichlorodibenzofuran was chosen as a model for low chlorinated congeners of PCDFs to ensure that complete dechlorination can be achieved for low chlorinated congeners using ball-milled ZVMg and ZVMg/AC in ethanol reduction treatment systems. 2,8-Dichlorodibenzofuran was exposed to the same conditions as OCDF and the dechlorination kinetics were studied over time. The degradation of 2,8-dichlorodibenzofuran was confirmed by the disappearance of the parent compound peak and the appearance of by-product peaks by GC-MS during the reaction time. The change in 2,8-dichlorodibenzofuran concentration over reaction time in ball-milled ZVMg and ZVMg/AC using ethanol solvent is graphically presented in Figure 14. Complete degradation of 2,8-dichlorodibenzofuran was achieved by both systems (after 7 days of the reaction by ball-milled ZVMg and 9 days when activated carbon was used in the system). It was noticed that the degradation of 2,8-dichlorodibenzofuran was very slow in the beginning (the first 12 hours) and it took time to get a noticeable decrease in its concentration. This is in contrast to the degradation of the highly chlorinated congener OCDF where the byproducts were formed within the first 5 minutes of the reaction.

2,8- Dichlorodibenzofuran degradation products

Figure 15 and Figure 16 represent the reductive dechlorination of 2,8-dichlorodibenzofuran and the formation of byproducts over ball-milled ZVMg and ZVMg/AC in acidified ethanol. Time points between zero and 12 hours were not plotted to improve readability since preliminary studies showed no significant change in the concentration occurring during those time intervals. After 1 day of the reaction, 50.5% of 2,8-dichlorodibenzofuran was reduced to monochlorodibenzofuran and dibenzofuran by ball-milled ZVMg; whereas, 70.5% reduction in 2,8-dichlorodibenzofuran concentration was achieved in the presence of activated carbon. By the 5th day, 2,8-dichlorodibenzofuran achieved 88.6% and 89.7% reduction (from its initial concentration) by the ball-milled ZVMg and ZVMg/AC systems, respectively. The 2,8-dichlorodibenzofuran concentration decreased over time and by the 9th day, no 2,8-dichlorodibenzofuran was detected in the reaction under ball-milled ZVMg. In this system, 2,8-dichlorodibenzofuran and all the formed monochlorodibenzofuran were converted to dibenzofuran, the chlorine-free compound. However, at the same time point (9 days), a trace amount of 2,8-dichlorodibenzofuran (~ 5.8%) was present in the reaction containing activated carbon and dibenzofuran was the major byproduct at that time (55.7%). The monochlorodibenzofuran accounted for 25.2% of the byproducts formed at 9 days. After 10 days, 2,8-dichlorodibenzofuran and the monochlorodibenzofuran congeners achieved complete removal in which they were converted to dibenzofuran and not detected by the GC-MS.

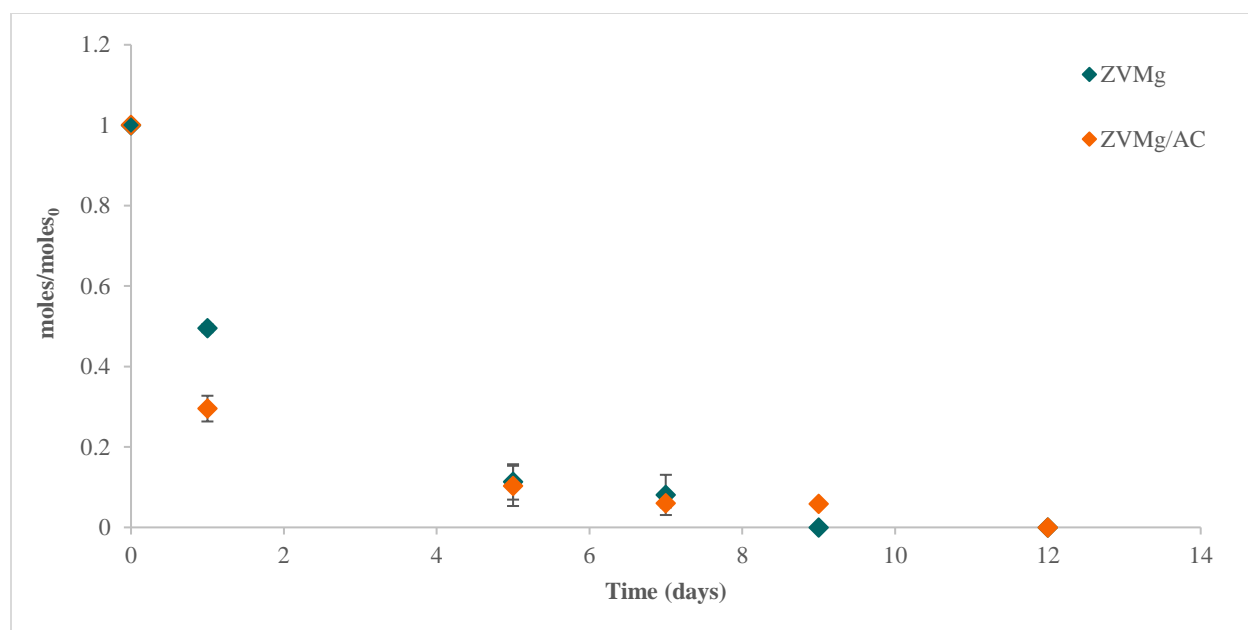


Figure 14: Reduction in 2,8-dichlorodibenzofuran concentration under ball-milled ZVMg and ZVMg/AC in acidified ethanol.

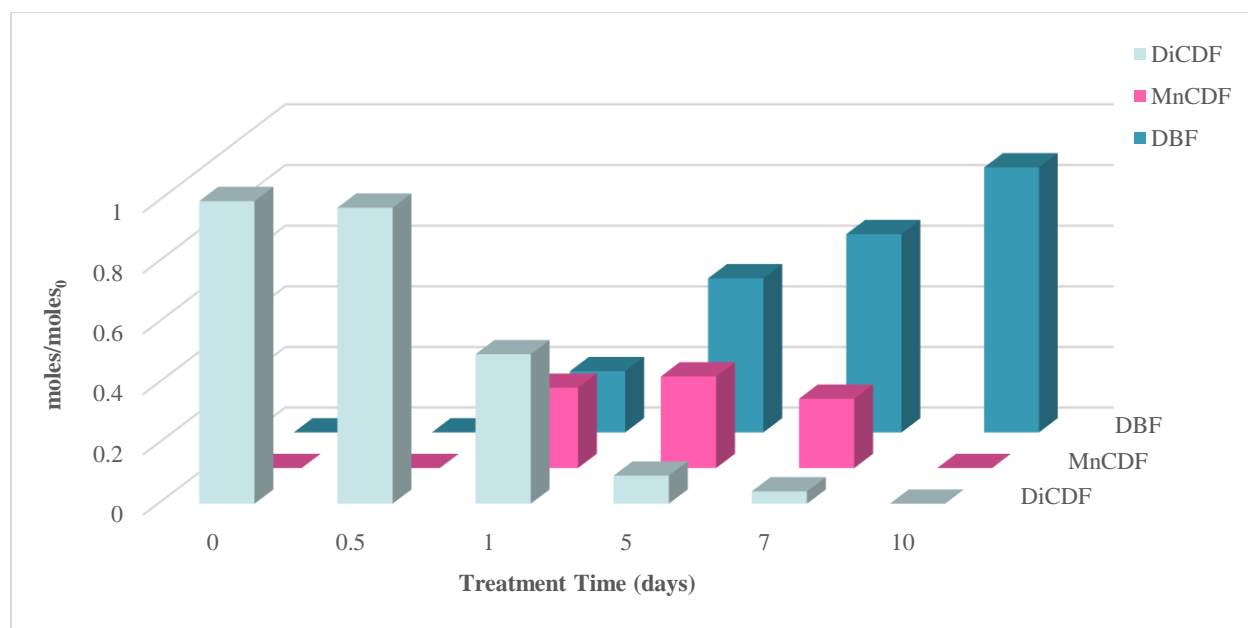


Figure 15: Reductive dechlorination of 2,8-dichlorodibenzofuran over ball-milled ZVMg in acidified ethanol.

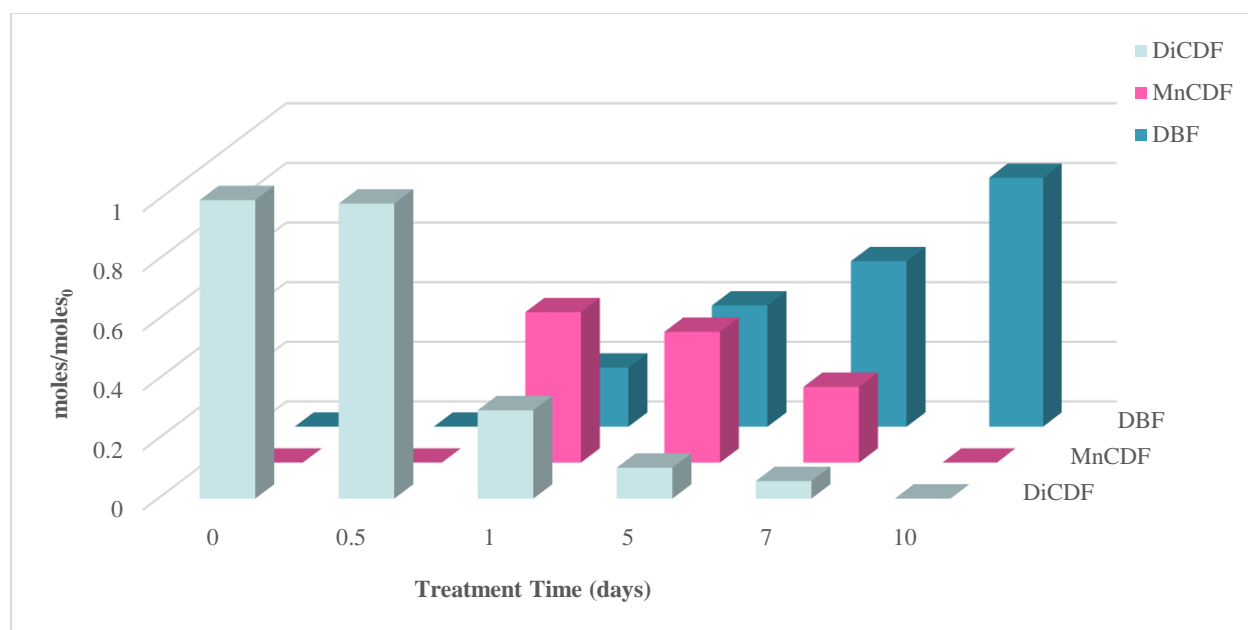


Figure 16: Reductive dechlorination of 2,8-dichlorodibenzofuran over ZVMg/AC in acidified ethanol.

2,8-Dichlorodibenzofuran dechlorination kinetics

OCDF degradation has shown a pseudo-first-order reaction with respect to the disappearance of the analyte. Furthermore, previous studies performed on low chlorinated biphenyl in a variety of solvent systems yielded pseudo-first-order kinetics in the presence of excess ZVM. For the degradation of 2,8-dichlorodibenzofuran, a similar trend was observed using acidified ethanol and ball-milled ZVMg in the present and absence of activated carbon.

Figure 17 and Figure 18 represent a pseudo-first-order decay model with respect to the disappearance of 2,8-dichlorodibenzofuran with ball-milled ZVMg and ZVMg/AC, respectively. Kinetic results of 2,8-dichlorodibenzofuran degradation with ball-milled ZVMg in the presence of activated carbon yielded a slightly faster rate than the degradation with only ball-milled ZVMg. A good explanation for that is that activated carbon enhanced the reaction by facilitating the

activation process which improved the reaction kinetics of the magnesium³⁸. The normalized pseudo-first-order rate constants obtained by both systems were $k = 0.3667 \text{ days}^{-1}$ for the ball-milled ZVMg system and $k = 0.3872 \text{ days}^{-1}$ for ZVMg/AC system. The values of the linear correlation coefficient were $R^2 = 0.9775$ and $R^2 = 0.9393$ for ball-milled ZVMg and ZVMg/AC, respectively.

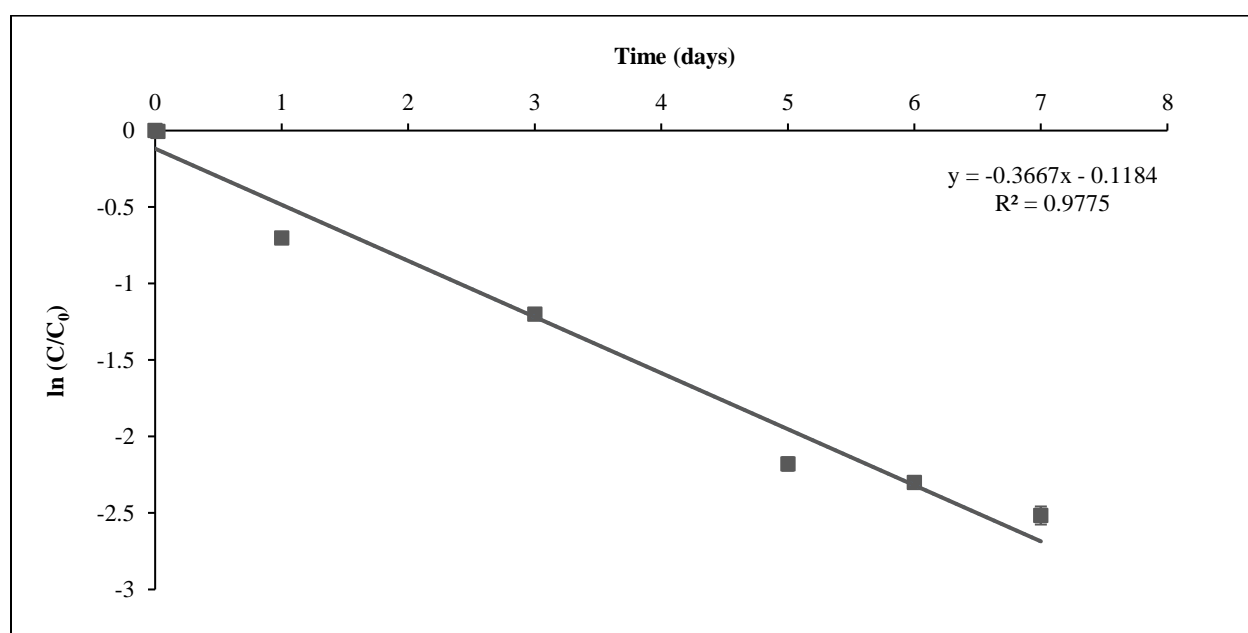


Figure 17: Pseudo-first-order plot of 2,8-dichlorodibenzofuran degradation using ZVMg in an acidified ethanol.

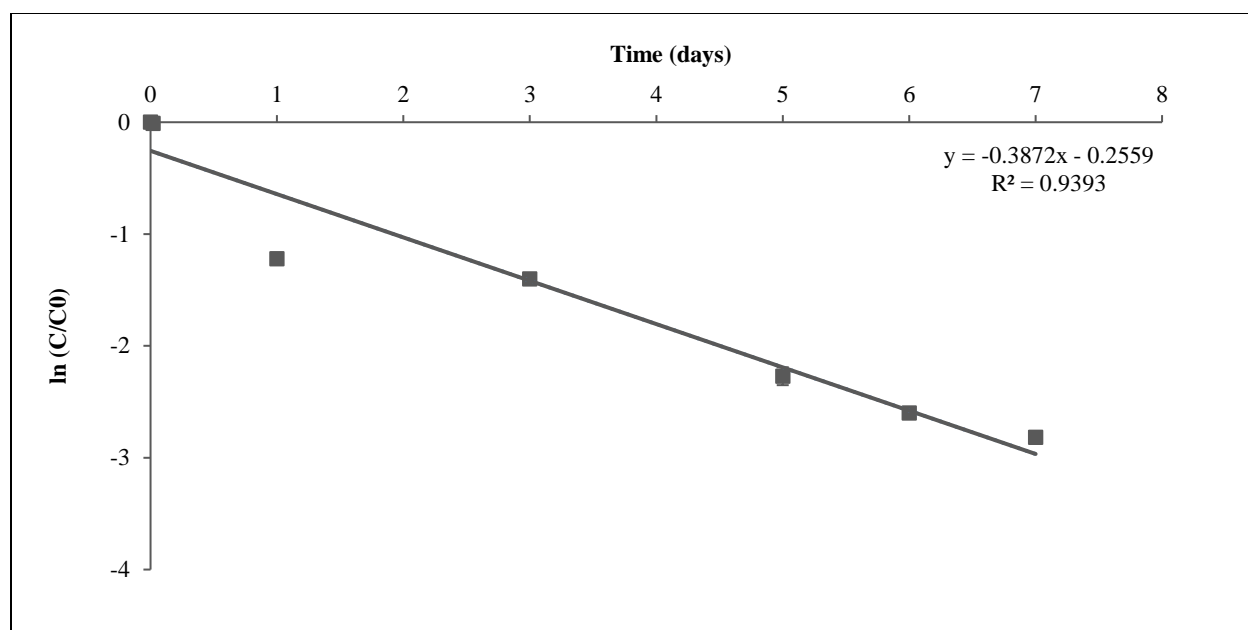


Figure 18: Pseudo-first-order plot of 2,8-dichlorodibenzofuran degradation using ZVMg/AC in an acidified ethanol.

Stability of the System Towards Dibenzofuran Degradation

The chlorine- free compound dibenzofuran was exposed to the same experimental conditions as OCDF and 2,8-dichlorodibenzofuran to examine the ability of the system to further degrade the parent compound dibenzofuran. The study was conducted for 10 days using ball-milled ZVMg in acidified ethanol. The result is illustrated in Figure 19. Dibenzofuran concentration was nearly constant during the study which means that DBF is very stable towards the degradation in ball-milled ZVMg and ethanol system. No significant DBF degradation occurred through the end of the study (10 days).

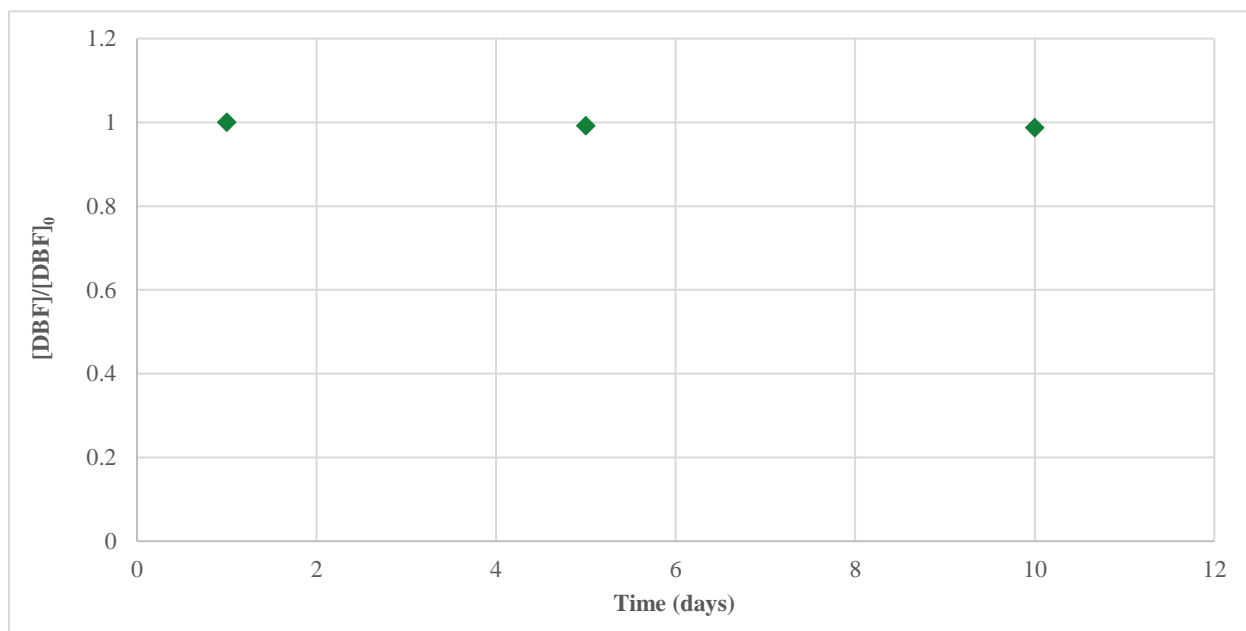


Figure 19: Stability of DBF in ball-milled ZVMg and acidified ethanol over time.

Conclusion

Novel reduction systems consisting of ball-milled ZVMg with and without activated carbon in acidified ethanol were evaluated in this chapter. The two examined systems showed good results in the degradation of high and low chlorinated congeners at ambient conditions. Complete removal of the highly chlorinated congener OCDF was achieved in both systems. The system of ball-milled ZVMg and ethanol resulted in complete conversion of OCDF and all the byproducts to dibenzofuran, the chlorine-free compound. Even though the presence of activated carbon has greatly enhanced the degradation kinetics, complete conversion to DBF was not obtained in this system. In these systems, chlorine atoms were substituted by hydrogen atoms in a stepwise process. It was also noted that high chlorinated dibenzofuran exhibited faster kinetics than low chlorinated dibenzofurans.

The reductive systems were also tested towards the degradation of the low chlorinated congener and 2,8-dichlorodibenzofuran was chosen for this study. Complete removal of 2,8-dichlorodibenzofuran was obtained by both systems. Although 2,8-dichlorodibenzofuran was resistant in the first 12 hours of the reaction, a great reduction in 2,8-dichlorodibenzofuran concentration was observed after 24 hours. No 2,8-dichlorodibenzofuran was detected after 10 days and 12 days in ball-milled ZVMg and ZVMg/AC systems, respectively. The parent compound dibenzofuran was stable with respect to the degradation using ball-milled ZVMg and acidified ethanol.

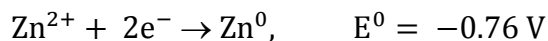
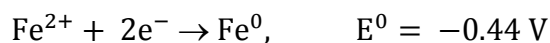
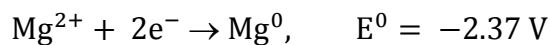
CHAPTER THREE: REDUCTIVE DECHLORINATION OF OCDF BY BALL-MILLED ZVMG AND ZVMG/AC USING ACIDIFIED ETHANOL/ETHYL LACTATE CO-SOLVENT SYSTEM

Introduction

Dioxins including poly-chlorinated dibenzofurans (PCDFs) and poly-chlorinated dibenzodioxins (PCDDs) are a family of halogenated aromatic hydrocarbons called persistent organic pollutants (POPs)¹. PCDFs and PCDDs are toxic pollutants that are produced unintentionally and enter the environment as unwanted byproducts from a variety of chemical and industrial activities⁴¹. They can be formed as a result of incomplete combustion, municipal and medical wastes, the use of chlorinated organics, chlorinated pesticides and herbicides, forest fires, and landfill fires^{42, 43}. In total, there are 75 PCDD congeners and 135 PCDF congeners¹. Among the 210 different congeners, 2,3,7,8-chlorine substituted congeners are the most toxic⁴⁴. Dioxins are known to be persistent in the environment, bioaccumulative, and resistant towards biological and chemical degradation^{41, 43, 45}. It has been reported that tetrachlorodibenzofuran and higher chlorinated congeners are extremely stable under environmental conditions⁴⁶. Therefore, dioxins have been detected in all compartments of the ecosystem^{47, 48}. Due to their lipophilicity, they accumulate in the food chain which is considered the primary route for human exposure to dioxins⁴⁵. Short-term and long-term exposure to dioxins can lead to serious health problems such as liver damage, birth defects, chloracne, reproductive and developmental problems⁴⁹, heart attack, alterations on the nervous system, immune deficiency^{21, 48, 50-52} and many other problems. They are also well-known endocrine disruptors⁵³. Due to the high toxicity of dioxins, they cause great scientific and public concerns. Therefore, it is essential to find an efficient method for dioxin

treatment. Several treatment options are available including incineration⁴⁵, bioremediation^{34, 36, 50}, radiolysis⁵⁴, supercritical water processes^{8, 55}, Fenton oxidation⁵⁶, electrochemical oxidation, photolysis, and photocatalysis^{57, 58}. However, each of these processes have some drawbacks. For example, bioremediation is known to be an environmentally friendly and a cost-effective technology. However, the low efficiencies, the incomplete degradation of high chlorinated congeners, and the slow kinetics associated with this process make it unfavorable for dioxin treatment⁴⁵. *Liu, et. al.* have demonstrated that OCDF degradation by microbial reductive dechlorination resulted in the formation of lower chlorinated congeners including HpCDF, HxCDF, PCDF, and TCDF. However, no congeners less than TCDF were detected⁵⁰. In another study OCDF was degraded by certain strains such as *Rhodococcus*, *Mesorhizobium*, *Micrococcus*, and *Bacillus* isolates. However, low degradation efficiencies were obtained (26- 43%)³⁶.

One area that has shown great potential in POP degradation is the use of zero-valent metals such as zero-valent iron (ZVI), zero-valent zinc (ZVZ), and zero-valent magnesium (ZVMg)^{8, 9, 38, 59}. Little research has been done using ZVZ due to the fact that hazardous zinc species are released from the zinc particles which can cause a great environmental toxicity⁹. Working with ZVI requires non-ambient environments such as elevated pressure and temperature and anaerobic conditions⁸. These limitations have opened up the attention to the use of ZVMg as an alternative. Many studies have been utilized ZVMg for the reductive dechlorination of numerous POPs. High efficiencies were obtained using ZVMg. The high reductive potential for Mg compared to iron and zinc as shown in the following equations¹² and the high efficiency of the treatment by ZVMg were deciding factors to make it the focus of this research.



Previous work done in chapter two on the degradation of octachlorodibenzofuran (OCDF) using ZVMg with and without activated carbon in ethanol as a solvent has resulted in complete OCDF degradation. The slow reaction kinetics with respect to OCDF removal in ball-milled ZVMg and the incomplete conversion of the products in ZVMg/AC systems have led us to test another solvent system. According to previous studies, the use of ethyl lactate as a co-solvent along with ethanol for the dechlorination of polychlorinated aromatic pollutants has shown numerous advantages in the degradation process^{39, 60}. Therefore, another solvent system was studied in this chapter to investigate the effect of the addition of ethyl lactate with ethanol with both ZVMg and ZVMg/AC. Ethyl lactate has been chosen since it is environmentally benign, non-toxic, cheap, biodegradable, and it enhanced the biodegradation of toxic halogenated compounds in soils⁶⁰⁻⁶². This chapter will focus on the treatment of octachlorodibenzofuran (OCDF) as a model compound to test the efficacy of the system of ZVMg and ethanol/ethyl lactate (90:10) to reductively dechlorinate the selected compound to less chlorinated congeners or a chlorine-free compound.

Experimental

Materials and Chemicals

Neat OCDF was obtained from Accustandard (New Haven, CT). Optima[®] grade toluene (99.95%) was purchased from Fisher Scientific. Absolute ethanol was purchased from Pharmco-

AAPER Ethyl L(-)-lactate (97%) and glacial acetic acid (99.8% purity) were acquired from ACROS Organics through Fisher Scientific, (Morris Plains, NJ). All chemicals were used without any further purification. Micro-scale magnesium powder (2-4 μm) and activated carbon (charcoal G-60) were purchased from Heart Metals Inc (Tamaqua, PA) and Matheson Coleman & Bell (Gardena, CA), respectively. Nylon filters with a pore size of 0.45 μm were acquired from Fisher Scientific (Pittsburg, PA).

ZVMg and ZVMg/AC Ball-milling Procedure

For the ball milling procedure, galvanized steel canisters were used. Each canister contains sixteen stainless steel ball bearings with a diameter of 1.6 cm and 85.0 g of ZVMg for ball-milled ZVMg and 76.5 g of ZVMg with 8.5 g of activated carbon for ZVMg/AC. The ball-milling was done for 30 minutes in an argon atmosphere using a Red Devil Paint Shaker Series 5400.

Dechlorination Procedure

Neat OCDF was dissolved in toluene and diluted to the desired concentration (20 $\mu\text{g mL}^{-1}$) in absolute ethanol/ ethyl lactate (90:10). For the dechlorination procedure, 0.25 g of ball-milled ZVMg or ZVMg/AC were added to 20 mL screw-top glass vials capped with PTFE lined caps. To each vial, 5 mL of OCDF solution was added. To initiate the dechlorination, glacial acetic acid (50 μL) was added to the reaction vials. The vials were placed on a Reciprocating Shaker table (Lab Companion Series K-57013) operated at 26 $^{\circ}\text{C}$ and 200 rpm speed until predetermined extraction time. All the experiments were done in duplicate. Control experiments were conducted without metal.

Samples were extracted using (5.0±0.1) mL of HPLC grade toluene and deionized water (5.0±0.1) mL added to the sample vial to induce separation of the toluene/ethanol: ethyl lactate. The resulting mixture was then shaken by hand for 2 minutes followed by centrifugation for 10 minutes. A second centrifugation was done for 30 minutes where the top layer was transferred to a clean vial and more deionized water was added to the solution. Finally, the top layer of the extract was collected and filtered with a Watman® 25-mm (0.45-µm pore size) nylon filter.

pH Study

A separate set of experiments was performed over 21 days to monitor change in pH. As described previously in the procedure section, 5 ml of ethanol solvent or ethanol/ethyl lactate (90:10) co-solvent were added to reaction vials having 250 mg of ZVMg or ZVMg/AC. Then, 50 µL of acetic acid were added to the reaction vials to initiate the reaction. At designated time points, 1mL aliquots of the reaction mixture were transferred into new vials and diluted with distilled water (1:10 dilution). Then, the pH of the solutions was measured using an Accumet Research AR15 pH meter. Finally, for determining the pH in the non-aqueous solvents, hydrogen ion concentrations were back-calculated.

Analysis

OCDF and other byproduct concentrations were analyzed by gas chromatography- mass spectrometry (GC-MS). For the quantitative analysis of the samples, an Agilent Technologies 6850 GC/MS system equipped with a Restek RTX®-5 column (30 m x 0.25 mm i.d., 0.25 µm film thickness) was used. Helium with a constant flow of 1.3 mL/min acted as the carrier gas. The injector temperature and the ion source temperature were held at 250 °C and 280 °C, respectively.

The injection volume was 1 μL and it was set in a splitless mode. The instrument parameters were as follows: the initial temperature was 140 $^{\circ}\text{C}$, then the column was ramped at 10 $^{\circ}\text{C}/\text{min}$ to 300 $^{\circ}\text{C}$. Identification of OCDF and the other congeners was based upon the retention times of known standards and verified via their mass spectrum.

Results and Discussion

Reductive Dechlorination of OCDF Under Ball-milled ZVMg with and Without AC in Ethanol/Ethyl Lactate (90:10) Co-solvent System

Kinetic studies of the degradation of OCDF with ball-milled ZVMg ZVMg/AC using an ethanol/ethyl lactate (90:10) co-solvent system were performed at room temperature in closed vials containing 20 ppm (45.07 μM) OCDF solution and acetic acid. The addition of the acid helps in neutralizing the oxide/hydroxide layer formed on the surface of the ZVMg, allowing more access to the reactive ZVMg; thus, increasing the reactivity of the reaction³⁸. Figure 20 illustrates the change in concentration of OCDF over time for the two systems (ball-milled ZVMg and ZVMg/AC in ethanol/ethyl lactate (90:10) co-solvent). The results of the reduction percentage in OCDF concentration under ball-milled ZVMg and ZVMg/AC in ethanol/ethyl lactate (90:10) are summarized in Table 4. Successful degradation of OCDF was achieved in the two systems and this was accompanied by the observation of less chlorinated congeners from the first minute of the reactions and confirmed by the analysis and characterization (GC–MS) of the formed byproducts during the reaction.

For the system consisting of ZVMg in acidified ethanol/ethyl lactate, 95.3% of OCDF was degraded to less chlorinated congeners within the first 3 minutes of the reaction. By 5 minutes of

the reaction, only a trace amount of OCDF was detected in the system with a reduction of 98.7% of its initial concentration. No OCDF was observed after 5 minutes (Figure 20)

When activated carbon was present in the system, degradation kinetics were improved (as in the first study where acidified ethanol was used as a solvent). OCDF dechlorination was faster by using activated carbon with 97.6% removal during the first 3 minutes. Complete OCDF degradation occurred after 3 minutes of reaction. After that time, OCDF was not detected by the GC-MS.

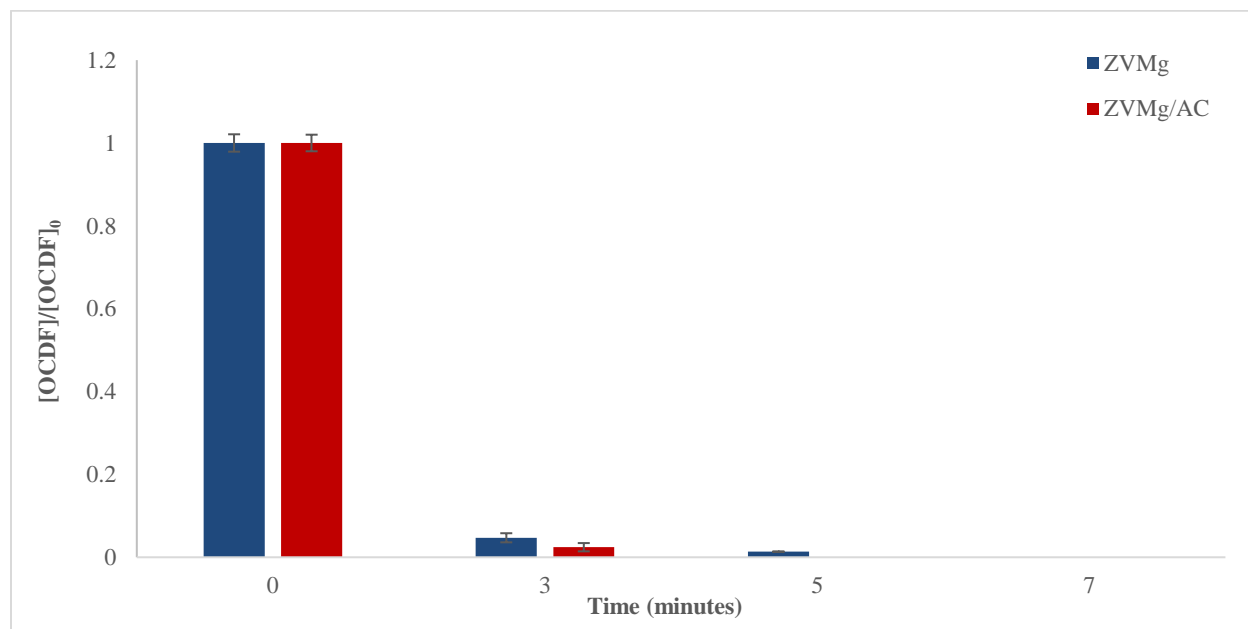


Figure 20: Total OCDF concentration in ball-milled ZVMg and ZVMg/AC in ethanol/ethyl lactate co-solvent system.

Table 4: % Reduction in OCDF concentration under ball-milled ZVMg and ZVMg/AC in ethanol/ethyl lactate (90:10).

Time (minutes)	OCDF Conversion (%)	
	ZVMg in ethanol/ethyl lactate	ZVMg/AC in ethanol/ethyl lactate
3	95.3	97.6
5	98.7	100
7	100	100

OCDF degradation was confirmed by the disappearance of OCDF peak in the GC-MS chromatogram and the detection of different byproduct peaks during the reaction time. The sequential formation of less chlorinated congeners indicates a stepwise dechlorination. Results of the appearance and disappearance of the different congeners obtained from the degradation of OCDF under ball-milled ZVMg and ZVMg/AC in ethanol/ethyl lactate (90:10) are summarized in Table 4. Figure 21 and Figure 22 represent the results of the reductive dechlorination of OCDF and the formation of byproducts over the course of the treatment (28 days). Some data points were not plotted in the figure to improve readability. However, complete time intervals can be found in the appendix as well as selected ion monitoring (SIM) parameters and example chromatograms, of the parent compound and byproducts. As presented in Figure 21, different chlorinated congeners including hepta-, hexa-, penta-, tetra-, tri-, and di-chlorodibenzofuran were produced by ball-milled ZVMg in ethanol/ethyl lactate (90:10) system within the first 3 minutes of the reaction. Monochlorodibenzofuran congener started to form within 1 hour and the chlorine- free congener (dibenzofuran) was detected in the system after 1 day. Contrary to the ZVMg in ethanol system (where complete OCDF degradation was achieved), the presence of

ethyl lactate inhibited the complete conversion of OCDF and its by-products to dibenzofuran.

However, faster kinetics for OCDF and the byproducts were observed in this system.

When activated carbon was used in the system as well as ethyl lactate, better performance was achieved. As demonstrated in Figure 22, the conversion and disappearance of OCDF and the other chlorinated byproducts (from hepta- to tri-chlorodibenzofuran) was faster than that observed in the absence of activated carbon.

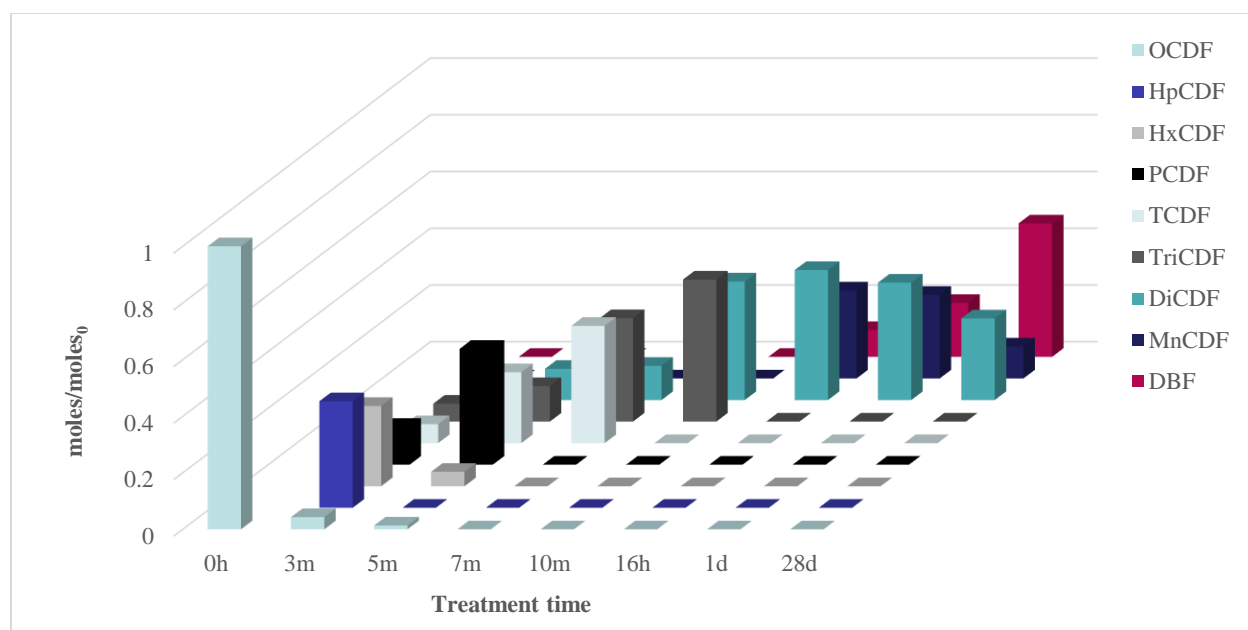


Figure 21: Reductive dechlorination of OCDF by ball-milled ZVMg in ethanol/ethyl lactate (90:10) co-solvent system.

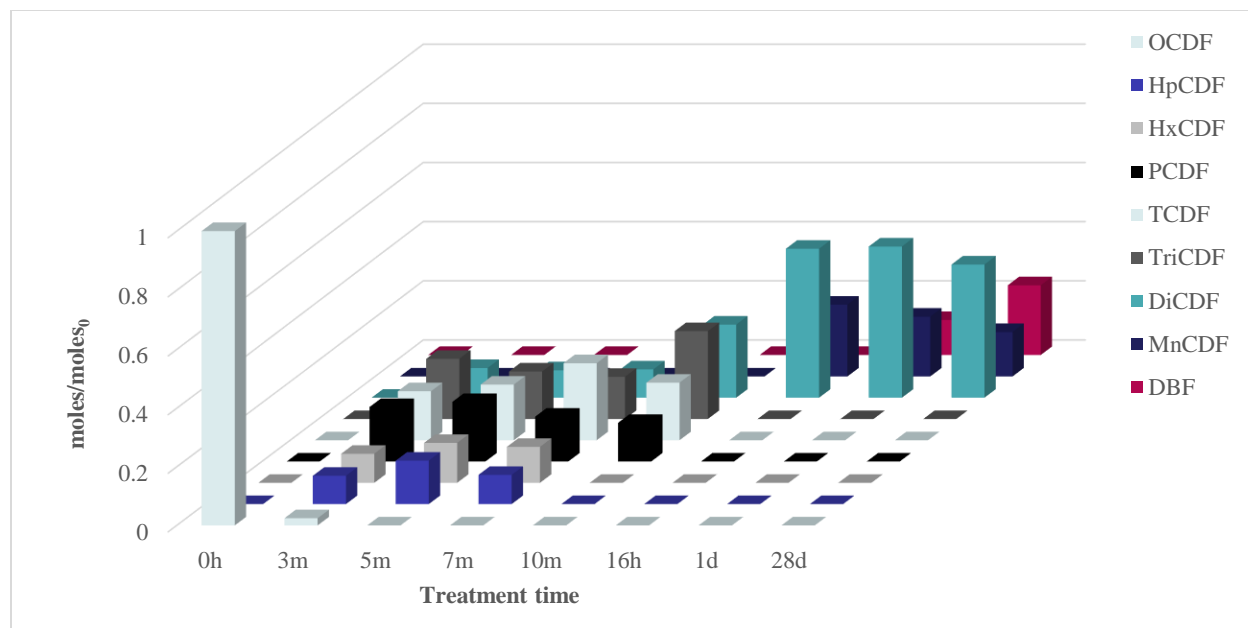


Figure 22: Reductive dechlorination of OCDF by ZVMg with activated carbon in ethanol/ethyl lactate (90:10) co-solvent system.

Table 5: Appearance and disappearance time of the different congeners obtained from the degradation of OCDF under ball-milled ZVMg and ZVMg/AC in ethanol/ethyl lactate (90:10).

Congener	ZVMg + ethanol/ethyl lactate		ZVMg/AC + ethanol/ethyl lactate	
	Appearance	Disappearance	Appearance	Disappearance
OCDF	0h	5m	0h	3m
HpCDF	3m	7m	3m	5m
HxCDF	3m	7m	3m	5m
PCDF	3m	15m	3m	5m
TCDF	3m	15m	3m	7m
TriCDF	3m	4h	3m	15m
DiCDF	3m	-	3m	-
MnCDF	1h	-	30m	-
DBF	1d	-	16h	-

Table 5 summarizes the results obtained from the study of the degradation of OCDF using ethanol/ethyl lactate and ball-milled ZVMg in the presence and absence of activated carbon with respect to the appearance and disappearance of the different congeners. Tetrachlorodibenzofuran, the most toxic congener, was formed within 3 minutes of the reaction in both systems. However, it was degraded within 7 minutes in the presence of activated carbon (in contrast to 15 minutes without activated carbon). Hepta-, and hexa-chlorodibenzofuran were observed in both systems at 3 minutes and degraded after 7 and 5 minutes with ZVMg and ZVMg/AC, respectively. Pentachlorodibenzofuran and trichlorodibenzofuran congeners were also formed during the first 3 minutes of the reaction; however, pentachlorodibenzofuran disappeared after 15 minutes without

and 5 minutes with activated carbon. Trichlorodibenzofuran was observed in the ZVMg system up to 4 hours; whereas, no trichlorodibenzofuran was detected after 15 minutes in the presence of activated carbon.

The Effect of the Addition of Ethyl Lactate as a Co-Solvent

Since pH measurements give information regarding the reaction mechanism of the metal over the time period of the reaction, separate experiments for each system were performed to determine the pH variation during the reaction time. Data obtained from the pH experiments will give a better understanding of the role of ethyl lactate on the activity of the magnesium. The pH of the different systems over time is presented in Figure 23. High pH values were observed in the systems where only acidified ethanol was used as a solvent. This confirms the formation of magnesium oxides/ethoxides in the system over time which in turn will deactivate the magnesium. The addition of 10% ethyl lactate to the system, reduced the polarity of the solution and kept the pH less basic during the first hour of the reaction. The lower pH indicates that less magnesium oxide/ethoxide is formed in the system. This means that the presence of ethyl lactate lowers the solution pH and helps in cleaning the magnesium surface, improving interactions between the analyte and the metal's active sites. It has been found that as ethyl lactate increased, pH decreased and the solution became more neutral. However, a high ethyl lactate concentration is unfavorable due to difficulties in the extraction of the analyte.

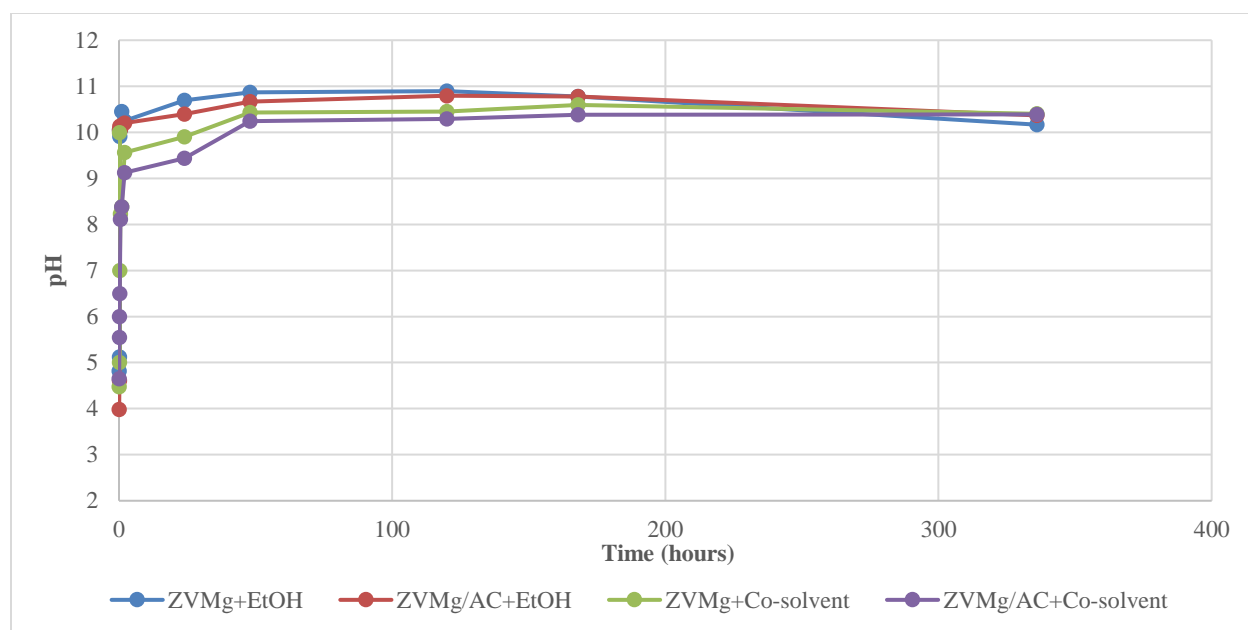


Figure 23: pH of the different systems over time.

The Role of the Addition of Activated Carbon

Activated carbon has shown numerous advantages in past studies towards the degradation of recalcitrant organic pollutants via hydrogenation. This improvement can be attributed to the protection layers offered by graphite to the metal surface which prevent the formation of the oxide layers. Scanning electron microscopy (SEM) were performed in ethanol/ ethyl lactate (90:10) solvent by Zullo, *et. al.* to compare the structure of ball-milled ZVMg before and after the dechlorination reaction with and without activated carbon³³. As obtained in this study, where SEM done in acidified ethanol, ball-milled ZVMg with activated carbon has less agglomerates than ball-milled ZVMg. The abundance of oxygen and carbon relative to magnesium increase with exposure time which is expected due to the formation of passivating oxide/ethoxide layers on the magnesium

surface. The enhanced reactivity of ball-milled ZVMg/AC may also be ascribed to the change in the average particle size of ball milled ZVMg/AC compared with un-milled and milled ZVMg (9 μm vs. 18 and 14 μm , respectively)³⁸. A Smaller particle sizes of ball milled ZVMg/AC leads to greater surface area, thus greater reactivity.

Degradation Kinetics and Mole Balance for the Degradation of OCDF by ZVMg and ZVMg/AC in Ethanol/Ethyl Lactate (90:10) Co-solvent System

In an effort to enhance the reduction systems consisting of ZVMg and ZVMg/AC in ethanol and make them more applicable adaptable to applications, ethyl lactate was added to the systems as a co-solvent and OCDF degradation kinetics were studied. Values of the natural log of OCDF concentration in ethanol/ethyl lactate (90:10) over ZVMg and ZVMg/AC were plotted at each time point and the results are presented in Figure 24 and Figure 25. Kinetics data obtained previously for ball-milled ZVMg and ZVMg/AC in ethanol systems have shown pseudo-first order- kinetics with respect to the analyte degradation rate. In this present study where a new dual system of ethanol/ethyl lactate (90:10) was used, a similar trend was observed.

The kinetics for OCDF degradation using ball-milled ZVMg/AC in ethanol/ethyl lactate were faster than the kinetics of the reaction using ball-milled ZVMg. This can be attributed to the fact that activated carbon facilitates the activation process leading to improved metal reaction kinetics³⁸. The normalized pseudo-first-order rate constants obtained for ethanol/ethyl lactate (90:10) co-solvent system were $k = 0.8727 \text{ min}^{-1}$ and $k = 1.2252 \text{ min}^{-1}$ for the reactions with ball-milled ZVMg and ball-milled ZVMg/AC, respectively.

The mole balance for the dechlorination of OCDF using ball-milled ZVMg and ZVMg/AC in ethanol/ethyl lactate (90:10) after 28 days of the degradation is presented in Figure 26.

Dichlorodibenzofuran, monochlorodibenzofuran, and dibenzofuran concentration were nearly constant in both systems after the first week up to the end of the study. No significant di- and monochlorodibenzofuran degradation occurred through the end of the study. Higher concentration of dichlorodibenzofuran (45.1%) was observed in the presence of activated carbon compared to only ball-milled ZVMg (28.8%). This can be attributed to the desorption effect of activated carbon which occurred more significant in the case of low chlorinated congeners which is also accounted for the decrease in the mole balance when activated carbon is used. The monochlorodibenzofuran congener corresponded to 11.3% and 15.0% of the final products of ball-milled ZVMg and ZVMg/AC systems, respectively. Higher conversion to DBF, the chlorine- free compound, was achieved by ball-milled ZVMg (47.0% vs. 23.6% for ZVMg/AC). The overall mole balances for ball-milled ZVMg and ZVMg/AC are 87.1% and 83.7, respectively.

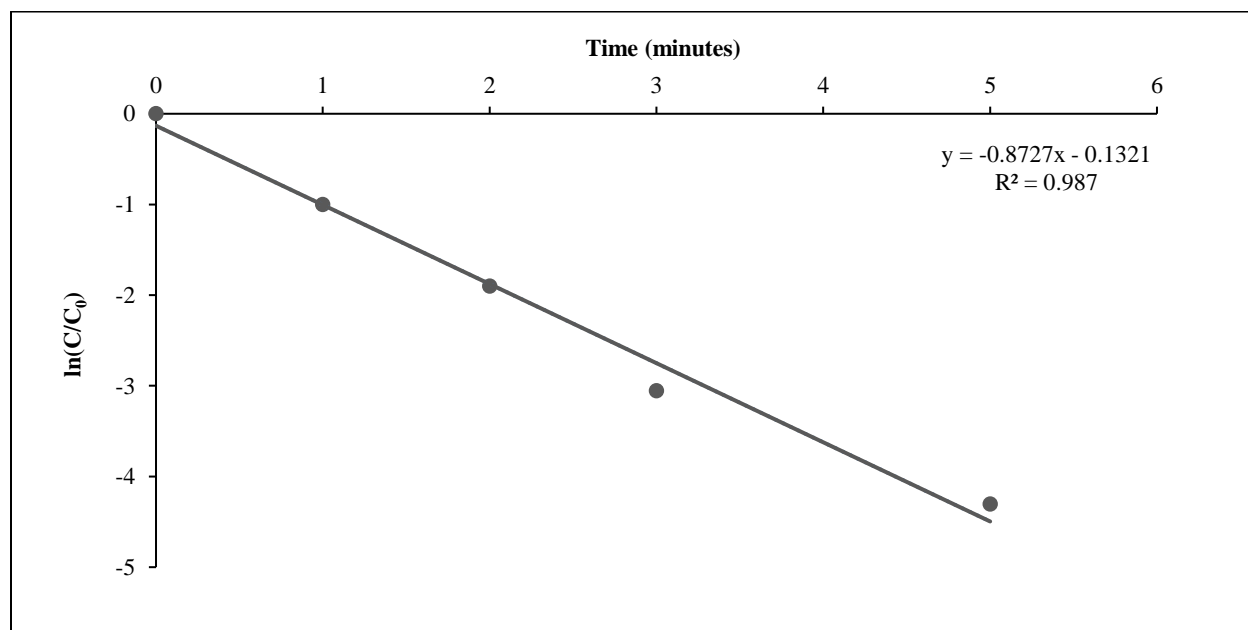


Figure 24: Pseudo-first-order kinetics plot for the degradation of OCDF over ZVMg in ethanol/ethyl lactate (90:10) system.

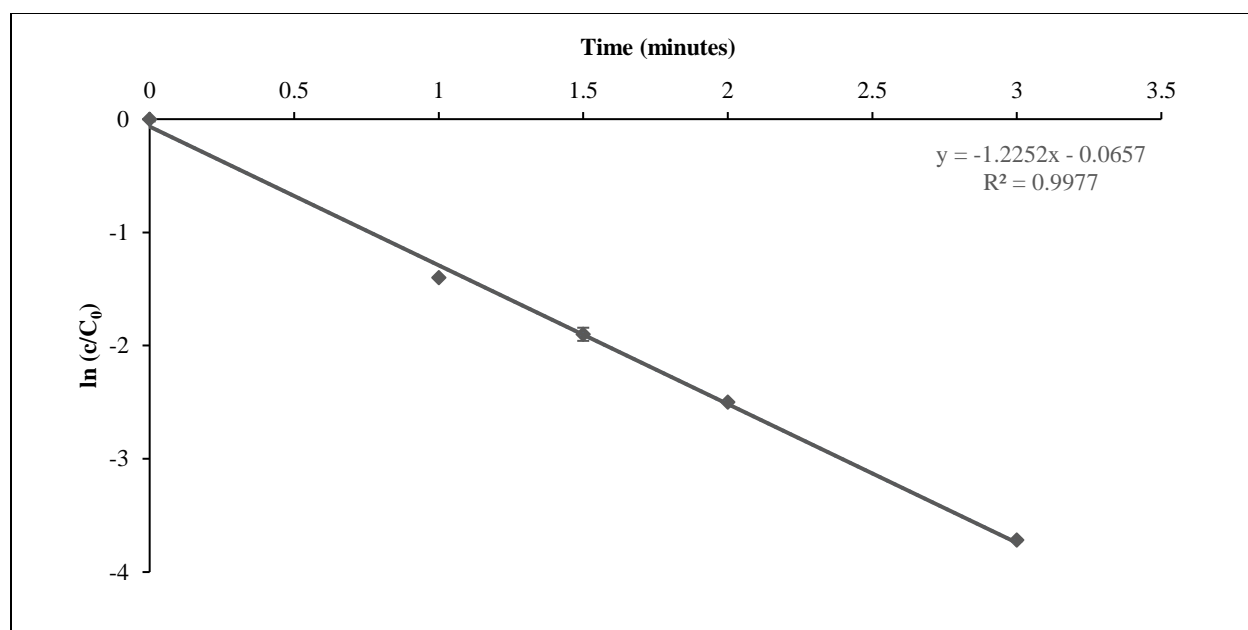


Figure 25: Pseudo-first-order kinetics plot for the degradation of OCDF over ZVMg/AC in ethanol/ethyl lactate (90:10) system.

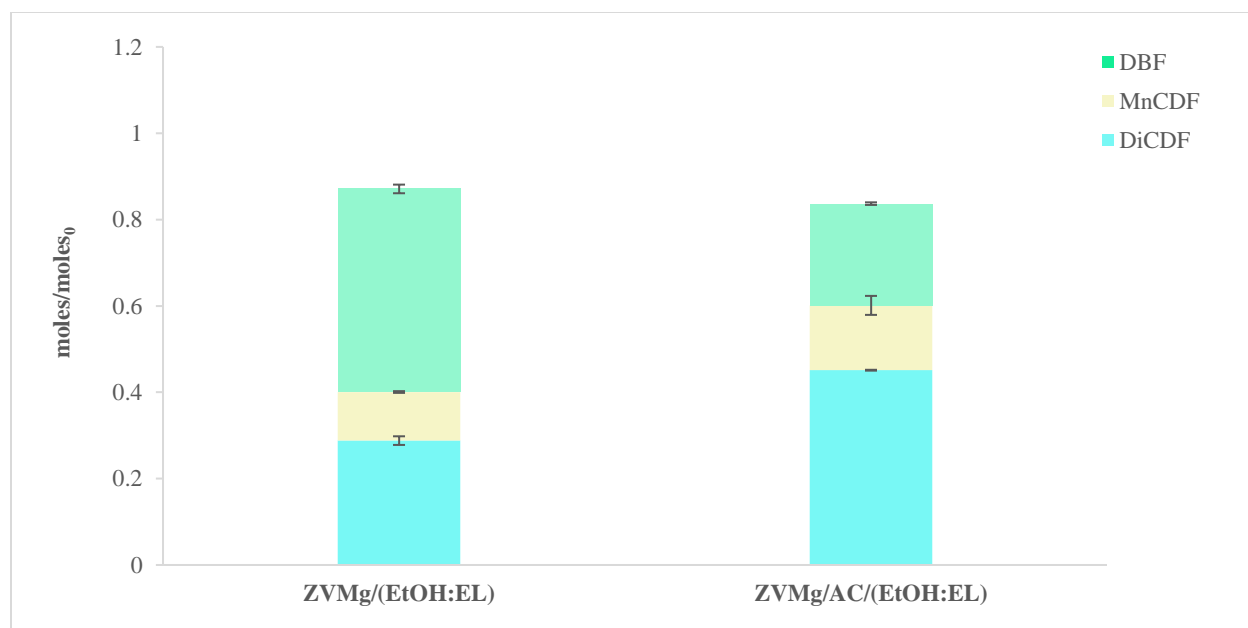


Figure 26: Mole balance for OCDF dechlorination using ball milled ZVMg and ZVMg/AC in ethanol/ethyl lactate (90:10) after 4 weeks of treatment.

Effect of the Addition of Ethanol or Acetic Acid on the Degradation Reaction

Experiments were conducted to examine whether re-spiking the system with glacial acetic acid (50 μ L) or with ethanol (5mL) enhances the dechlorination process of OCDF in the ball-milled ZVMg and ethanol/ethyl lactate (90:10) system. Moreover, the re-spike experiments were performed in an effort to completely transform all chlorinated byproducts to dibenzofuran. For this study, two systems were designed. In both systems, OCDF was degraded as previously described (5 mL of OCDF solution in ethanol/ethyl lactate (90:10) + 250 mg of ball-milled ZVMg + 50 μ L of glacial acetic). Samples were placed on a shaker table for 1 week. Then, half of the samples were re-spiked with 50 μ L of glacial acetic acid while the other half were re-spiked with 5 mL ethanol. At designated time points (1, 2 and 3 weeks after re-spiking), samples were collected and analyzed by GC-MS. The results are illustrated in Figure 27 and Figure 28. After 1 week of treatment with ethanol/ethyl lactate (90:10) and before re-spiking the samples, OCDF was completely degraded to dichlorodibenzofuran, monochlorodibenzofuran, and dibenzofuran. One week after re-spiking, there was a significant decrease in dichlorodibenzofuran concentration associated with an increase in the concentrations of monochlorodibenzofuran and dibenzofuran in both systems. Figure 27 demonstrates that the addition of acetic acid slightly enhances the degradation of the dichlorodibenzofuran congener compared to the addition of ethanol.

When the samples were analyzed 2 weeks after the re-spike, dichlorodibenzofuran and monochlorodibenzofuran were further degraded which was confirmed by a decrease in their concentrations and an increase in dibenzofuran concentration. The samples were also analyzed after 3 weeks and the concentrations of dichlorodibenzofuran, monochlorodibenzofuran, and dibenzofuran stayed more or less constant in both systems. It can be concluded that the re-spike

process with either acetic acid or ethanol was beneficial in converting a high percentage of the formed by-products (di- and mono-chlorodibenzofuran) to dibenzofuran. At the end of this study, trace concentrations of di- and mono-chlorodibenzofuran were detected in both systems; however, dibenzofuran was the major by-product. No complete transformation to dibenzofuran was observed by either system.

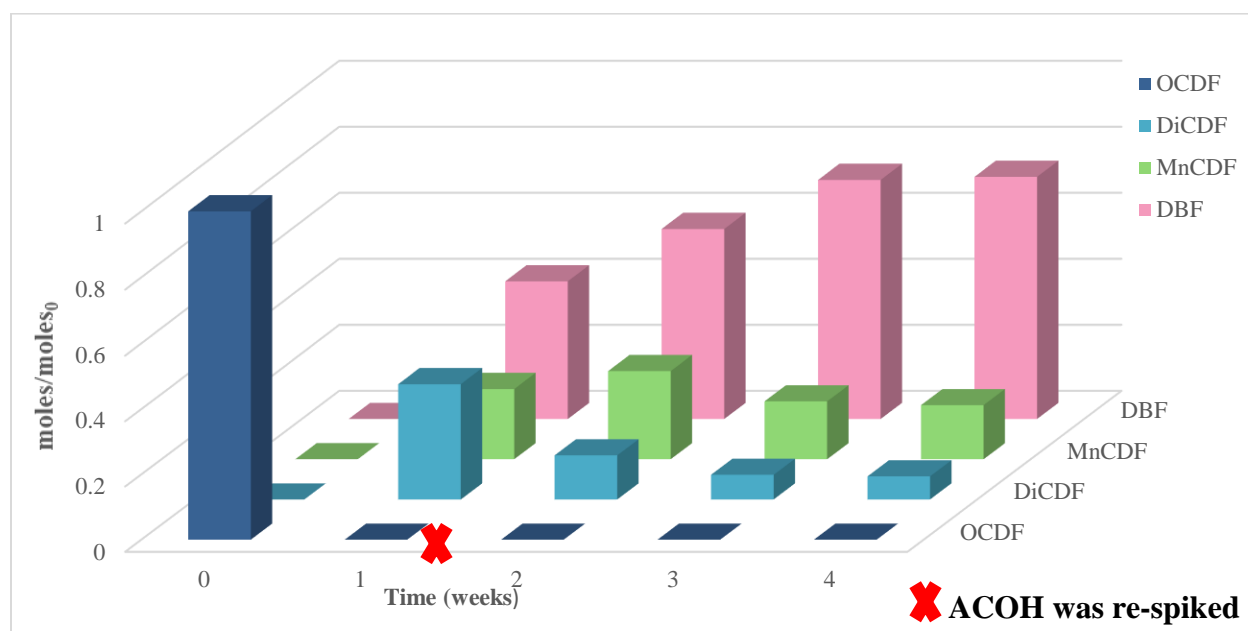


Figure 27: Degradation of OCDF in ball-milled ZVMg and ethanol/ethyl lactate (90:10) with the addition of acetic acid.

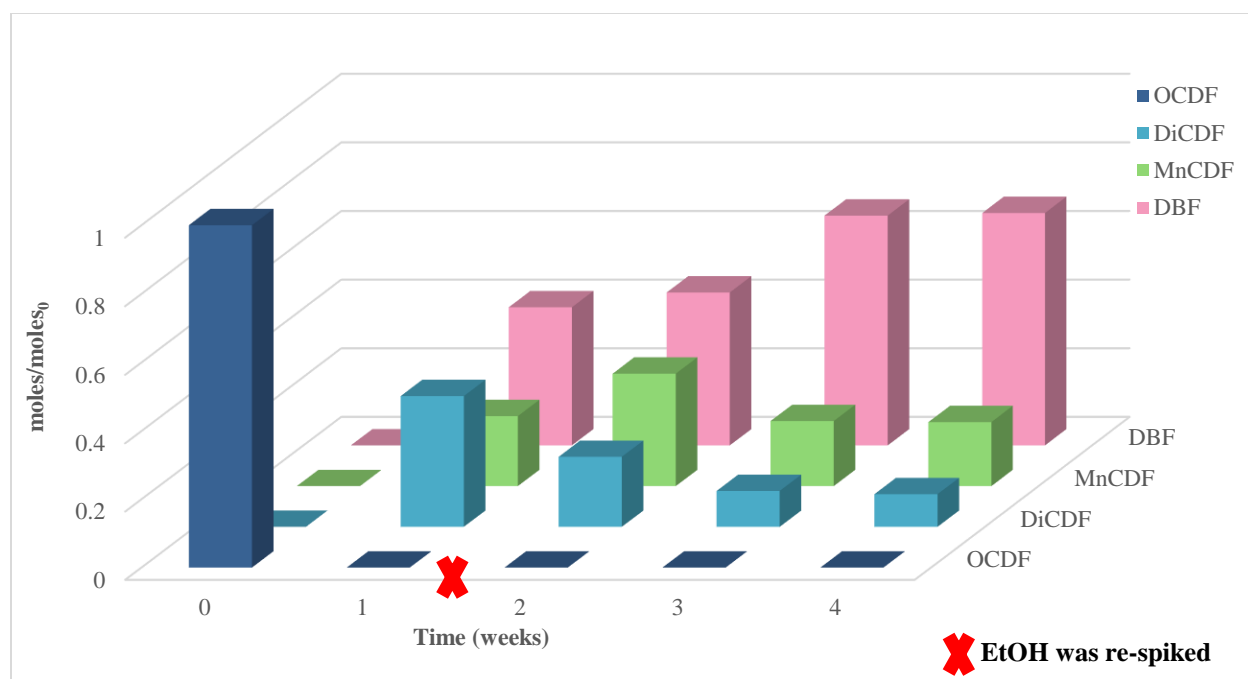


Figure 28: Degradation of OCDF in ball-milled ZVMg and ethanol/ethyl lactate (90:10) with the addition of ethanol.

Conclusion

A new solvent system consisting of absolute ethanol and ethyl lactate (90:10) was used in this chapter to evaluate the advantages of the addition of ethyl lactate as a co-solvent on the degradation efficiency of OCDF. Complete OCDF degradation was obtained in this solvent system with ball-milled ZVMg and ZVMg/AC. In this study, results on the degradation kinetics of OCDF and other congeners (hepta- to tri-chlorodibenzofuran) indicate the presence of activated carbon enhances the degradation process and faster OCDF removal kinetic were therefore obtained. However, no complete conversion to dibenzofuran was achieved in the presence of ethyl lactate.

Time-course measurements of pH indicate that the addition of 10% ethyl lactate lowers the pH of the solution as compared to ethanol. This keeps the magnesium active for a longer time, in contrast to the use of only ethanol where magnesium oxides/ethoxides are formed in the system over time (as confirmed by the high pH values), deactivating the magnesium.

When the systems of ethanol/ethyl lactate (90:10) and ball-milled ZVMg were studied after re-spiking the reaction vials with 50 μ L glacial acetic acid or 5 mL ethanol after one week of the treatment, enhanced results were obtained. However, complete conversion to dibenzofuran was still not achieved in either system. The major advantage of the re-spiking process was that a high percentage of di- and mono-chlorodibenzofuran were converted to dibenzofuran, with acetic acid yielding a greater formation of dibenzofuran.

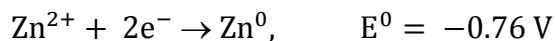
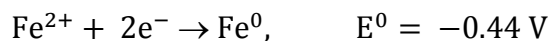
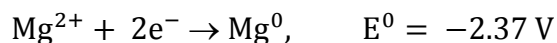
CHAPTER FOUR: REDUCTIVE DECHLORINATION OF OCDF UNDER BALL-MILLED ZVMG AND ZVMG/AC IN ACIDIFIED 2-BUTOXYETHANOL

Introduction

Polychlorinated dibenzofurans (PCDFs) with a generic formula $C_{12}H_nCl_{8-n}O$ are a major group of persistent organic pollutants (POPs). This class of tricyclic aromatic hydrocarbons contains 135 congeners that are known to be highly toxic and have been classified as human carcinogens by the International Agency for Research on Cancer (IARC)³⁵. PCDFs have never been produced intentionally; however, they are produced as unwanted byproducts from different anthropogenic and natural activities which makes it difficult to regulate PCDF production. Industrial combustion processes including metal smelters, coal-fired power plants, cement kilns, and waste incinerators are the primary emission sources of PCDFs⁴. Due to their lipophilicity, they have a high potential to bioaccumulate in the food chain. As a result, ingestion is considered the predominant human exposure pathway. PCDF exposure poses a great hazard to the environment and human health. PCDF exposure can lead to serious health problems such as endocrine disruption, reproductive problems, immunotoxicity, liver damage, and cardiovascular disorders^{34, 49, 52}. Based on some of the epidemiologic studies done in France and the United States, low level exposure to PCDFs may lead to an increased risk of non-Hodgkin's lymphoma (NHL)⁶³. Therefore, scientific and public concerns have been aroused all over the world due to the toxicity and negative effects of PCDFs on the environment and human health.

The Stockholm Convention establishes that POPs should be destroyed or irreversibly transformed in order to reduce or eliminate their release to the environment⁶. Several technologies have been adopted for the remediation and degradation of PCDFs. These technologies include advanced oxidation processes (for example, Fenton and Fenton-like reactions, photolysis, and photocatalysis), microbial degradation, thermal, and chemical processes⁴⁵. However, the high cost and energy, and/or the low efficiencies associated with these treatments have led to the development of alternative technologies⁶⁴. One of the most effective methods that has shown great potential in the degradation and removal of POPs is the use of zero-valent metals^{8, 9, 11, 38}. The use of zero-valent metals for the reductive dechlorination of recalcitrant organic pollutants has attracted significant attention for *in situ* remediation since it is a rapid, environmentally friendly, and cost-effective process.

The use of zero-valent magnesium is favorable due to the advantages of magnesium over other metals used for the reductive dechlorination such as iron and zinc³⁸. Magnesium has the greatest reactivity when compared with iron and zinc as demonstrated by their reductive potentials given in the following equations¹²



Furthermore, magnesium has the capability to reductively dechlorinate chlorinated compounds even after exposure to oxygen, due to the formation of a self-limiting oxide layer on the magnesium surface allowing the metal to work under ambient conditions. This is in contrast to

iron metal which requires anaerobic conditions due to the formation of the oxide layer on the iron surface inhibiting the dechlorination process.

Previous studies done in chapter two and three were conducted in two different solvent systems (ethanol and ethanol/ethyl lactate (90:10)). Each system was examined over ball-milled ZVMg and ZVMg with activated carbon to evaluate the efficacy of the systems to dechlorinate different PCDF congeners. For the fully chlorinated congener OCDF, complete degradation was achieved by all the studied systems. It was noticed that when ball-milled ZVMg in ethanol was used, the chlorine atoms of OCDF and all the formed byproducts were removed and complete conversion to the chlorine free compound dibenzofuran was achieved. However, the kinetics of this system were slow compared with the other systems. In the case of the other three systems (ZVMg/AC in ethanol, ball-milled ZVMg with and without AC in ethanol/ethyl lactate (90:10)), although faster kinetics were achieved, no complete conversion to dibenzofuran was accomplished. In this chapter, a new solvent was introduced in an effort to enhance the degradation process and overcome the limitations of the other systems studied in the previous chapters. This new solvent is 2-butoxyethanol.

2-Butoxyethanol is derived from the glycol ether family, with a chemical formula of $\text{BuOC}_2\text{H}_4\text{OH}$. The chemical structure of 2-butoxyethanol is presented in Figure 29. 2-Butoxyethanol is an organic polar solvent. Two functional groups are present in 2-butoxyethanol which are the ether and alcohol groups. This solvent has the ability to dissolve both hydrophobic as well as water-soluble substances. 2-Butoxyethanol is widely used as a solvent for inks, paints, cleaning products, and surface coatings. It has also received approval by the U.S. FDA to be used as a food additive⁶⁵ (direct or indirect) including in stabilizers, antimicrobial agents, adhesives,

and defoamers. Furthermore, it is used in pharmaceuticals, herbicides, and many consumer products such as soaps, hair dyes, industrial and household cleansers, and cosmetics⁶⁶⁻⁶⁸.

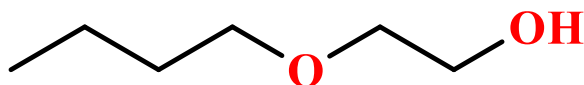


Figure 29: Molecular structure of 2-butoxyethanol.

The green solvent 2-butoxyethanol was chosen for this study since it can serve as a solvent and a great proton donor for OCDF hydrodechlorination. The overall goal for this chapter is to evaluate the efficiency of employing a 2-butoxyethanol reduction system in the degradation of the high-chlorinated congener OCDF as well as the low-chlorinated congener 2,8-dichlorodibenzofuran under mild conditions. The study was done in the presence of ball-milled ZVMg and ball-milled ZVMg with activated carbon. Kinetics of the reductive dechlorination of both congeners were examined and the degradation byproducts were identified. Furthermore, this chapter includes a proposed degradation pathway for 2,8-dichlorodibenzofuran.

Experimental

Chemicals and Materials

Neat OCDF and 2,8-dichlorodibenzofuran congeners in solid form were purchased from Accustandard and their stock solutions were prepared in 2-butoxyethanol. 2-Butoxyethanol 99%, ACROS Organics was obtained from Fisher Scientific. Neat dibenzofuran standard, 1,2,3,4,6,7,8-heptachlorodibenzofuran, 2,3,4,7,8-pentachlorodibenzofuran, and 2,3,4,8-tetrachlorodibenzofuran standard solutions were also acquired from Accustandard. Optima[®] grade

toluene and glacial acetic acid (≥ 99.8) were obtained from Fisher Scientific and Acros Organics, respectively. Micro-scale un-milled magnesium ($\sim 4 \mu\text{m}$) and activated carbon (charcoal G-60) were acquired from Heart Metals (Tamaqua, PA) and Matheson Coleman & Bell (Gardena, CA). They were used as received. All chemicals were of high purity (≥ 99.8). Nylon filters of $0.45 \mu\text{m}$ pore size were supplied from Fisher Scientific (Pittsburg, PA).

Preparation of Ball-milled ZVMg and ZVMg/AC Bimetal

The mechanical ball-milling process for ZVMg was done by adding 85.0 g of magnesium powder to the galvanized steel canisters containing sixteen stainless steel ball bearings (1.6 cm diameter). Canisters are 5.03 cm in internal diameter and 17.80 cm in length. The ball-milling was done in an argon atmosphere for 45 minutes using a Red Devil 5400 Series Paint Shaker. A similar procedure was followed for the preparation of the ball-milled ZVMg with activated carbon using 76.5 g of ZVMg and 8.5 g of activated carbon.

Dechlorination of PCDFs in 2-Butoxyethanol

Solutions containing $20 \mu\text{g mL}^{-1}$ of OCDF or $20 \mu\text{g mL}^{-1}$ of 2,8-dichlorodibenzofuran were prepared in 2-butoxyethanol. 5 mL of the standard solution was added to 20 mL glass vials containing 0.25 mg of ball-milled ZVMg or ZVMg/AC. Then, 50 μL of glacial acetic acid was added to each vial. The vials were placed on a Lab Companion Reciprocating Shaker Table (Series K-57013) at 200 rpm.

Sample Extraction

Samples were extracted by adding 5 mL toluene to each vial and the vials were shaken by hand for 2 minutes. Then, the mixture was transferred into another vial (40 mL). For each vial, 12 mL of a mixture containing sulfuric acid (0.3 M) and acetic acid (6.3 M) was added to protonate the ether-oxygen in 2-butoxyethanol. After that 5 mL of deionized water was added to the vials and the mixture was shaken by hand for 2 minutes followed by centrifugation for 20 minutes. Two more water washes were performed and the top organic layer was collected, filtered and saved for further analysis. All experiments were done in duplicate. Control experiments were conducted without metal.

Analysis

PCDFs present in samples were analyzed by gas chromatography with mass spectrometry on an Agilent Technologies 7990 GC/MS system equipped with an autosampler. The column used was a Restek RTX®-5 column (0.25 mm i. d., 0.25 μ m film thickness) and the carrier gas was helium with a constant flow set to 2 mL/min. The injector temperature was set at 250 °C and the ion source temperature was set to 280 °C. The initial oven temperature was 140 °C, then the column was ramped at 3 °C /min to 300 °C for OCDF analysis and to 200 °C for 2,8-dichlorodibenzofuran analysis. Injection volume was set at 1 μ L and it was performed in splitless mode. Identification of PCDF congeners was based upon the retention times of known standards and verified via their mass spectra. For unavailable standards, identification was done by comparing the mass spectra to reference spectra catalogued in the National Institute of Standards and Technology (NIST).

Computational Method

In this research, the Gaussian 09 software package was used for all DFT calculations. B3LYP functionals and 6-31G (d,p) basis set were applied for all optimization and frequency calculations. In order to further improve the accuracy, the Polarizable Continuum Model (PCM) was applied for systems with solvent. For ethanol, the static and dynamic dielectric constants were set to 24.852 and 1.853, respectively. For 2-butoxyethanol, the two dielectric constants were set to 5.30 and 2.008, respectively.

Results and Discussion

2-Butoxyethanol has become an attractive proton source for reductive reactions. 2-Butoxyethanol is highly acidic due to the presence of the ether group (electron withdrawing group) in its structure. Therefore, the influence of this new solvent on the reductive dichlorination of OCDF with ball-milled ZVMg with and without activated carbon was studied. As shown in Figure 30, the reaction of OCDF in acidified 2-butoxyethanol and ball-milled ZVMg or ZVMg with activated carbon produces dibenzofuran, magnesium chloride, and magnesium 2-butoxyethoxide.

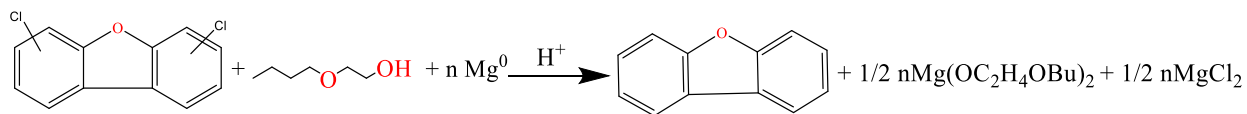


Figure 30: Reductive dechlorination reaction of OCDF in acidified 2-butoxyethanol.

Efficacy of 2-butoxyethanol for the Dechlorination of OCDF in Ball-Milled ZVMg and ZVMg/AC

In order to investigate the efficiency of the new solvent to reductively dechlorinate OCDF, two separate experiments were conducted at room temperature for OCDF ($20\ \mu\text{g mL}^{-1}$) in acidified 2-butoxyethanol and ball-milled ZVMg with and without activated carbon. In both systems, satisfactory results were obtained. Full OCDF degradation was achieved within the first 7 minutes of the reaction in both systems. Results of the reduction in OCDF concentration over time for both systems are presented in Figure 31 and summarized in Table 6. In the ball-milled ZVMg system, approximately 62% and 78% reduction in OCDF concentration was achieved after 3 and 5 minutes of the reaction, respectively. Faster degradation for the same concentration of OCDF was obtained in the first 5 minutes when activated carbon was used. In this system, 70.9% and 81.0% of OCDF initial concentration were reduced within 3 and 5 minutes of the treatment, respectively.

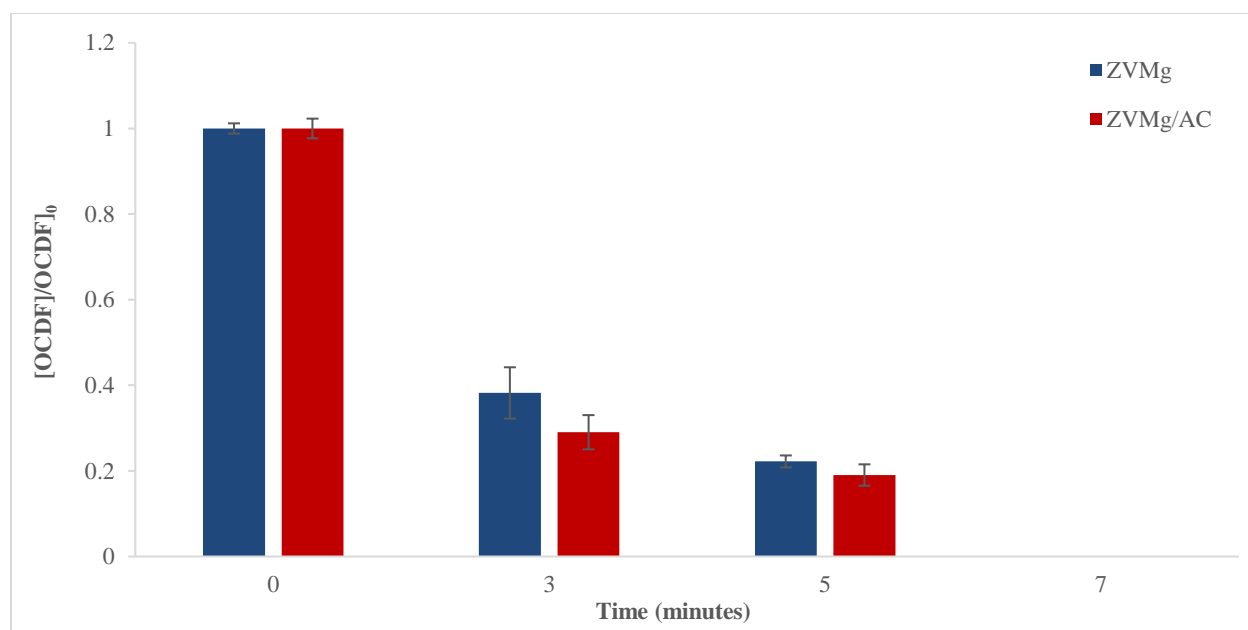


Figure 31: Reduction in OCDF concentration over time using ball-milled ZVMg and ZVMg/AC in acidified 2-butoxyethanol.

Table 6: % reduction in OCDF concentration under ball-milled ZVMg and ZVMg/AC in 2-butoxyethanol.

Time (minutes)	OCDF Reduction (%)	
	Ball-milled ZVMg in 2-butoxyethanol	ZVMg/AC in 2-butoxyethanol
3	61.8	70.9
5	77.8	81.0
7	100	100

Characterization and Identification of OCDF Degradation Products

Products for the degradation of OCDF in 2-butoxyethanol were characterized and identified by GC-MS. An analysis of the distribution of products from the reductive dechlorination of OCDF over ball-milled ZVMg and ZVMg/AC are presented in Figure 32 and Figure 33 and summarized in Table 7. The presented mole balance was calculated as the ratio of the total PCDF congeners measured at each sampling point to the initial OCDF moles measured in the system. For the degradation of OCDF by ball-milled ZVMg, hepta-, hexa-, penta-, tetra-, and tri-chlorodibenzofuran congeners started to form within the first 3 minutes of the reaction. After 5 minutes, heptachlorodibenzofuran was not detected in the system; whereas, hexa-, penta-, and tetra-chlorodibenzofuran were degraded after 10 minutes of the reaction. Trichlorodibenzofuran was removed after 15 minutes. Dichlorodibenzofuran was formed within 10 minutes and was observed by the GC-MS until the end of this study (4 weeks). In case of monochlorodibenzofuran, it was initially observed at the 1 hour time point and disappeared after 4 days. Dibenzofuran, the chlorine-free congener, was formed within 20 hours and its concentration increased over time. After 1 week, its concentration was almost constant up to the end of this study (Figure 32).

The results obtained for OCDF degradation when activated carbon was added to the system are presented in Figure 33. As shown in the figure, OCDF was completely removed from the system after 5 minutes of the reaction and this was accompanied by the observation of less chlorinated congeners. As in the previous system (ZVMg and 2-butoxyethanol), hepta-, hexa-, penta-, tetra-, and tri-chlorodibenzofuran congeners were formed during the first 3 minutes. Hepta-, hexa-, and penta-chlorodibenzofuran congeners were completely degraded after 5 minutes, while tetra- and tri-chlorodibenzofuran congeners were degraded after 10 and 30 minutes, respectively.

Di- and mono-chlorodibenzofuran congeners were formed within 5 minutes and 4 hours, respectively. However, the dichlorodibenzofuran was more stable and exists in the system until the end of the treatment time. After 2 weeks of the treatment, no monochlorodibenzofuran was detected by the GC-MS. It is important to mention that the systems of ZVMg with and without activated carbon in 2-butoxyethanol were effective in removing the last chlorine atom of the monochlorodibenzofuran congener, converting it to dibenzofuran in contrast to other previous systems (ZVMg/AC in ethanol, ZVMg and ZVMg/AC in ethanol/ethyl lactate) where the monochlorodibenzofuran congener existed in the systems until the end of the treatment time.

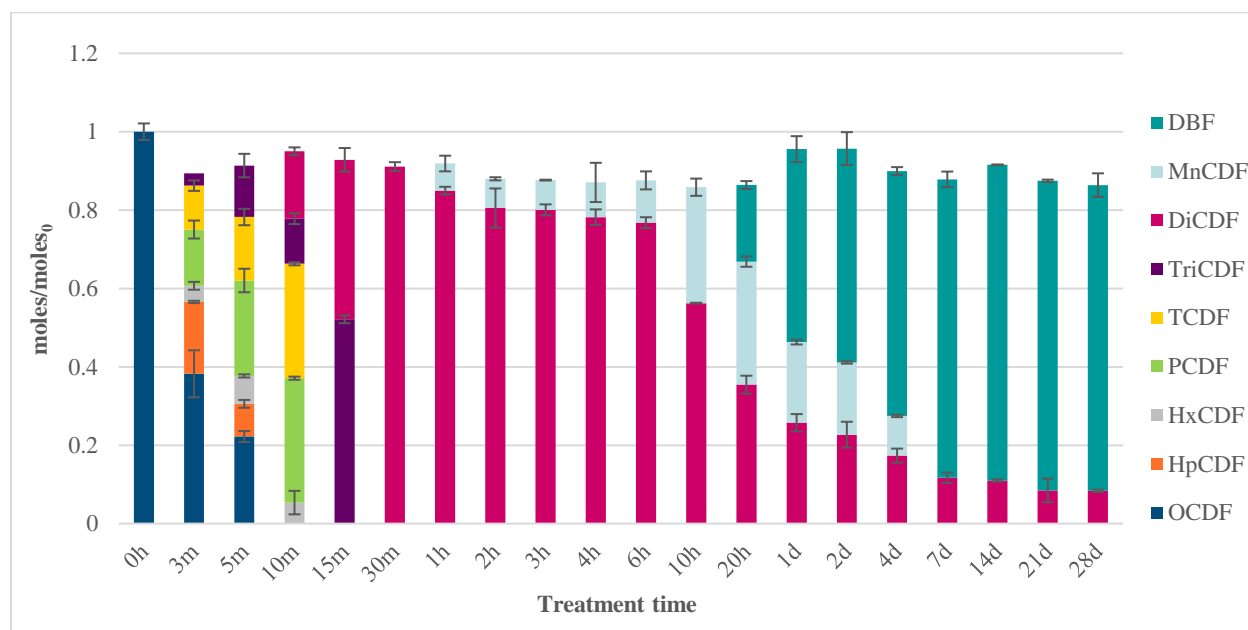


Figure 32: Distribution of OCDF and the dechlorination products in acidified 2-butoxyethanol over ball-milled ZVMg.

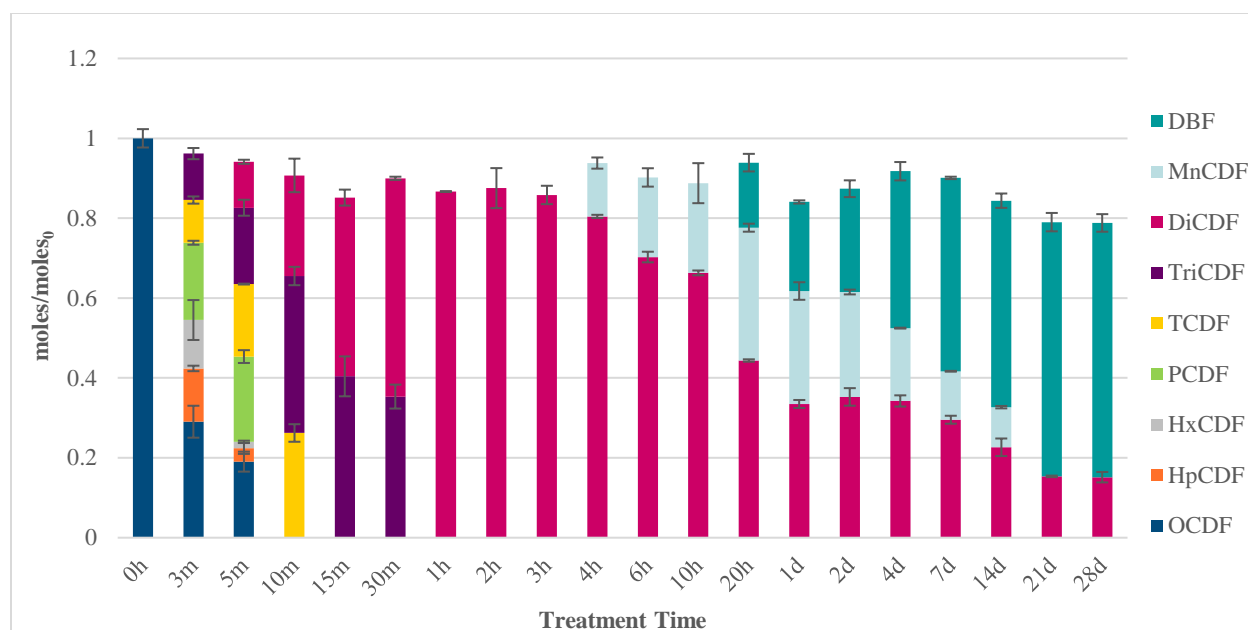


Figure 33: Distribution of OCDF and the dechlorination products in acidified 2-butoxyethanol over ZVMg/AC.

Table 7: Appearance and disappearance of the different congeners obtained from the degradation of OCDF under ball-milled ZVMg and ZVMg/AC in 2-butoxyethanol.

Congener	Ball-milled ZVMg + 2-butoxyethanol		ZVMg/AC + 2-butoxyethanol	
	Appearance	Disappearance	Appearance	Disappearance
OCDF	0h	5m	0h	5m
HpCDF	3m	5m	3m	5m
HxCDF	3m	10m	3m	5m
PCDF	3m	10m	3m	5m
TCDF	3m	10m	3m	10m
TriCDF	3m	15m	3m	30m
DiCDF	10m	-	5m	-
MnCDF	1h	4h	4h	2w
DBF	20h	-	20h	-

Degradation Kinetics and Mole Balance for the Degradation of OCDF by ZVMg and ZVMg/AC

Results from previous kinetic studies done on the degradation of OCDF in different solvent systems using excess ZVM have shown a pseudo-first-order decay model with respect to the disappearance of the analyte. A similar result was obtained in the 2-butoxyethanol system. Figure 34 and Figure 35 present the pseudo-first-order plots with respect to the disappearance of OCDF treated by ball-milled ZVMg and ZVMg/AC in acidified 2-butoxyethanol. The system containing activated carbon exhibited faster kinetics than the system containing only ball-milled ZVMg. The observed enhancement was expected since the presence of activated carbon facilitates the activation process, leading to improved reaction kinetics³⁸. Full OCDF removal was accomplished after 5 minutes of the reaction with pseudo-first-order rate constants of $k = 0.3021 \text{ min}^{-1}$ and $k = 0.3380 \text{ min}^{-1}$ for the reactions of ZVMg and ZVMg/AC, respectively.

It was noticed that by using 2-butoxyethanol as a solvent, complete conversion to dibenzofuran was not accomplished with either ball-milled ZVMg or ZVMg/AC. In ball-milled ZVMg, nearly 78.0% conversion to dibenzofuran was achieved compared to 63.6% conversion in the presence of activated carbon. Dichlorodibenzofuran remained present in very low concentrations in both systems with a percentage of 8.4% without and 15.2% with activated carbon. The mole balances for the degradation of OCDF in acidified 2-butoxyethanol over a 4-week study were 86.4% and 78.8% using ball-milled ZVMg and ZVMg/AC, respectively (Figure 36).

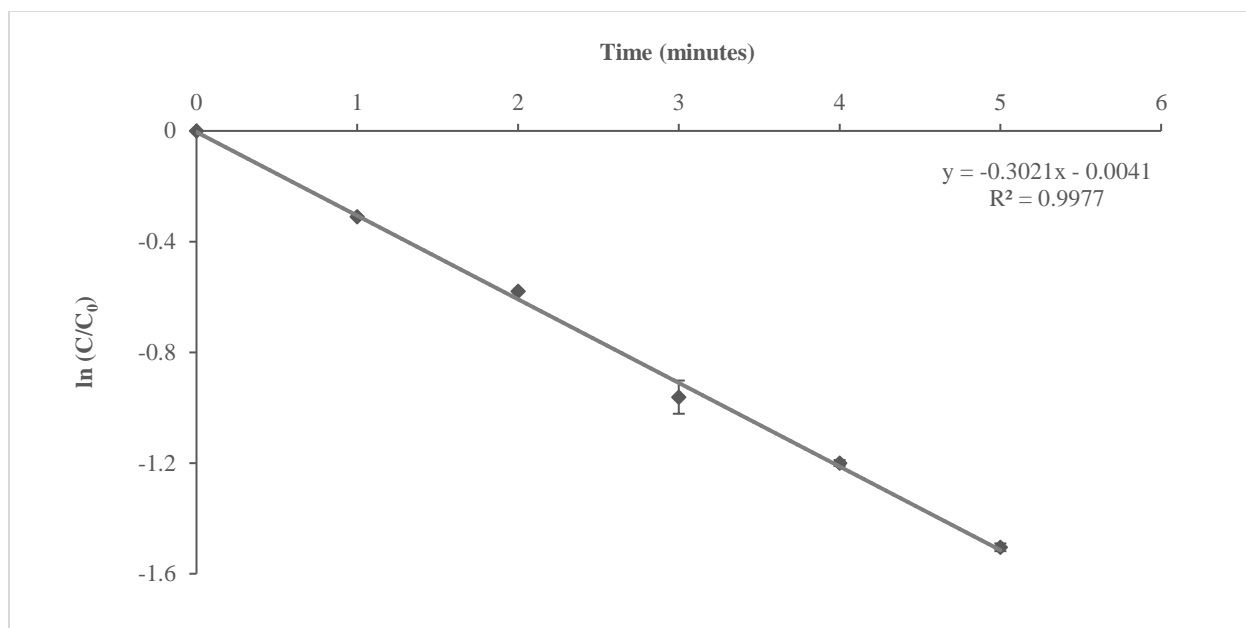


Figure 34: Pseudo-first-order decay model for the degradation of OCDF using ball-milled ZVMg in an acidified 2-butoxyethanol.

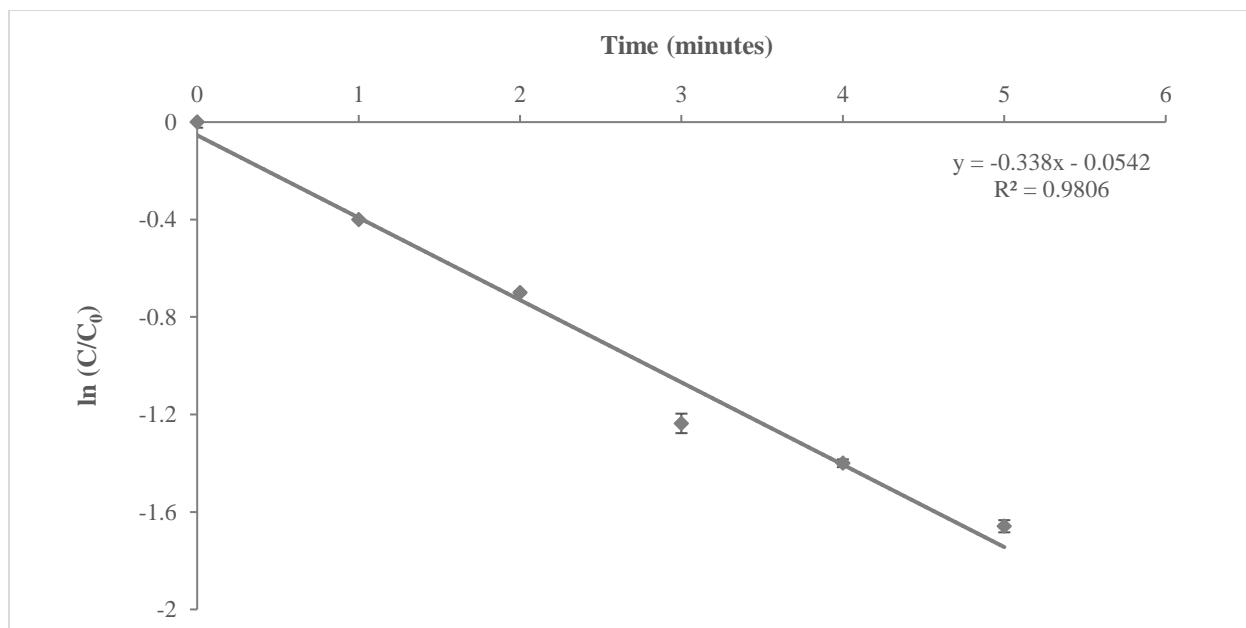


Figure 35: Pseudo-first-order decay model for the degradation of OCDF using ball-milled ZVMg/AC in an acidified 2-butoxyethanol.

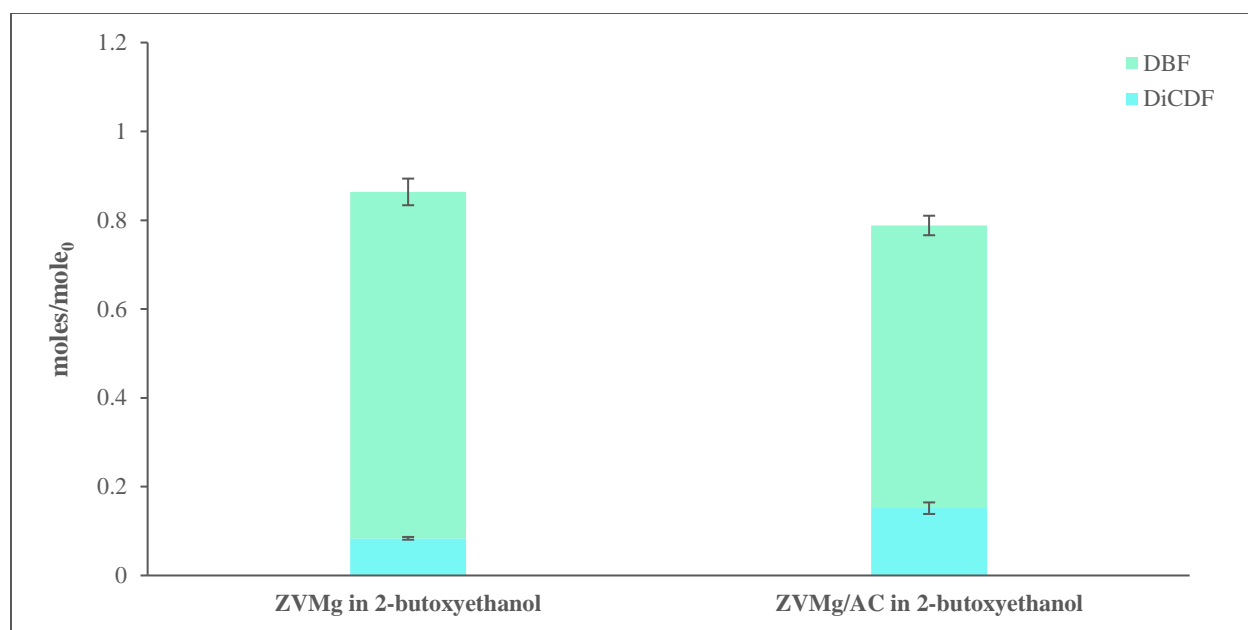


Figure 36: Mole balance for the degradation of OCDF in 2-butoxyethanol over ZVMg and ZVMg/AC after 4 weeks.

Proposed Pathway for OCDF Dechlorination

Figure 38 presents a schematic of the proposed pathway for the reductive dechlorination of OCDF. The same intermediates were observed on all OCDF experiments previously described. This pathway was based on the characterization of the observed byproducts at different times of the reaction by GC-MS. PCDF congeners were identified based upon ion mass to charge (m/z) ratios and comparison to retention times of available standards. Although not all of the products of OCDF degradation could be unequivocally identified (due to the lack of commercially available standards), chlorinated congeners that were not available as standards were identified based on their mass spectra. It was assumed that the congener with the largest peak area observed in the analysis of the degraded samples was the main degradation product. Thus, the main degradation pathway was determined on the basis of the main products. Only the main dechlorination pathway is discussed even though some minor peaks were detected in this study. Since the molecule is symmetric, the removal of the first chlorine atom from a given position on either ring will result in the formation of the same congener. Thus, four possible heptachlorodibenzofuran congeners could be formed. The activation energies for the first step (the removal of the first chlorine atom) were calculated using Gaussian 09 as described previously. The results shown in Figure 37 and Table 8. The result in Figure 37 indicates that the removal of the chlorine atom in the 1 or 9 position has the lowest activation energy compared to the removal of a chlorine from other positions. This is in agreement with the experimental results. Therefore, the first step of the dechlorination includes the removal of a chlorine atom from the 9 position forming 1,2,3,4,6,7,8-HpCDF in a similar manner to previous studies done on the degradation of OCDF^{57, 69, 70}. *Heliman et al.* has mentioned that steric crowding occurs at the 1 and 9- positions of OCDF. Therefore, the loss of

the chlorine in the 1 or 9-position is preferable since it serves to relieve the steric strain in the molecule⁶⁹.

Based on the identified penta- and tetra-chlorodibenzofuran intermediates, three possible hexa-CDF congeners could be formed from the removal of the second chlorine atom. These congeners are 2,3,4,6,7,8-HxCDF, 1,2,3,4,7,8-HxCDF, and 1,2,3,6,7,8-HxCDF. These congeners were not confirmed by the GC-MS owing to the lack of authentic standards. However, 2,3,4,6,7,8-HxCDF was deduced to be the probable dechlorination product of 1,2,3,4,6,7,8-HpCDF based on the identified penta- and tetra-CDF as well as the calculated activation energies (Table 8).

A specific TriCDF congener was also not confirmed by the GC-MS, but it was deduced based on the identified 2,3,7,8-TCDF and 2,8-DiCDF. Therefore, the activation energies for the removal of a chlorine atom from 2,3,7,8-TCDF and formation of the trichlorodibenzofuran congener were calculated using computational methods. There are two possible trichlorodibenzofuran congeners that could be formed: 2,3,7- trichlorodibenzofuran or 2,3,8- trichlorodibenzofuran. The computational studies were done for both congeners in acidified ethanol and in acidified 2-butoxyethanol and the results obtained for both solvents agreed with the experiments performed. The results are shown in Table 8 for acidified ethanol and Table 9 for acidified 2-butoxyethanol. The results revealed that the activation energy for the removal of a chlorine from the 7 position is lower than the removal of a chlorine from the 8 position. The results agreed with expectations based on the identified tetra- and di-CDF congeners.

Three possible diCDF congeners could be formed upon the removal of a chlorine atom from 2,3,8-triCDF: 2,3-dichlorodibenzofuran, 2,8-dichlorodibenzofuran, and 2,7-dichlorodibenzofuran. The activation energies for the formation of these congeners were also

calculated. It has been found that the energy required for removal of a chlorine from the 3 position is lower than the removal of a chlorine from the 8 or 2 positions. The calculations agree with the experimental results obtained in this study.

The formation of mono-CDF could result from the loss of the chlorine in the 2 or 8 position, but the symmetry of the molecule results in both producing 2-MnCDF before the formation of DBF. The main dechlorination pathway was 1,2,3,4,6,7,8,9-OCDF \rightarrow 1,2,3,4,6,7,8-HpCDF \rightarrow 2,3,4,6,7,8-HxCDF \rightarrow 2,3,4,7,8-PeCDF \rightarrow 2,3,7,8-TCDF \rightarrow 2,3,8-TriCDF \rightarrow 2,8-DiCDF \rightarrow 2-MnCDF \rightarrow DBF.

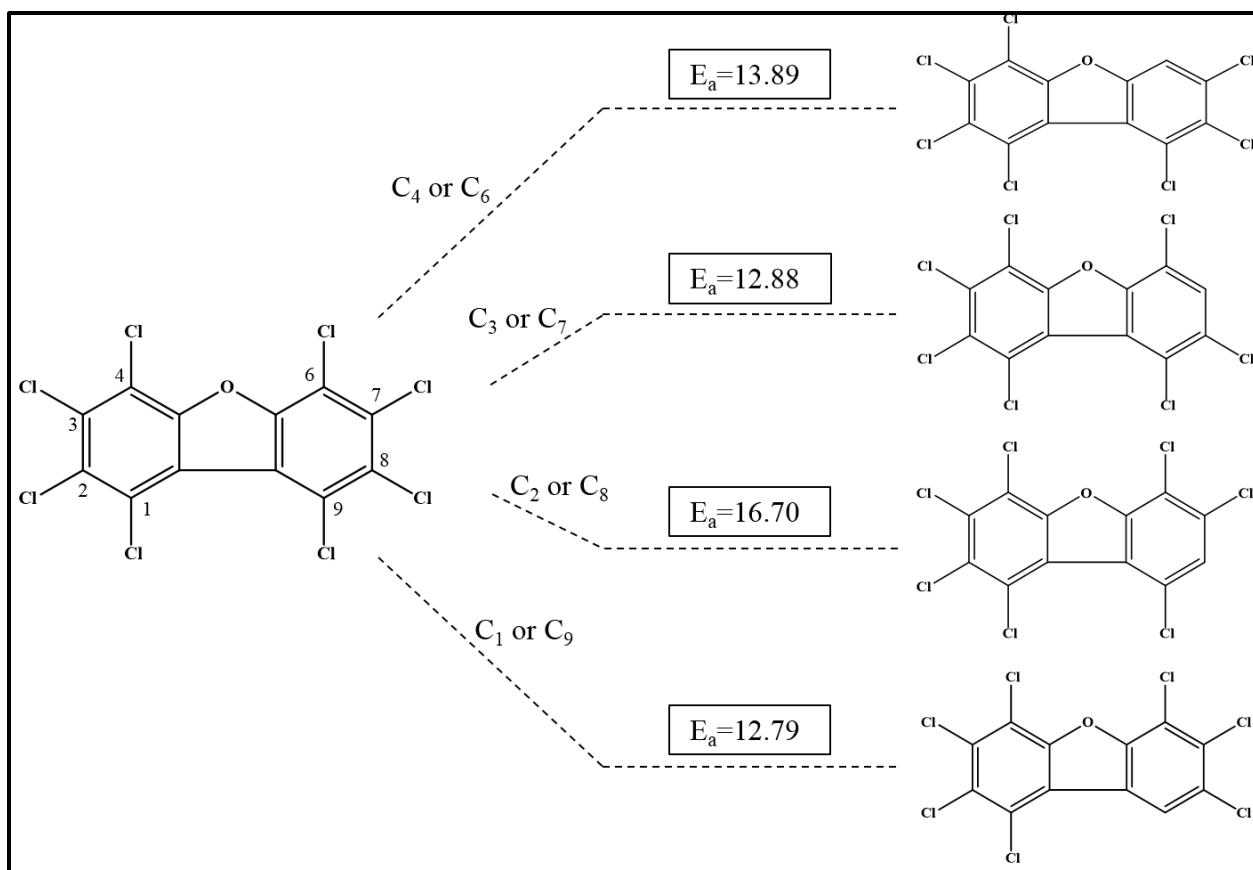


Figure 37: Activation energies for the degradation of OCDF and the formation of heptachlorodibenzofuran congeners.

Table 8: Activation energies of some of OCDF degradation products in acidified ethanol.

Reactant	Product	Ea (kcal/mol)
1,2,3,4,6,7,8,9-OCDF	1,2,3,4,6,7,8-HpCDF	12.79
1,2,3,4,6,7,8,9-OCDF	1,2,3,4,6,7,9-HpCDF	16.7
1,2,3,4,6,7,8,9-OCDF	1,2,3,4,6,8,9-HpCDF	12.88
1,2,3,4,6,7,8,9-OCDF	1,2,3,4,7,8,9-HpCDF	13.98
1,2,3,4,6,7,8-HpCDF	1,2,3,6,7,8-HxCDF	27.55
1,2,3,4,6,7,8-HpCDF	2,3,4,6,7,8-HxCDF	26.74
1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8-HxCDF	28.49
2,3,7,8-TCDF	2,3,7-TriCDF	22.6
2,3,7,8-TCDF	2,3,8-TriCDF	18.49
2,3,8-TriCDF	2,3-DiCDF	22.81
2,3,8-TriCDF	2,8-DiCDF	18.81
2,3,8-TriCDF	2,7-DiCDF	22.94

Table 9: Activation energies of some of 2,3,7,8-TCDF and 2,3,8-TriCDF degradation products in acidified 2-butoxyethanol.

Reactant	Product	Ea (kcal/mol)
2,3,7,8-TCDF	2,3,7-TriCDF	52.81
2,3,7,8-TCDF	2,3,8-TriCDF	24.61
2,3,8-TriCDF	2,3-DiCDF	29.44
2,3,8-TriCDF	2,8-DiCDF	25.23
2,3,8-TriCDF	2,7-DiCDF	56.03

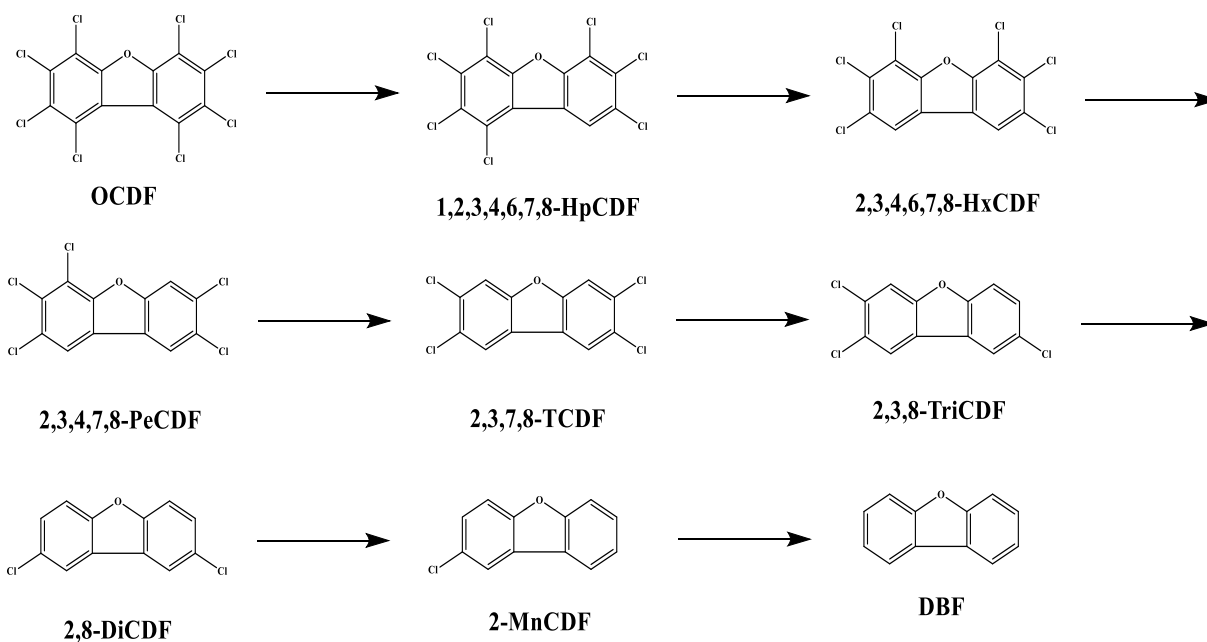


Figure 38: Schematic of the proposed pathway for the dechlorination of OCDF over ball-milled ZVMg or ZVMg/AC in acidified ethanol.

Efficacy of the System to Dechlorinate the Low Chlorinated Congener 2,8-Dichlorodibenzofuran

To ensure that the systems of ball-milled ZVMg with and without activated carbon in 2-butoxyethanol are able to dechlorinate low chlorinated congeners, 2,8-dichlorodibenzofuran was exposed to the same experimental conditions as OCDF and the dechlorination kinetics were studied. The degradation of 2,8-dichlorodibenzofuran was confirmed by the disappearance of the parent compound peak and the appearance of byproduct peaks over time using the GC-MS. The change in concentration of 2,8-dichlorodibenzofuran versus reaction time in ball-milled ZVMg and ZVMg/AC using 2-butoxyethanol as the solvent is graphically presented in Figure 39. Complete degradation of 2,8-dichlorodibenzofuran was achieved by both systems (7 days of the reaction by ball-milled ZVMg and 9 days when activated carbon was used in the system). About 30.5% reduction in 2,8-dichlorodibenzofuran concentration was accomplished within the first 12 hours of the reaction with ball-milled Mg; whereas, 39.7% reduction was achieved in the presence of activated carbon. The major product found in the first 3 days of treatment were dibenzofuran for ZVMg and monochlorodibenzofuran for ZVMg/AC. Distributions of the dechlorination products are shown in Figure 40 and Figure 41 for ball-milled ZVMg and ZVMg/AC, respectively. Time points between zero and 12 hours were not plotted to improve readability, since preliminary studies showed no significant change in concentration occurred during those time intervals. The figures indicate that, by the fifth day of the treatment, the majority of 2,8-dichlorodibenzofuran (95.8%) was converted to dibenzofuran in the ZVMg and 2-butoxyethanol system. At the same time, trace amounts of 2,8-dichlorodibenzofuran and monochlorodibenzofuran were detected in the system (~3.8%). When activated carbon was added to the system, the amount of dibenzofuran and monochlorodibenzofuran detected after 5 days of reaction were 57.8% and 37.0%,

respectively. Only a trace amount of 2,8-dichlorodibenzofuran was detected (~2.6%) and complete transformation was obtained after 7 days of treatment.

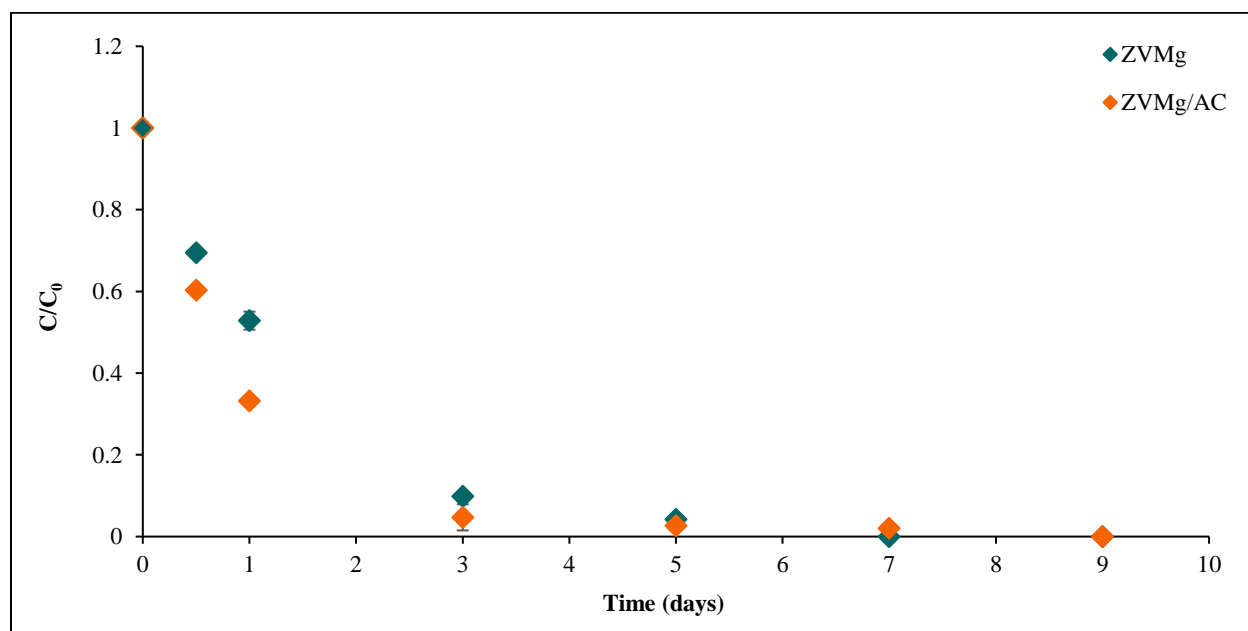


Figure 39: Reductive dechlorination of 2,8-dichlorodibenzofuran under ball-milled ZVMg and ZVMg/AC in 2-butoxyethanol.

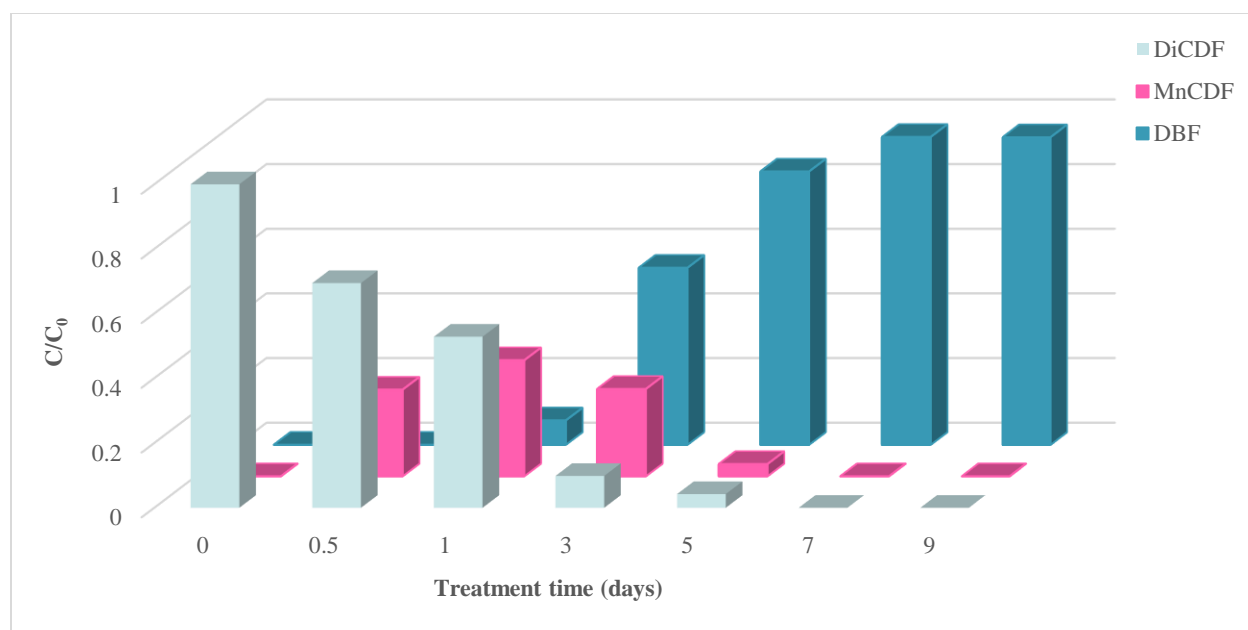


Figure 40: Degradation products of 2,8-dichlorodibenzofuran under ball-milled ZVMg in acidified 2-butoxyethanol.

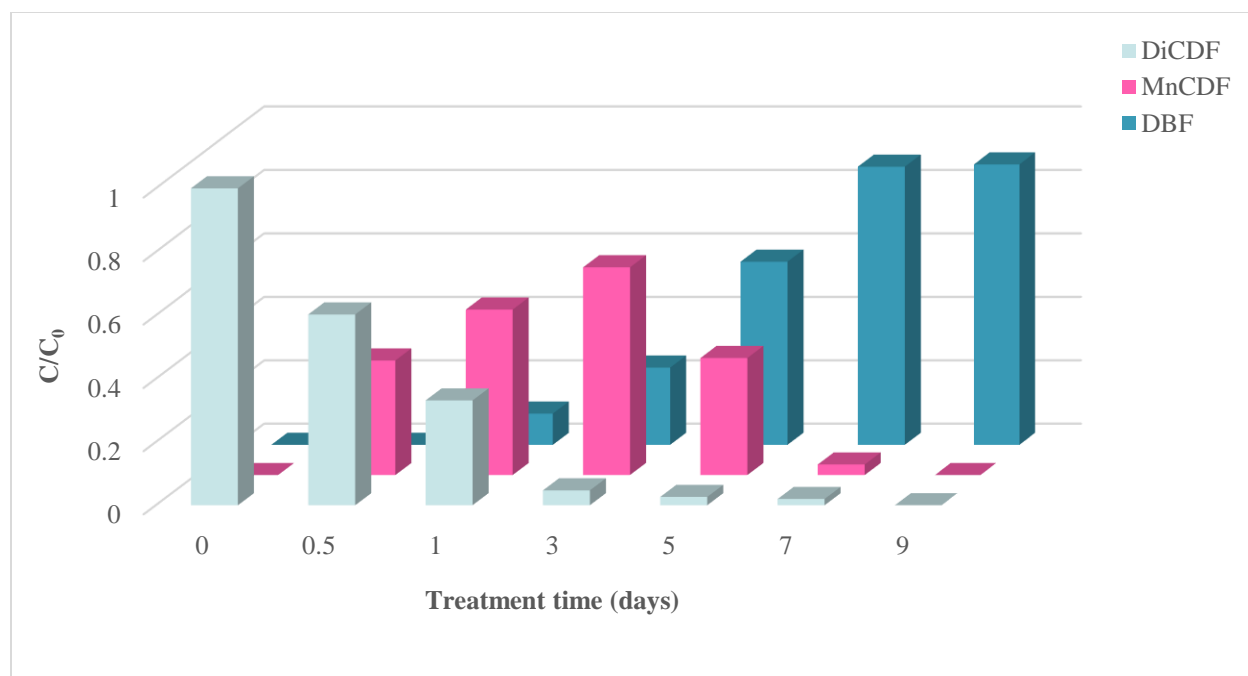


Figure 41: Degradation products of 2,8-dichlorodibenzofuran under ball-milled ZVMg/AC in acidified 2-butoxyethanol.

2,8-Dichlorodibenzofuran dechlorination kinetics

As observed in the previously discussed dechlorination of 2,8-dichlorodibenzofuran using ethanol as the solvent, a similar result was obtained in the current system where 2-butoxyethanol was used as the solvent. This result is also in accordance with previous studies conducted on OCDF in ethanol as well as studies performed on low-chlorinated biphenyl congeners in a variety of solvent systems, which yielded pseudo-first-order kinetics with respect to the reduction in analyte concentration in the presence of excess ZVM^{12,33}. Figure 42 and Figure 43 represent the pseudo-first-order decay model with respect to the disappearance of 2,8-dichlorodibenzofuran in the presence of ball-milled ZVMg and ZVMg/AC, respectively. As was observed previously (in the case of OCDF degradation), the results of 2,8-dichlorodibenzofuran degradation with ball-milled ZVMg in the presence of activated carbon yielded faster kinetics than the degradation with only ball-milled ZVMg. A good explanation is that activated carbon enhances the reaction by facilitating the activation process, which leads to improved reaction kinetics³⁸. The normalized pseudo-first-order rate constants obtained by both systems were $k = 0.6619 \text{ days}^{-1}$ for the ball-milled ZVMg system and $k = 0.7249 \text{ days}^{-1}$ for the ZVMg/AC system.

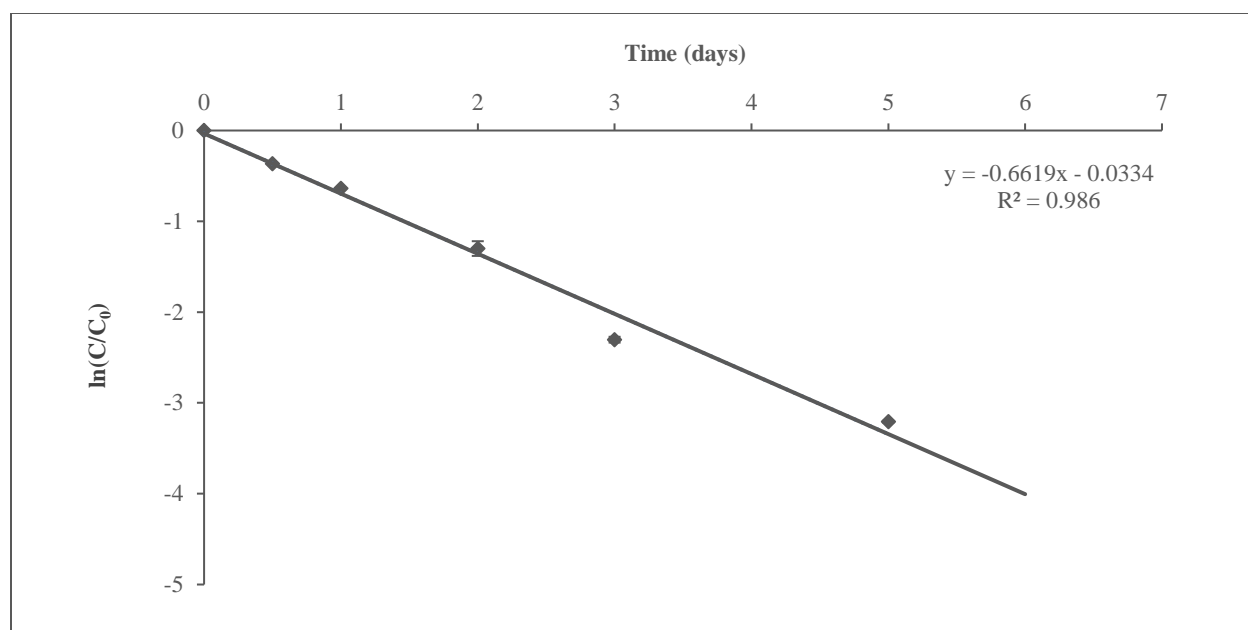


Figure 42: Pseudo- first-order plot for the degradation of 2,8-dichlorodibenzofuran over ball-milled ZVMg in an acidified 2-butoxyethanol.

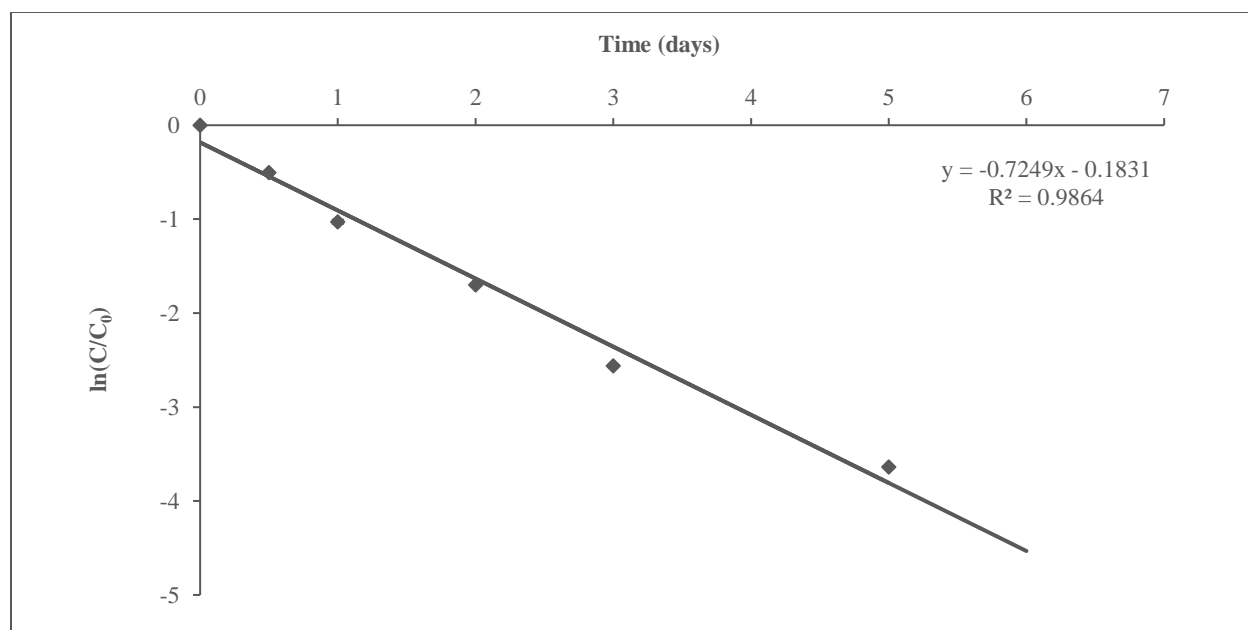


Figure 43: Pseudo- first-order plot for the degradation of 2,8-dichlorodibenzofuran over ball-milled ZVMg/AC in an acidified 2-butoxyethanol.

Conclusion

A new solvent was tested in this chapter towards the degradation of OCDF. This new solvent, 2-butoxyethanol, was chosen since it is environmentally benign, biodegradable, and it has two functional groups: an ether and an alcohol. Reductive dechlorination of OCDF was achieved with both ball-milled ZVMg and ZVMg/AC. Complete OCDF removal was obtained after 5 minutes of the reaction under ball-milled ZVMg with and without activated carbon. Kinetic results showed a pseudo-first-order decay model for both systems with faster kinetics in the presence of activated carbon. The mole balances after 4 weeks of treatment were 86.4% for ball-milled ZVMg and 78.8% for ZVMg with activated carbon.

The reductive dechlorination of the low chlorinated congener 2,8-dichlorodibenzofuran was studied also using 2-butoxyethanol solvent. Satisfactory degradation was achieved for ball-milled ZVMg with and without activated carbon with faster degradation in the presence of activated carbon. Complete 2,8-dichlorodibenzofuran removal was achieved after 5 and 7 days with ball-milled ZVMg and ZVMg/AC, respectively.

The mole balance achieved by using 2-butoxyethanol was the lowest among all the studied systems in chapters two and three. This is due to some difficulties observed during the extraction process. More work should be done in order to find out the best extraction method and improve the systems to make them more applicable for large scale in situ remediation of OCDF contamination.

CHAPTER FIVE: REDUCTIVE DEGRADATION OF 2,4,6-TRINITROTOLUENE USING BALL-MILLED ZVMG IN ACIDIFIED ETHANOL

Introduction

Nitroaromatics compounds are a group of toxic compounds that have aroused significant concerns¹³. Among these explosive compounds, 2,4,6-trinitrotoluene (TNT) has been historically produced on an enormous scale²⁵. TNT is commonly used for military applications and in explosive compositions¹⁴. TNT is also used in mining and industrial applications¹⁵. TNT can be introduced to the surroundings through different sources including the disposal of industrial production wastes. TNT manufacturing, storage, and use are also important sources for the introduction of TNT to the environment. TNT is very stable chemically and thermally and its solubility in water is very low (130 mg/L)¹⁶. In 2001, the US EPA declared that the removal of TNT pollution is a priority⁷¹ and TNT levels in water should not exceed 0.001 ppm²⁴. In 2004, TNT was listed by the US EPA as a pollutant of great concern²³. It has been found that TNT possess mutagenic, poisonous, and carcinogenic properties and exposure to TNT can lead to serious health problems such as cataracts, liver damage, aplastic anemia, skin irritation, toxic hepatitis, and hepatomegaly^{17, 21}.

TNT is very stable and recalcitrant due to the presence of multiple nitro groups. Thus, its degradation is very challenging. Several remediation techniques have been developed to remediate nitro explosive contaminants, including TNT. Some examples of the available remediation techniques are microbial remediation⁷², oxidation processes²⁴, phytoremediation⁷³, and nickel catalysis³⁰. The use of zero-valent metals (ZVM) such as zero-valent iron (ZVI) has been applied

to the remediation of nitro explosives. The use of iron is limited since it requires an anaerobic environment with controlled temperature and pH³¹. Remediation processes utilizing the use of hydrogenation catalysts allow the treatment of explosive contaminants under ambient conditions. Nickel and palladium are the most commonly known hydrogenation catalysts. Even though the use of these catalysts has some advantages, hydrogen gas is required in these treatments³⁰, which makes it impractical for *in situ* remediation of TNT contamination. As a result, researchers have searched for an alternative to ZVI, and one metal of interest is zero-valent magnesium (ZVMg). Using ZVMg to remediate TNT and nitro-based compounds is promising due to the great reduction potential of ZVMg (-2.37 V vs. SHE) over ZVI (-0.44 V vs. SHE)³⁸. Furthermore, ZVMg can form a self-limiting oxide layer in contrast to the ready corrosion of ZVI⁷⁴. Researchers in the Industrial and Environmental Laboratory at the University of Central Florida (UCF) have studied the degradation of TNT in water samples using bimetal systems, including mechanically alloyed Mg/Pd, Fe/Pd, and Fe/Ni. The results showed that all the tested systems were able to reduce TNT under ambient conditions with varying reactivities⁷⁵. In this chapter, a new reductive system consisting of ZVMg and acidified ethanol will be tested towards the degradation of TNT.

Experimental

Chemicals and Materials

TNT standard solution was obtained from Accustandard and prepared by diluting the standard in ethanol to the desired concentration. 2-amino-4, 6-dinitrotoluene, 4-amino-2, 6-dinitrotoluene, and 2, 4-dinitrotoluene standard solutions were also obtained from Accustandard. Glacial acetic acid (≥ 99.8 purity) was purchased from Acros Organics through Fisher Scientific.

Toluene (Optima[®] grade) was acquired from Fisher Scientific. Micro-scale un-milled magnesium (2-4 μm) was supplied by Heart Metals (Tamaqua, PA). Nylon filters with 0.45 μm pore size were purchased from Fisher Scientific (Pittsburg, PA).

Preparation of Ball-milled ZVMg and ZVMg/AC

Mechanically ball-milled ZVMg and ZVMg with activated carbon were prepared by adding 85.0 g of ZVMg or 76.5 g magnesium mixed with 8.5 g of activated carbon, respectively, to galvanized steel canisters that are 17.80 cm in length and 5.03 cm in internal diameter. Each canister was filled with sixteen stainless steel balls (1.6 cm diameter). The ball-milling was done under an argon atmosphere for 45 minutes using a Red Devil 5400 twin arm paint shaker.

Degradation of TNT in acidified ethanol

Degradation experiments were performed in duplicate by adding 5 mL of TNT solution ($10\ \mu\text{g mL}^{-1}$) to 20 mL glass screw-top vials containing 250 mg of ZVMg and 50 μL of glacial acetic acid. These vials were placed on a Reciprocating Shaker table (Lab Companion K-57013) at a speed of 200 rpm and 26 $^{\circ}\text{C}$ until a predesignated extraction time. Blank experiments were carried out in parallel without metal.

Sample Extraction

Samples were extracted by adding 5 mL toluene to each vial and shaking by hand for 2 minutes. Then, the samples were placed in an ultrasonic bath (VWR Scientific Aquasonic Model 750D). After 30 minutes sonication, samples were centrifuged and the toluene/TNT layer was washed twice with deionized water. The organic layer was filtered by a Whatman[®] 25-mm nylon

syringe filter (0.45 μm pores) attached to a disposable syringe and stored in the refrigerator for further analysis.

Analysis

Analysis of the residual TNT and its degradation products was performed on an Agilent Technologies 6850 (series II) GC-MS coupled with an Agilent 5975 mass spectrometer and equipped with an autosampler and a Restek RTX®-5 column (30 m x 250 μm x 0.25 μm). Helium was acted as the carrier gas, with a constant flow of 2 mL/min and an average gas velocity of 53.6 cm/s. Injection volume was set at 1 μL and it was performed in splitless mode. The ion source temperature was held at 280 °C and the injector temperature was held at 250 °C. The initial oven temperature was 100 °C and it was held for 1 minute. Then, the column was ramped at 3 °C/minute to 180 °C and held for 3 minutes. Identification of the byproducts was based upon the retention times of known standards and verified via their mass spectra.

Results and Discussion

TNT Reduction by Ball-Milled ZVMg and ZVMg with Activated Carbon in Acidified Ethanol

Initial studies utilizing ball-milled ZVMg with and without activated carbon in acidified ethanol were conducted to evaluate the efficiency of the system towards TNT degradation. The results of the degradation of TNT by ball-milled ZVMg and ZVMg/AC in ethanol are presented in Figure 44. As observed in the figure, TNT was degraded successfully after 30 minutes and 120 minutes with ball-milled ZVMg and ZVMg/AC, respectively. As in the previous studies of OCDF degradation, the presence of activated carbon enhanced the degradation of TNT. Identification of the byproducts was done using GC-MS. The identified TNT decomposition byproducts were 2-

amino-4, 6-dinitrotoluene, 4-amino-2, 6-dinitrotoluene, and 2, 4-dinitrotoluene. Many studies have observed the formation of 2,4,6-triaminotoluene (TAT) as the major product of TNT reduction by ZVI¹⁴. TAT is known to be more toxic than TNT. However, analysis of the products formed in this study demonstrated no presence of the hazardous product TAT in any of the samples using ball-milled ZVMg with or without activated carbon.

The three products (2-amino-4, 6-dinitrotoluene, 4-amino-2, 6-dinitrotoluene, and 2, 4-dinitrotoluene) were observed at various concentration in both systems for a period of time. Their concentrations increased over time, then decreased until they were removed from both systems. The results of the formed byproducts over time in the presence of ball-milled ZVMg or ZVMg with activated carbon are illustrated in Figure 45 and Figure 46, respectively. Results obtained from ball-milled ZVMg indicate the formation of 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene within 5 minutes of reaction in both systems. These two compounds were degraded by ZVMg after 210 minutes, whereas, in ZVMg/AC, 2-amino-4, 6-dinitrotoluene was degraded after 180 minutes and 4-amino-2, 6-dinitrotoluene was degraded after 210 minutes of the reaction. 2,4-Dinitrotoluene was detected at 30 and 15 minutes under ZVMg and ZVMg/AC, respectively, and it was not detected in either system after 180 minutes.

The obtained results demonstrate that ball-milled ZVMg and ZVMg/AC systems were successfully degraded TNT. The decay in the formed byproducts 2-amino-4, 6-dinitrotoluene, 4-amino-2, 6-dinitrotoluene, and 2, 4-dinitrotoluene indicate that these products were further transformed to other products (still unknown products). Work is continuing in order to investigate the final products of TNT reduction and to determine if the use of ball-milled ZVMg and ZVMg/AC in acidified ethanol is applicable for *in situ* remediation of TNT contaminants.

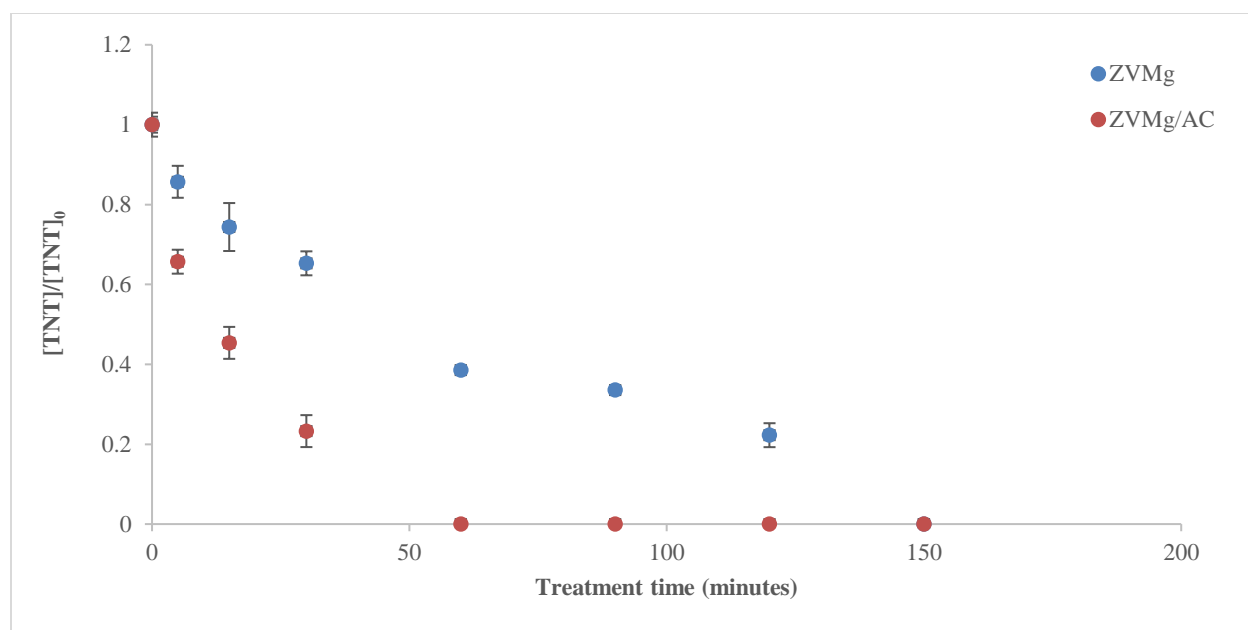


Figure 44: Degradation of TNT under ball-milled ZVMg and ZVMg/AC in acidified ethanol.

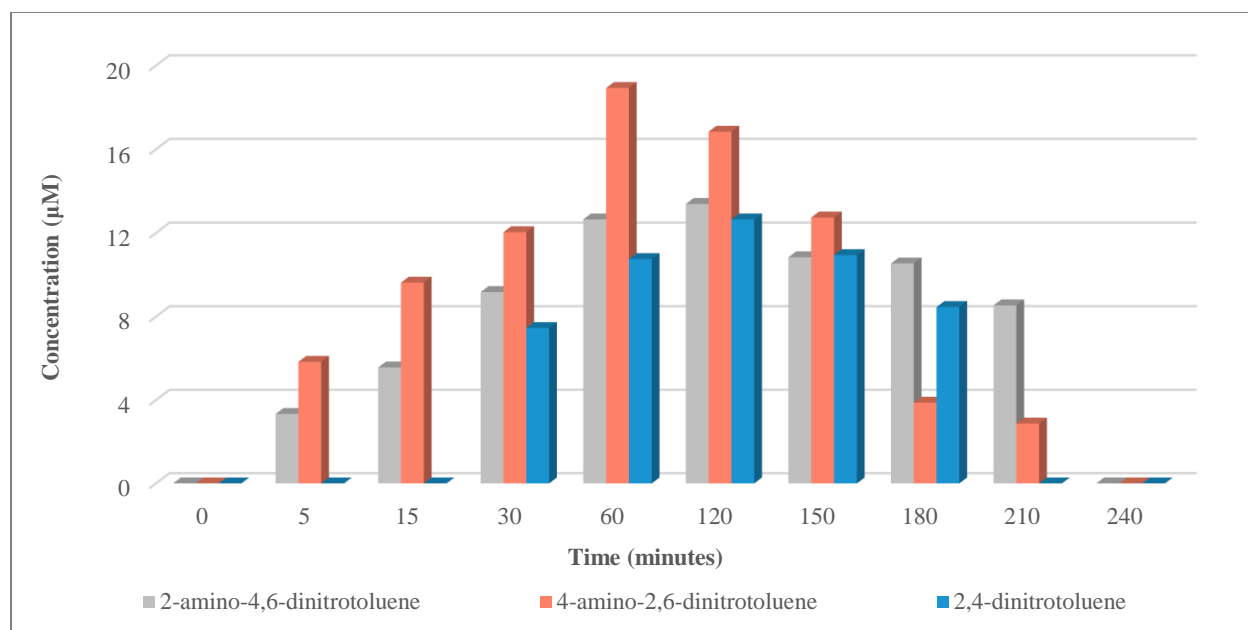


Figure 45: Distribution of TNT degradation byproducts over ball-milled ZVMg and ethanol.

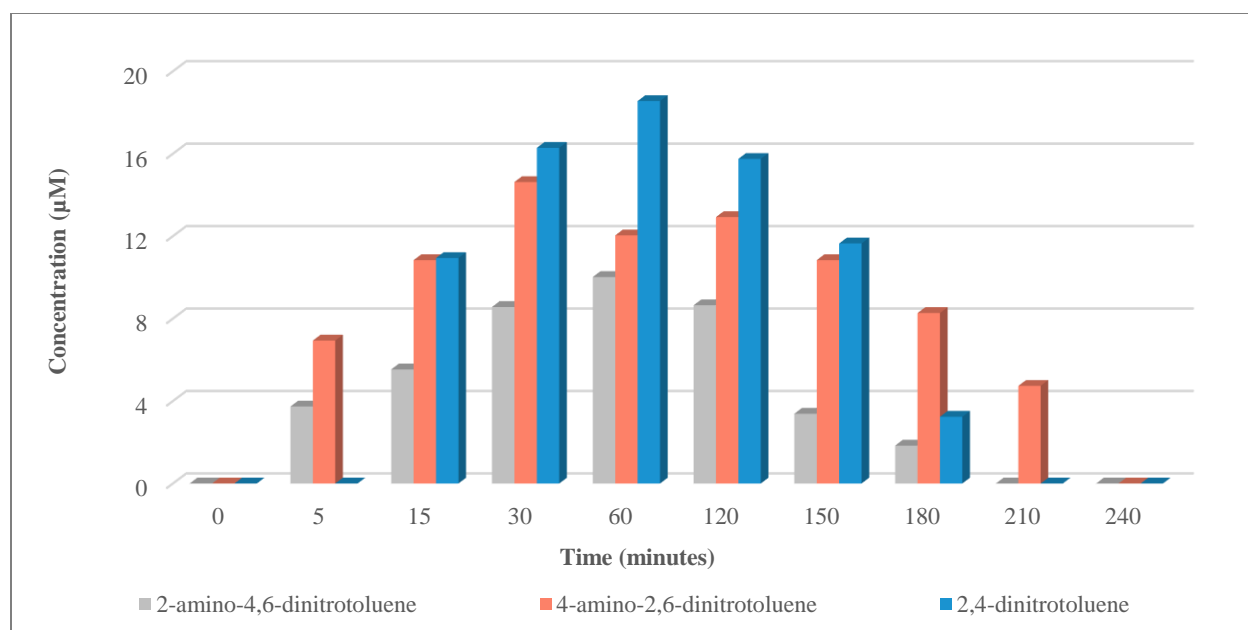


Figure 46: Distribution of TNT degradation byproducts over ZVMg/AC and ethanol.

TNT Reduction Kinetic Studies

Similar to OCDF degradation, TNT decay follows a pseudo-first-order decay model as shown in Figure 47 and Figure 48. The results are in accordance with previous studies done on the degradation of TNT using different treatment methods⁷⁵. Faster kinetics were observed in the presence of activated carbon. This enhancement occurred due to the protection provided by the carbon to the magnesium surface, preventing the formation of oxide/ethoxide layers on the metal surface. This results in improved reactivity of the metal surface and enhanced degradation. The obtained pseudo-first-order rate constants were $k = 0.0124 \text{ minutes}^{-1}$ and $k = 0.0458 \text{ minutes}^{-1}$ for the reactions with ball-milled ZVMg and ZVMg/AC, respectively. The linear correlation coefficients for the two systems were $R^2 = 0.9819$ for ball-milled ZVMg and $R^2 = 0.9866$ for ZVMg with activated carbon.

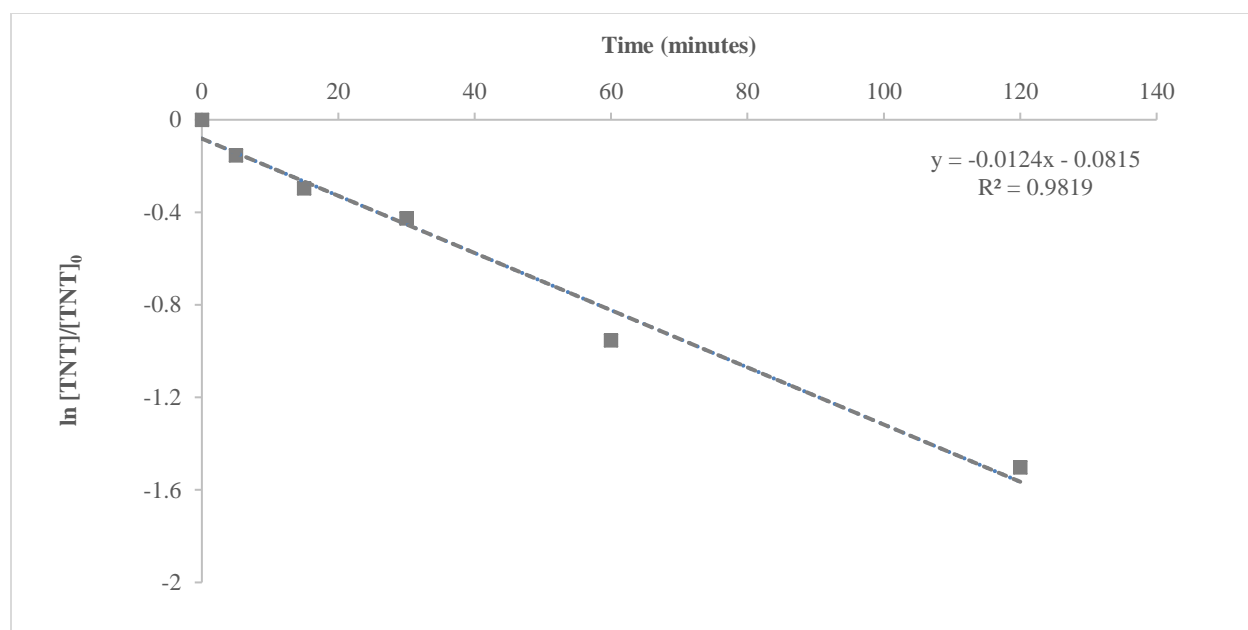


Figure 47: Pseudo-first-order decay model for TNT degradation in ball-milled ZVMg and ethanol.

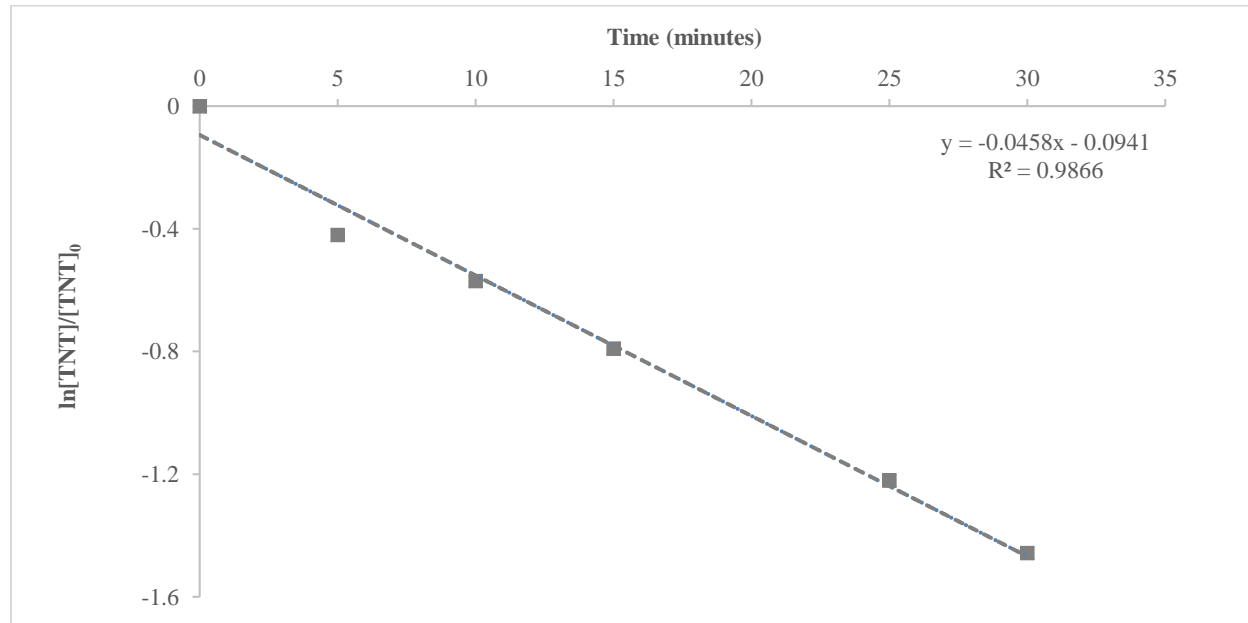


Figure 48: Pseudo-first-order decay model for TNT degradation in ZVMg/AC and ethanol.

TNT Reduction Pathways

Due to the presence of the electronegative nitro groups, π electrons in the aromatic ring of TNT are withdrawn. This makes the aromatic ring electrophilic. The nitrogen and the oxygen atoms in the nitro group are electronegative; however, the oxygen atom is more electronegative than the nitrogen. Thus, the bond between the two atoms is polarized and the nitrogen atom bears a partially positive charge. This partially positive charge as well as the high electronegativity of the nitrogen makes the nitro group easily reducible. Reduction of the nitro groups of TNT is well documented in the literature^{22, 76, 77}.

The reduction of the nitro group in nitroaromatic compounds could occur via single-electron transfer or two-electron transfer. The single-electron transfer mechanism includes the formation of a nitro anion radical which could react with oxygen, forming a superoxide radical which is then oxidized back to the parent compound via a futile cycle. In the case of two-electron transfer, the mechanism will go through the formation of a nitroso derivative which is considered the first putative intermediate. Since radicals are not produced in this process, it is known to be insensitive to oxygen. The process may continue by two consecutive electron transfers to produce a hydroxylamine and an aromatic amine. It has been found that the mutagenic effect of TNT is reduced when the nitro groups undergo complete reduction to amino groups. The mechanism for the reduction of the nitro groups in nitroaromatic compounds via one- and two-electron transfers are shown by Spain (1995)⁷⁸.

In general, it has been reported that the reduction of the first nitro group on TNT occurs rapidly and more easily than that of the remaining nitro groups, the nitro group in the *para* position is reduced more readily than the nitro groups in the *ortho* positions²². Nitroaromatic compounds

including TNT can undergo nonenzymatic reduction by different reductants such as iron, ferredoxin, and sulfhydryl compounds⁷⁸.

Another possible mechanism for the reductive degradation of TNT is via the formation of a Meisenheimer-complex. The aromatic ring of TNT is electron deficient due to the presence of the electron-withdrawing nitro group. Therefore, the ring is susceptible to nucleophilic attack by a hydride ion followed by a release of nitrite as shown by *Esteve-Núñez, et al.* (2001)²². *Haidour, et al.* have shown that a hydrid-Meisenheimer complex was transformed *in vitro* to 2,4-dinitrotoluene and an unidentified product^{22, 79}.

The use of magnesium with methanol or ethanol has been shown to successfully reduce a variety of functional groups. Mg/MeOH or Mg/EtOH are good sources for a single-electron transfer in reductive reactions via a hydrogen transfer mechanism promoted by the magnesium. In this study, a pathway for the transformation of TNT under ball-milled ZVMg and ZVMg/AC in acidified ethanol was proposed based on literature and the detected byproducts. This pathway is presented in Figure 49. A reduction of the nitro group in the *ortho* or *para* position could occur leading to the formation of 2-hydroxylamino-4, 6-dinitrotoluene or 4-hydroxylamino-2, 6-dinitrotoluene. These intermediates were documented in the literature; however, they were not observed in this study. The formed intermediates were then transformed into 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene. The presence of these two compounds was experimentally confirmed. The transformation of 2-amino-4,6-dinitrotoluene to 2,4-dinitrotoluene was also observed in this study. This pathway is similar to a pathway previously described by *Gordon, et al.* for the degradation of TNT. However, 2,6-dinitrotoluene was not detected in this study⁸⁰.

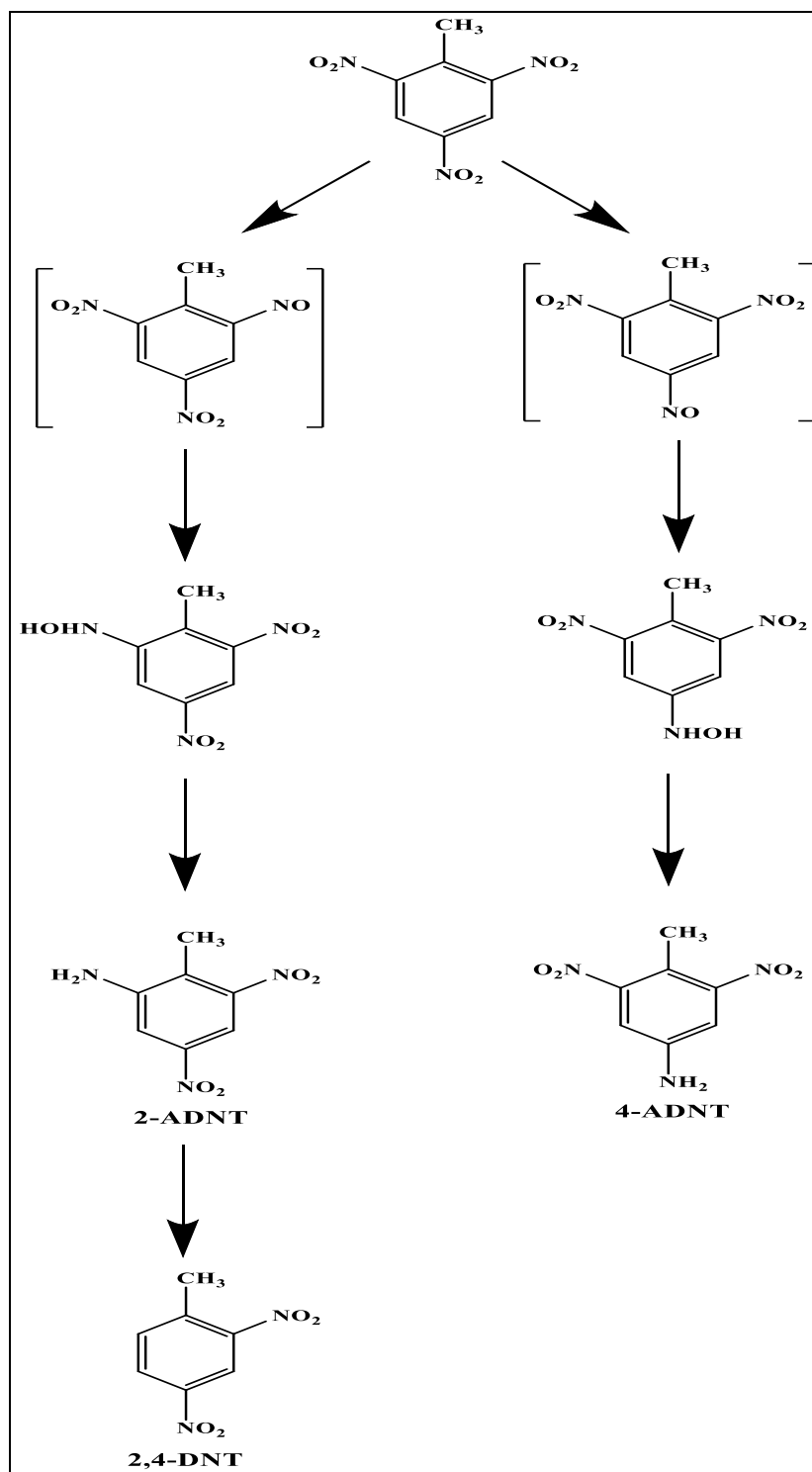


Figure 49: Proposed pathway for TNT degradation.

Conclusion

The use of ball-milled ZVMg with and without activated carbon in acidified ethanol has been shown to reductively degrade TNT at ambient conditions. Complete TNT removal was achieved after 30 minutes in ZVMg with activated carbon and 120 minutes in ZVMg. Faster kinetics were exhibited for TNT degradation in the presence of activated carbon.

The identified byproducts for TNT degradation were 2-amino-4, 6-dinitrotoluene, 4-amino-2, 6-dinitrotoluene, and 2, 4-dinitrotoluene. A degradation pathway was proposed based on literature and the observed byproducts by GC-MS. These products were formed then diminished which means that ball-milled ZVMg and ZVMg/AC were able to degrade these products, as well as TNT, to further unidentified products. The reduction of TNT using ZVMg has not resulted in the formation of TAT, a more hazardous product than the parent compound TNT. Therefore, this method appears to be promising for *in situ* remediation of TNT contamination. However, to verify if the method is suitable for field application, further research must be done in order to determine the final products of these reactions.

APPENDIX A: SUPPORTING INFORMATION FOR CHAPTER TWO

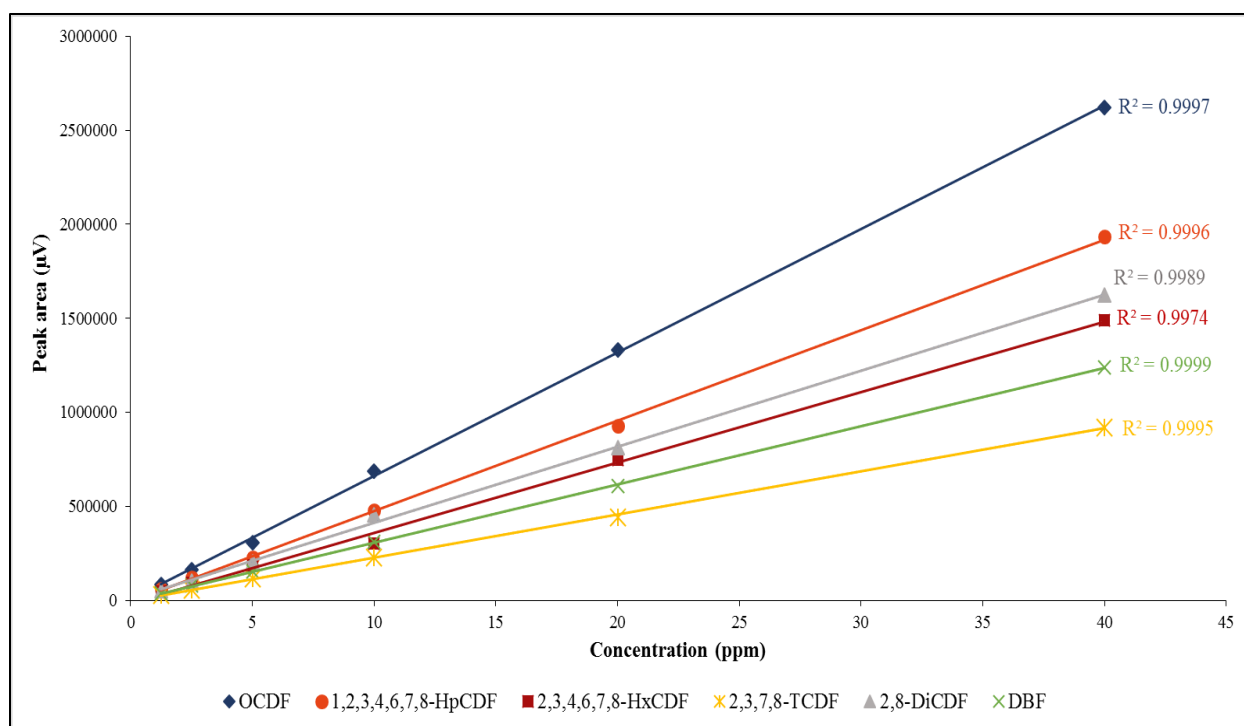


Figure 50: GC-MS peak area as a function of OCDF and its byproduct concentrations.

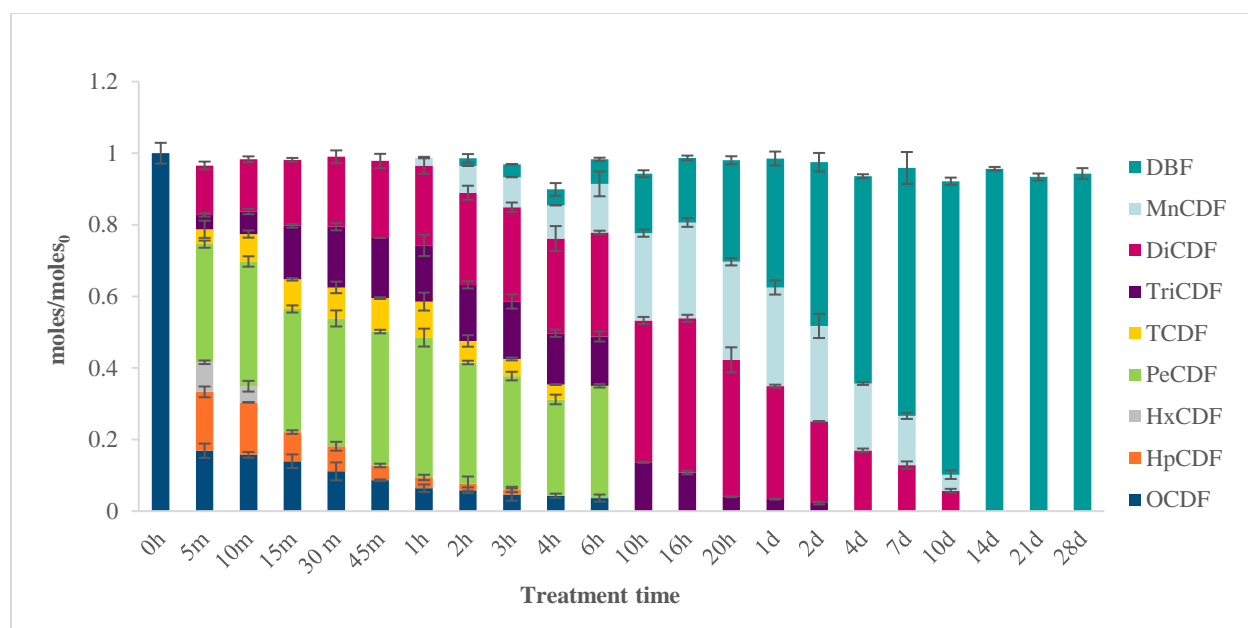


Figure 51: Dechlorination of OCDF under ball-milled ZVMg and acidified ethanol.

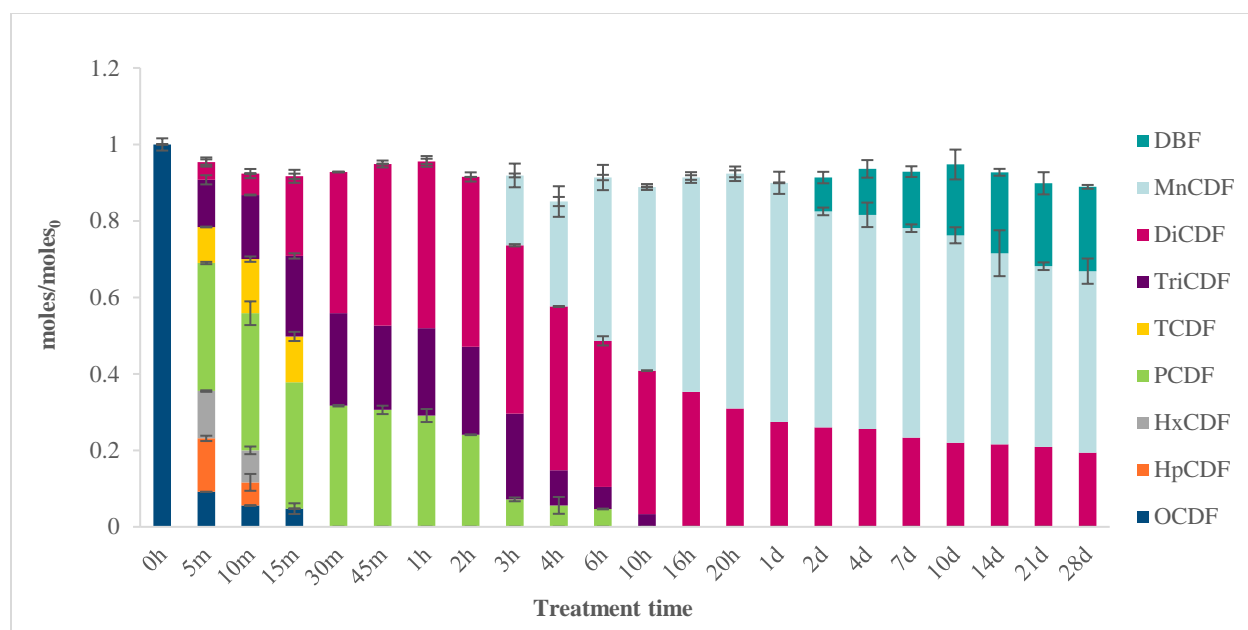
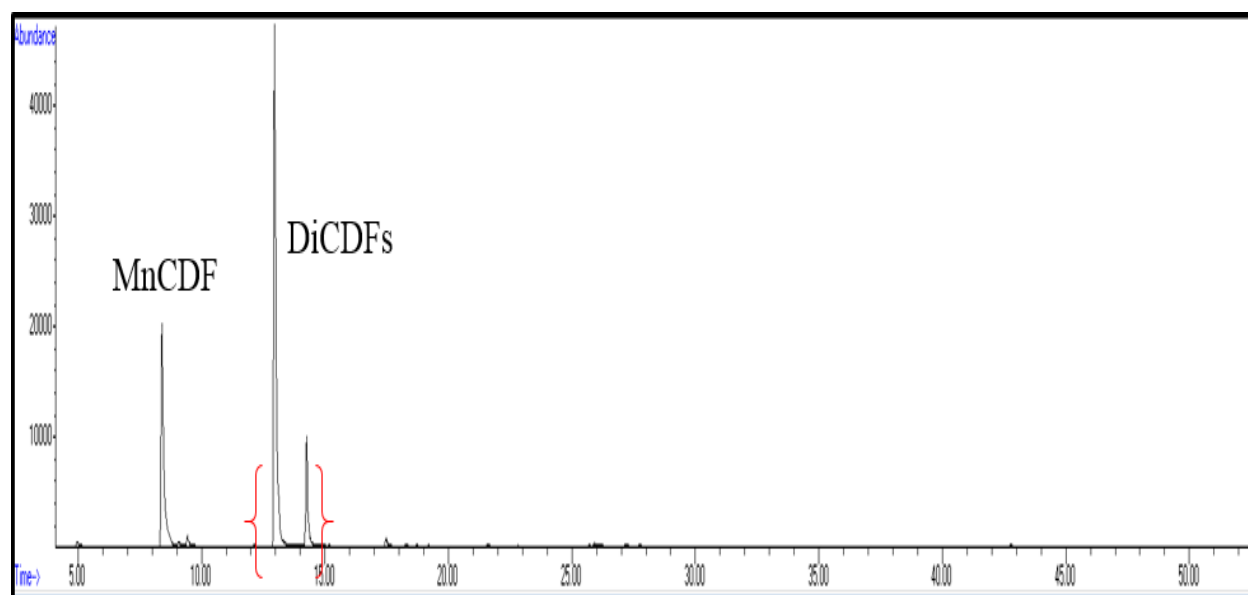
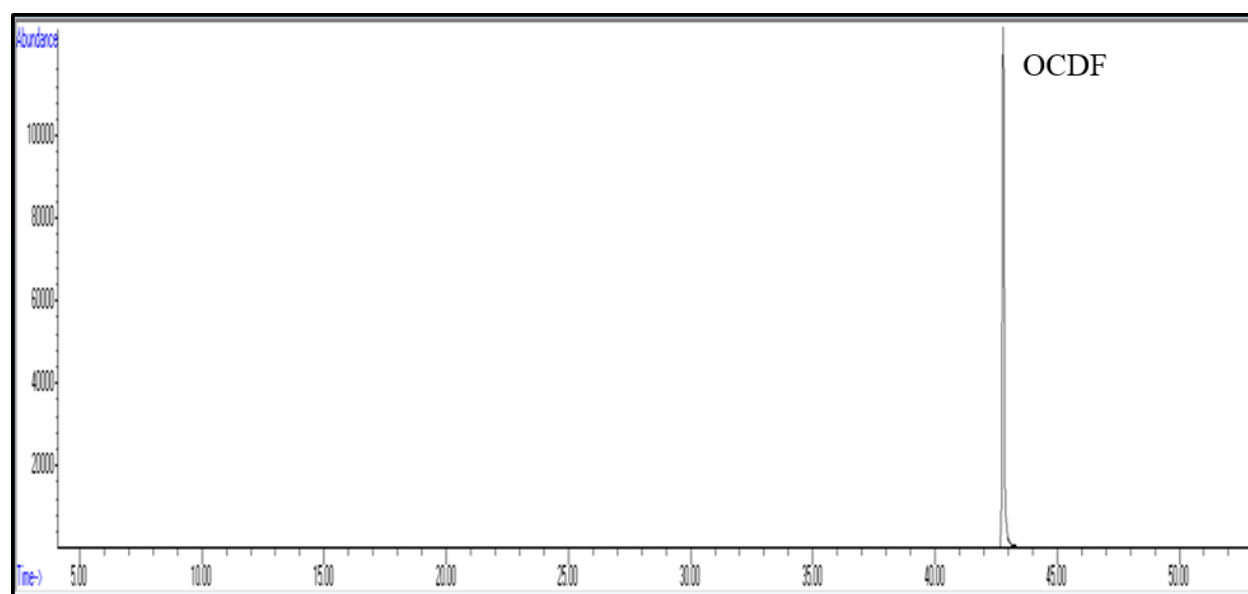


Figure 52: Dechlorination of OCDF under ball-milled ZVMg/AC and acidified ethanol.



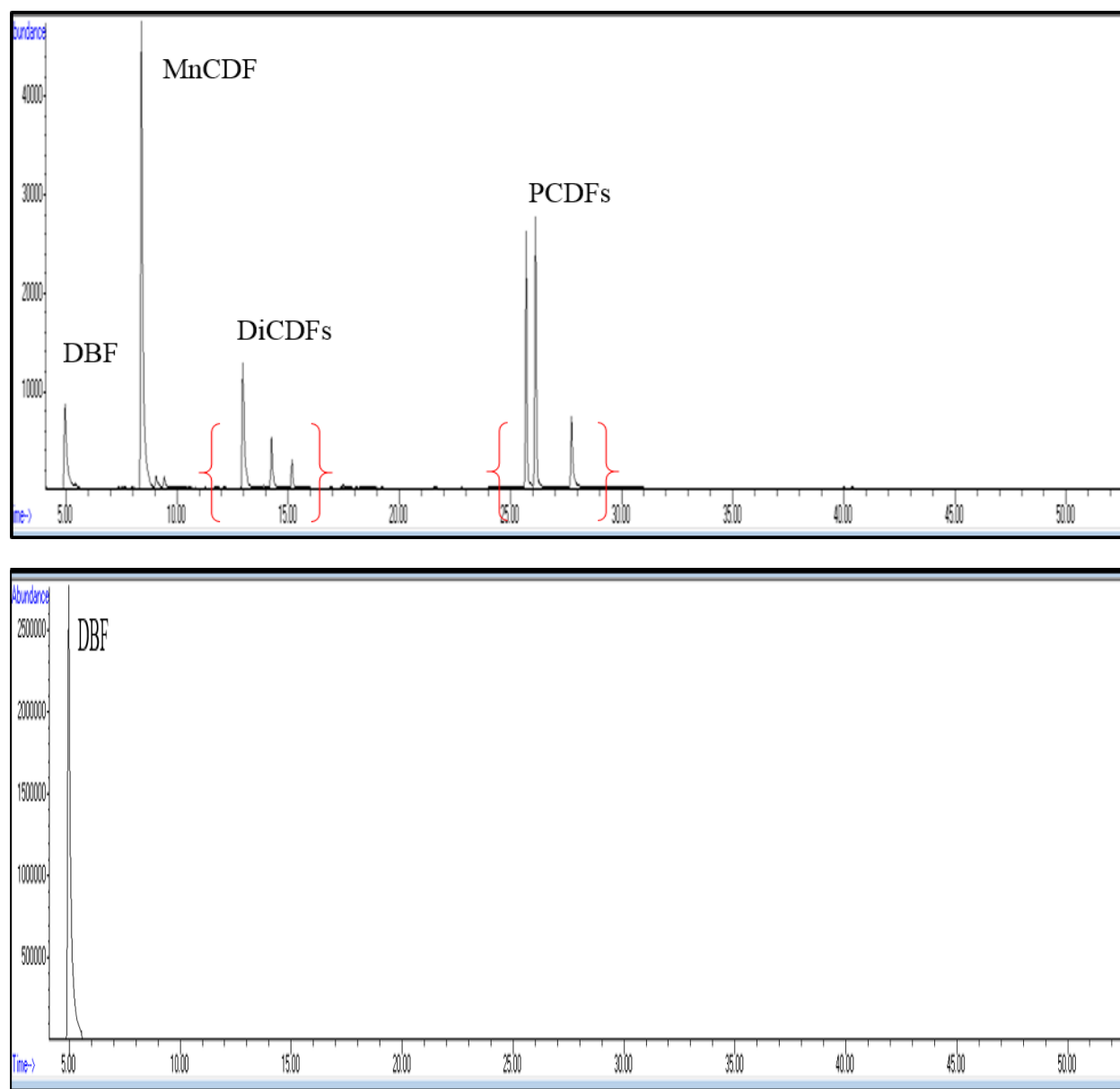


Figure 53: GC-MS chromatograms for the degradation of OCDF.

APPENDIX B: SUPPORTING INFORMATION FOR CHAPTER THREE

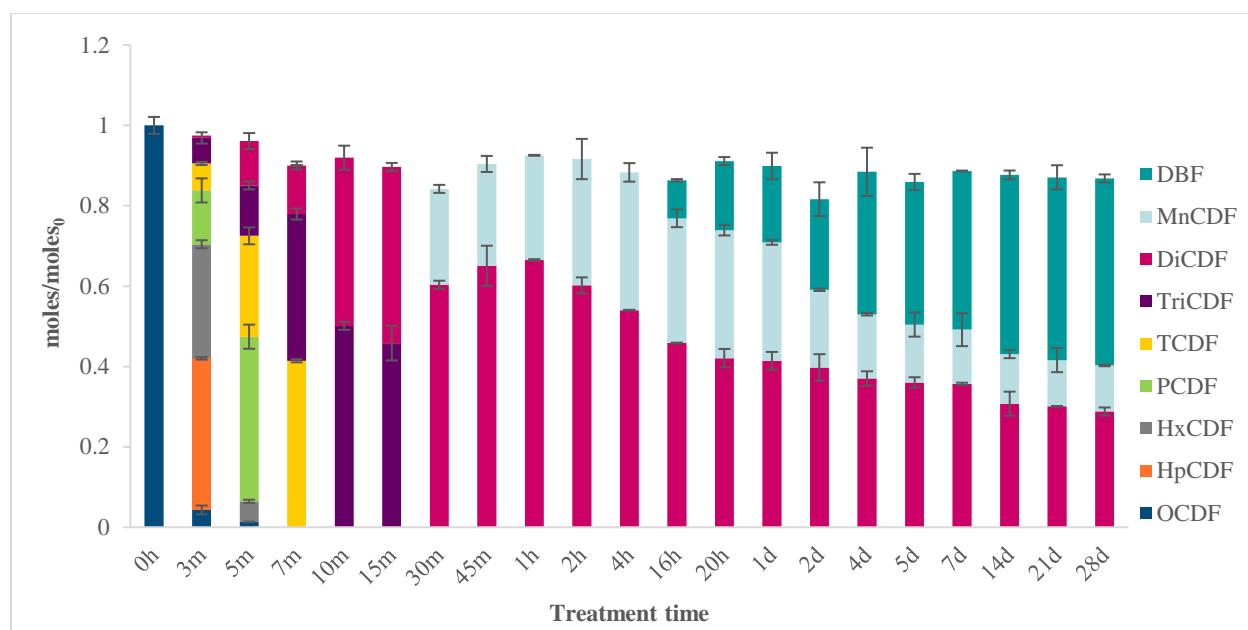


Figure 54: OCDF Degradation under ball-milled ZVMg and acidified ethanol/ethyl lactate (90:10).

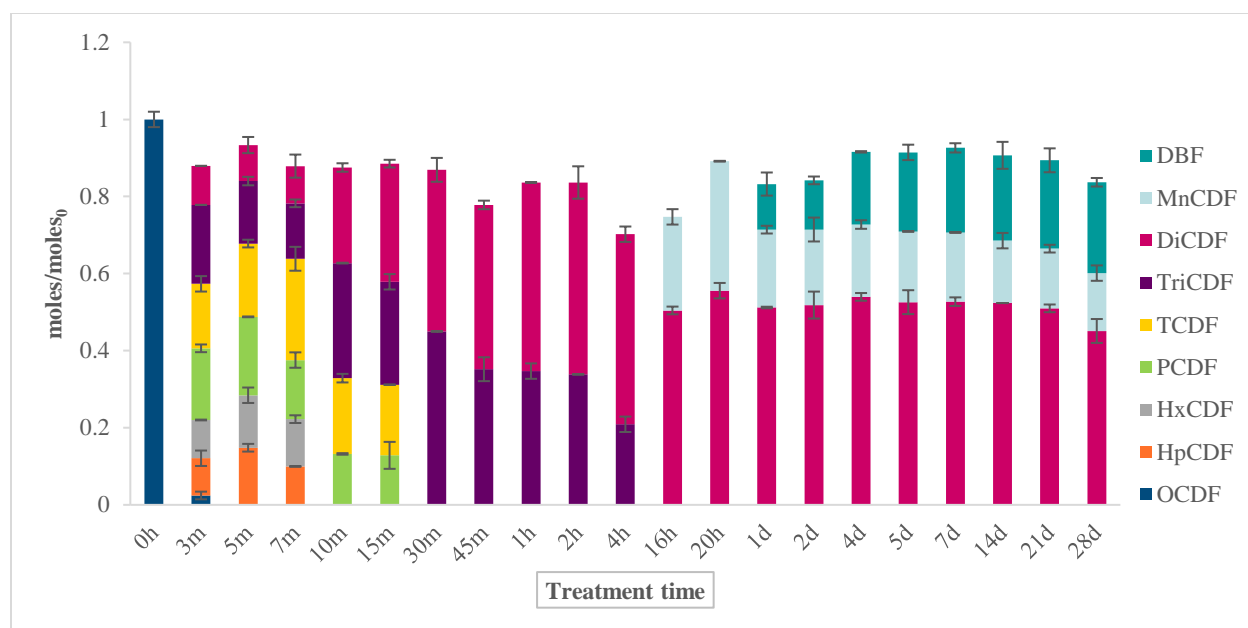


Figure 55: OCDF degradation under ZVMg over activated carbon and acidified ethanol/ethyl lactate (90:10).

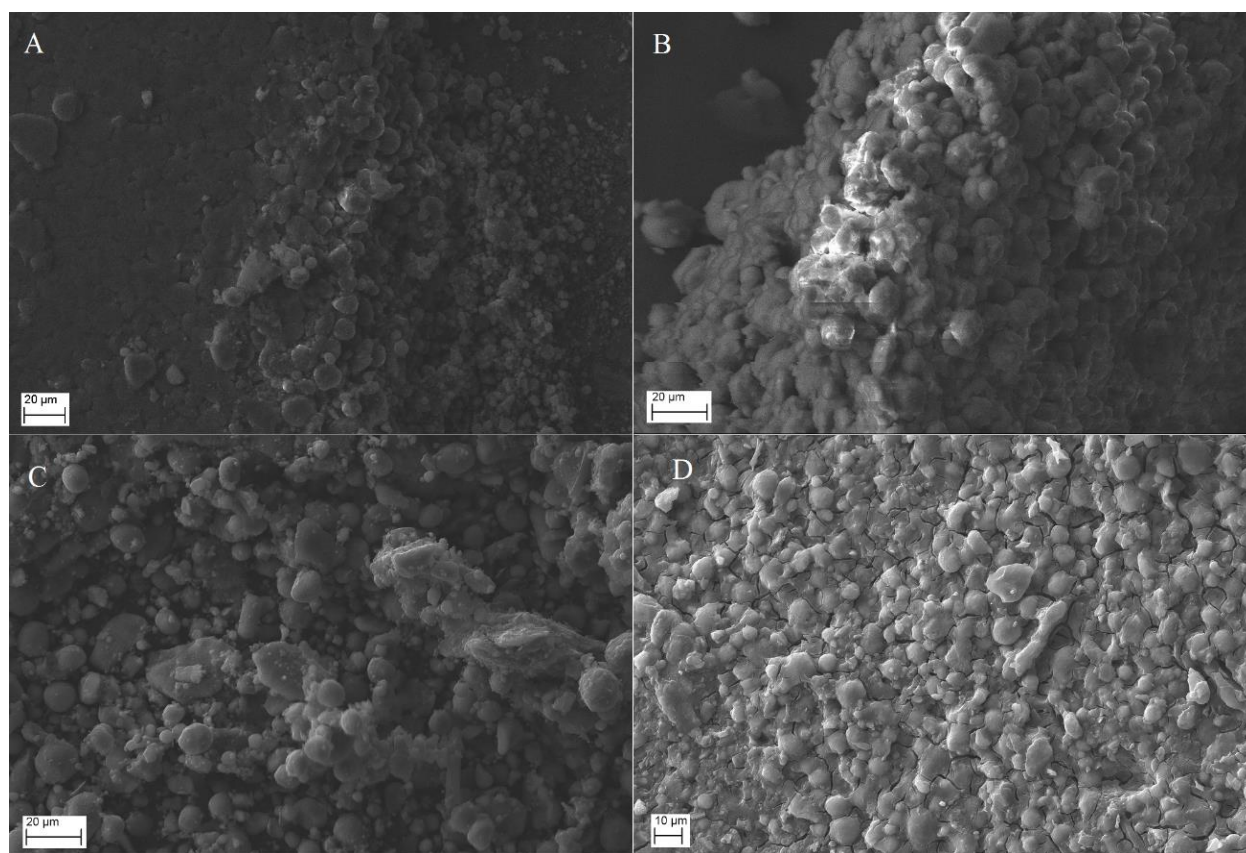
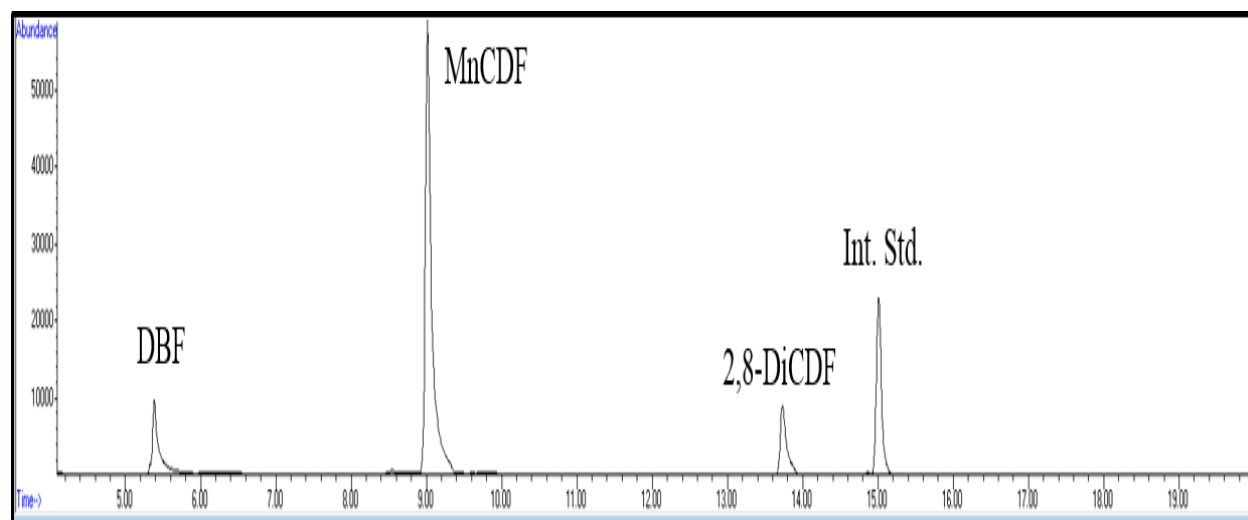
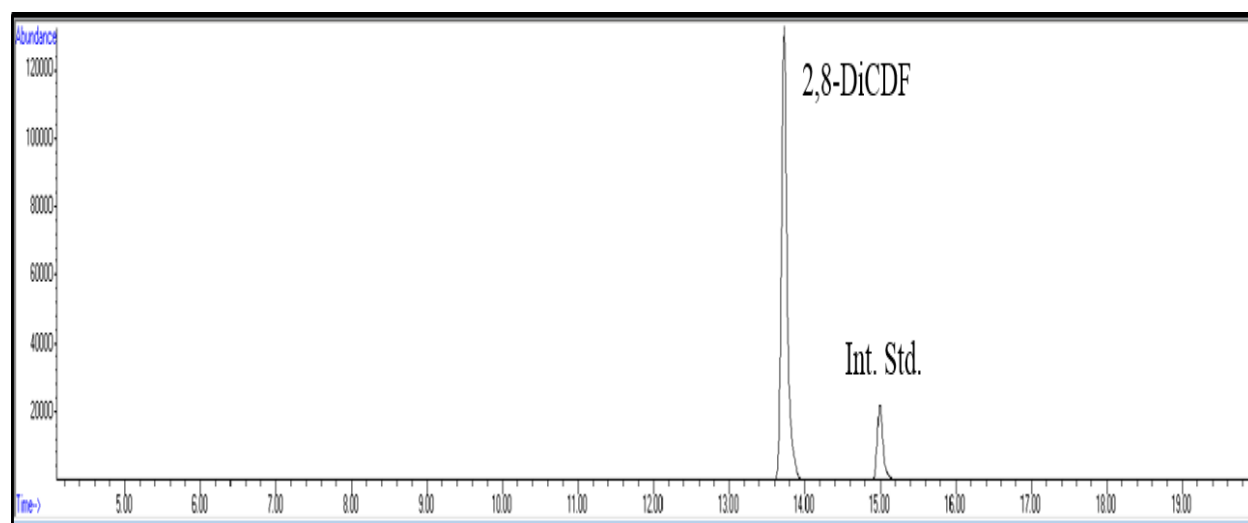


Figure 56: Images of A) ball-milled ZVMg before reaction, B) ball-milled ZVMg after 24 hours exposure to PCB solution in ethanol/ethyl lactate (90:10), C) ball-milled ZVMg/AC before reaction, and D) ball-milled ZVMg/AC after 24 hours exposure to PCB solution in ethanol/ethyl lactate (90:10).

APPENDIX C: SUPPORTING INFORMATION FOR CHAPTER FOUR



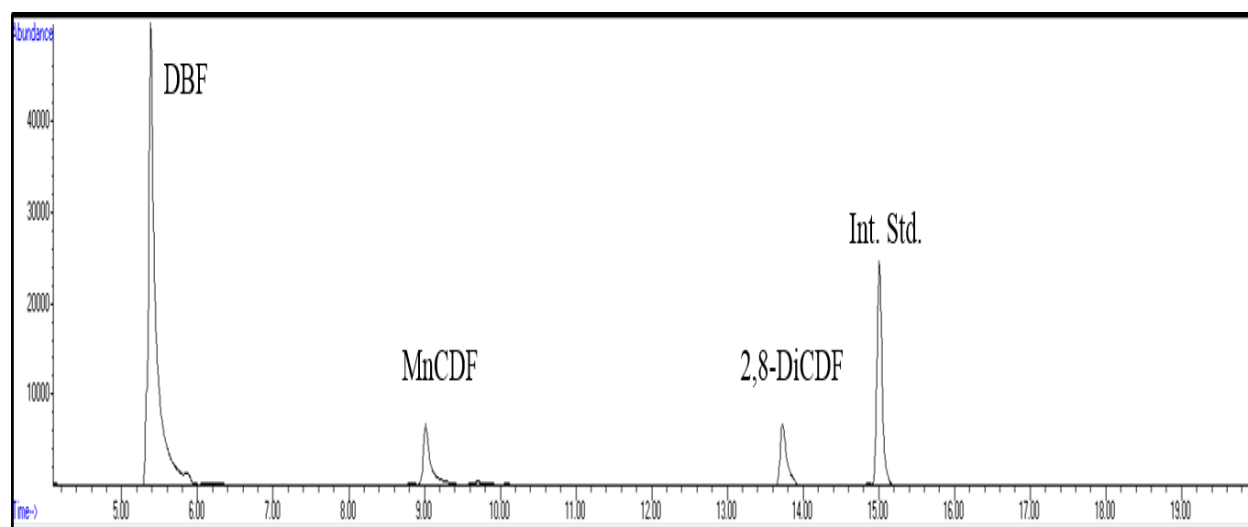


Figure 57: GC-MS chromatograms for the degradation of 2,8-dichlorodibenzofuran.

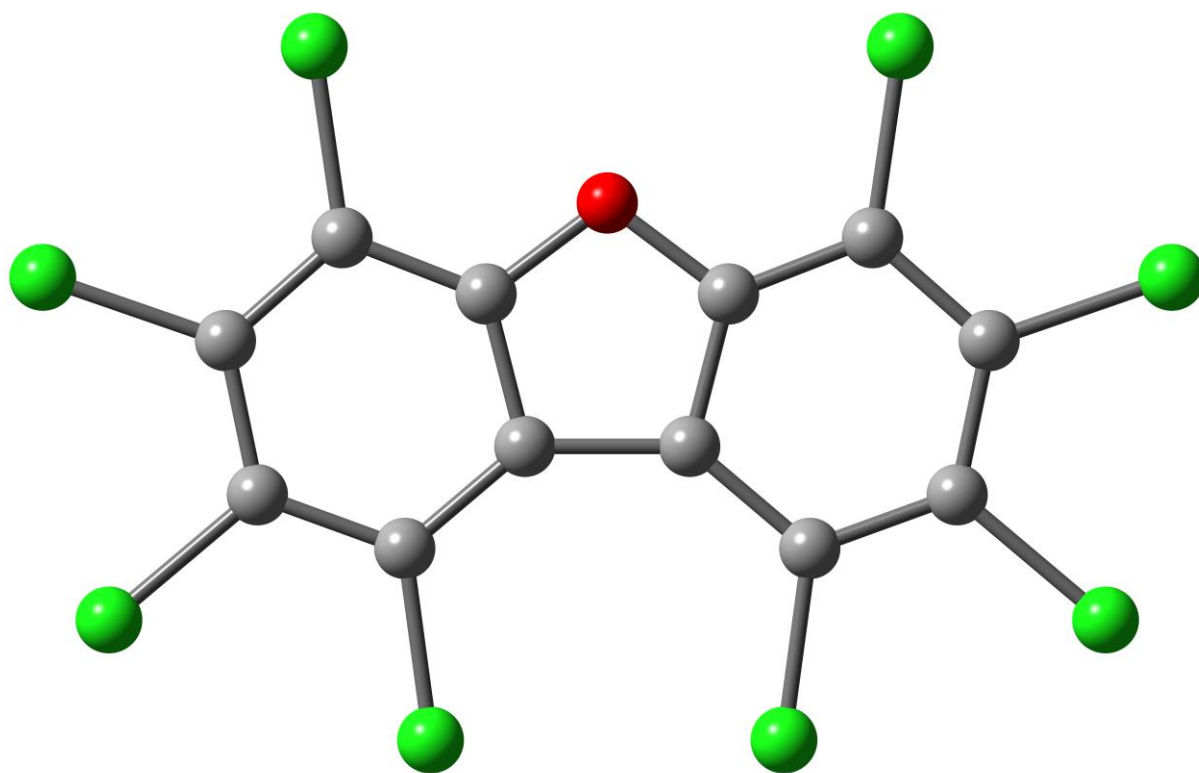


Figure 58: Minimum energy conformation of octachlorodibenzofuran.

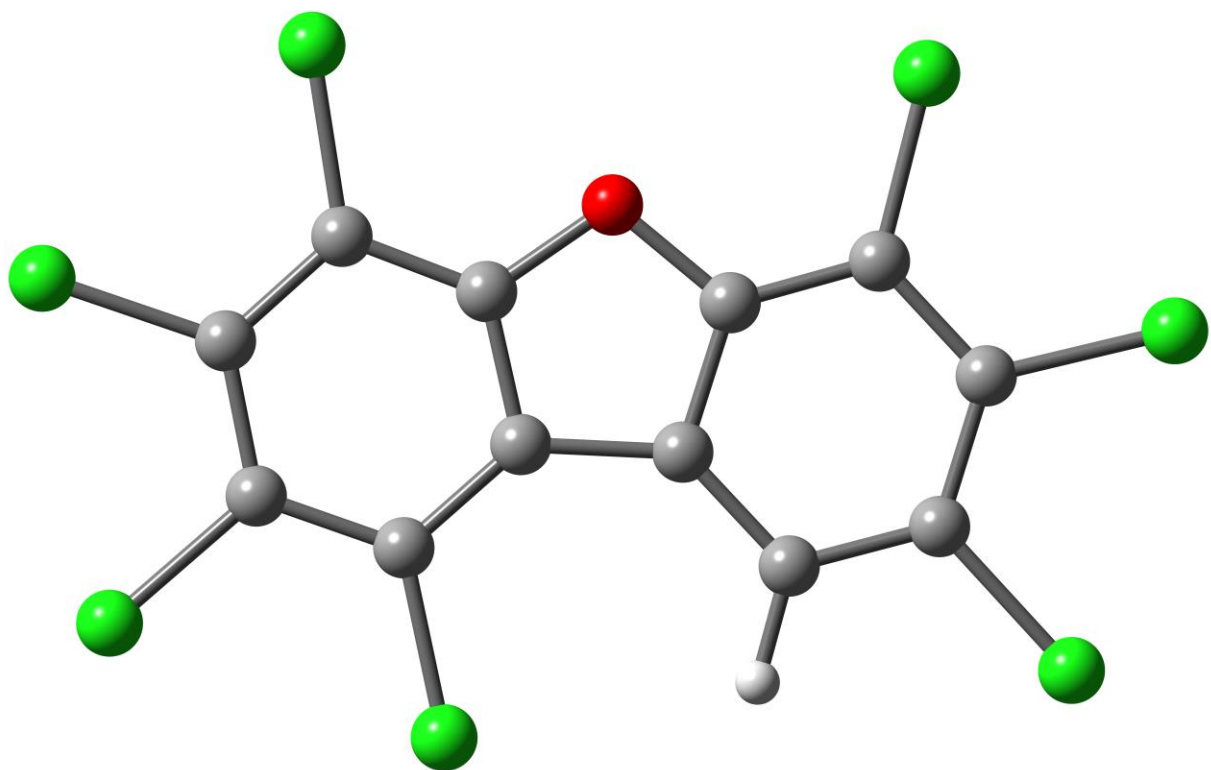


Figure 59: Minimum energy conformation of 1,2,3,4,6,7,8-heptachlorodibenzofuran.

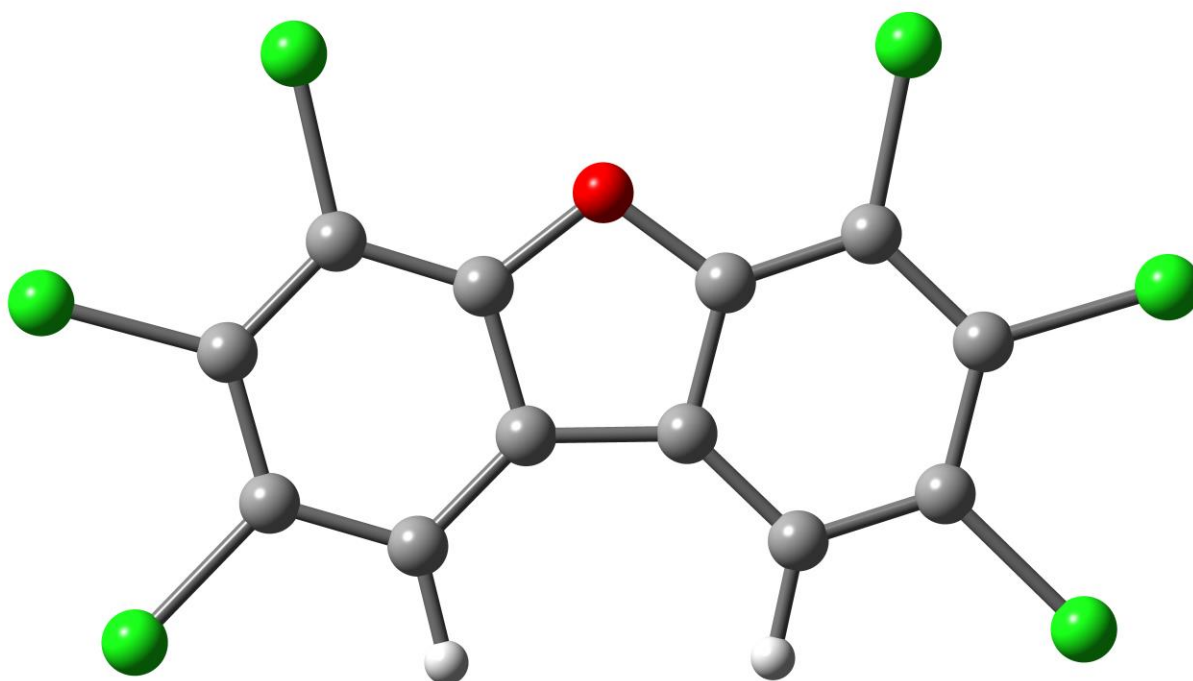


Figure 60: Minimum energy conformation of 2,3,4,6,7,8-hexachlorodibenzofuran.

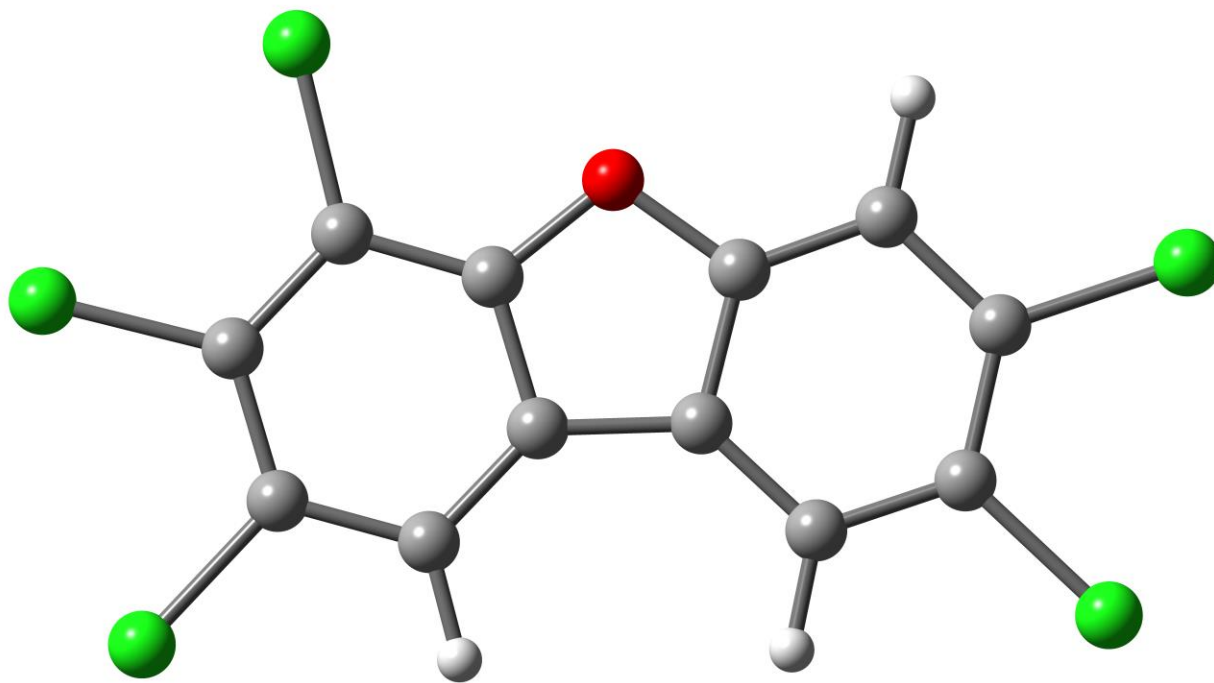


Figure 61: Minimum energy conformation of 2,3,4,7,8-pentachlorodibenzofuran.

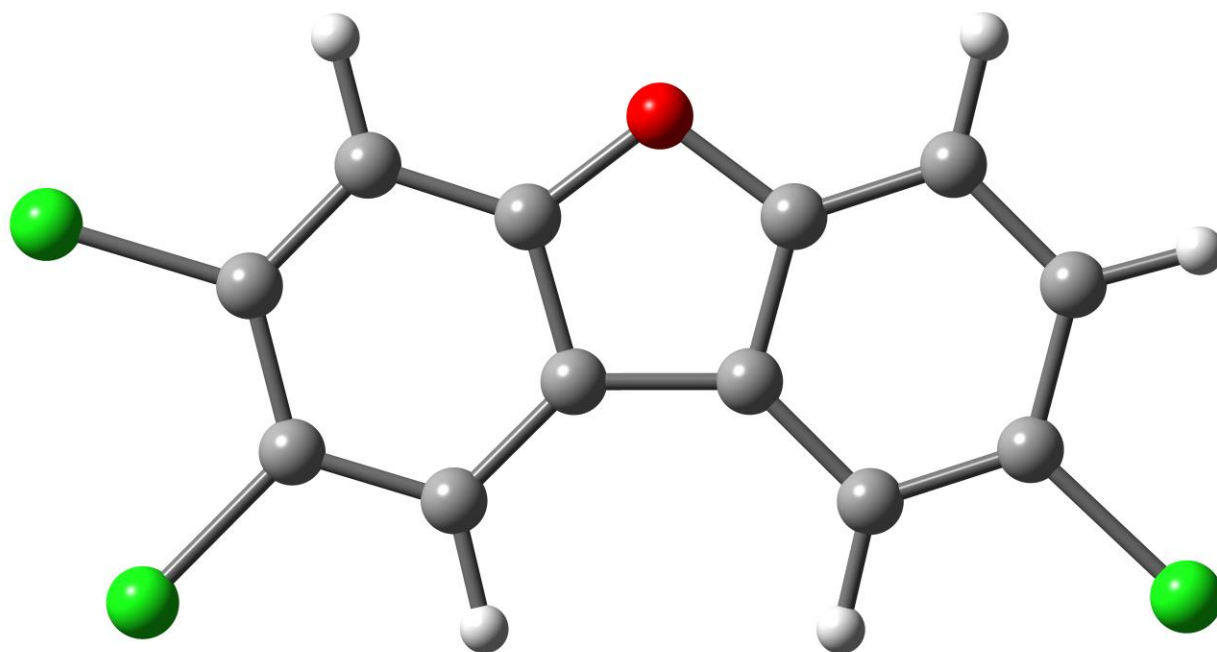


Figure 62: Minmum energy conformation of 2,3,8-trichlorodibenzofuran.

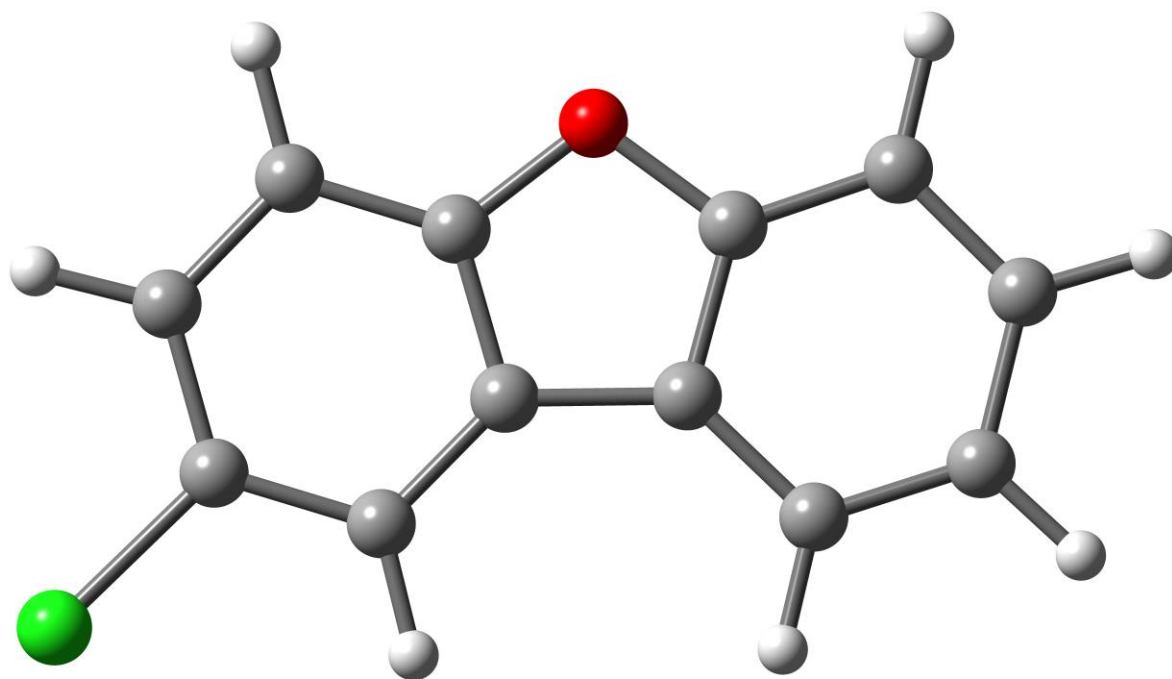


Figure 63: minimum energy conformation of 2-monochlorodibenzofuran.

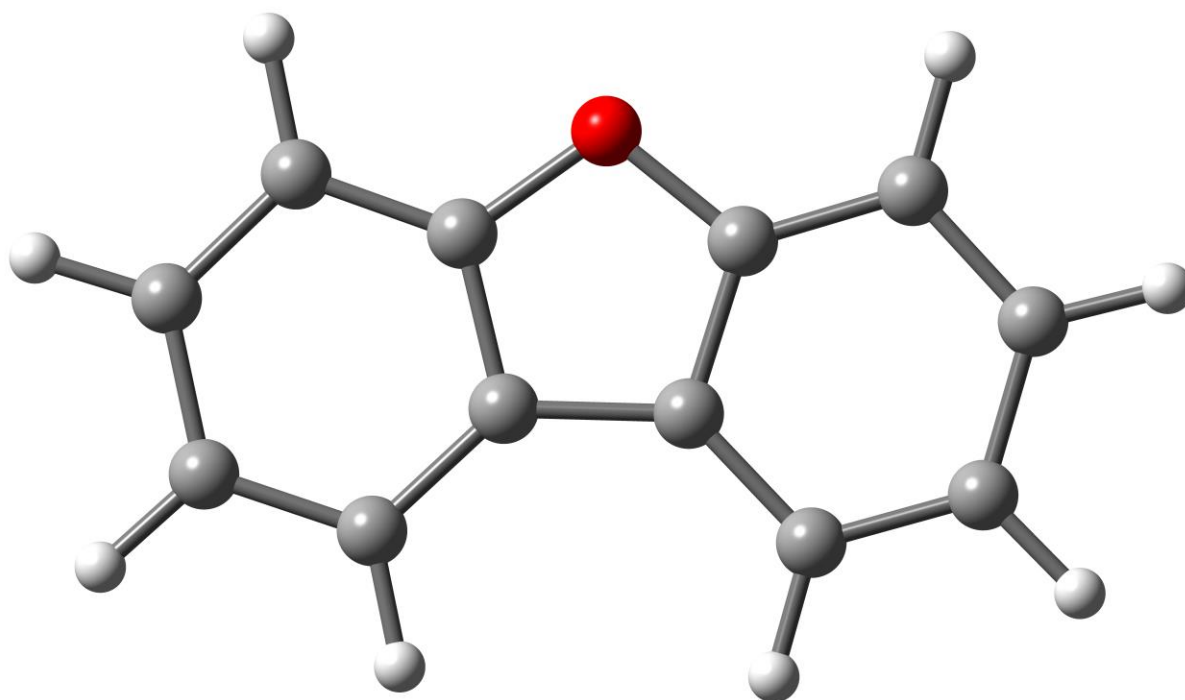


Figure 64: Minimum energy conformation of dibenzofuran.

APPENDIX D: SUPPORTING INFORMATION FOR CHAPTER FIVE

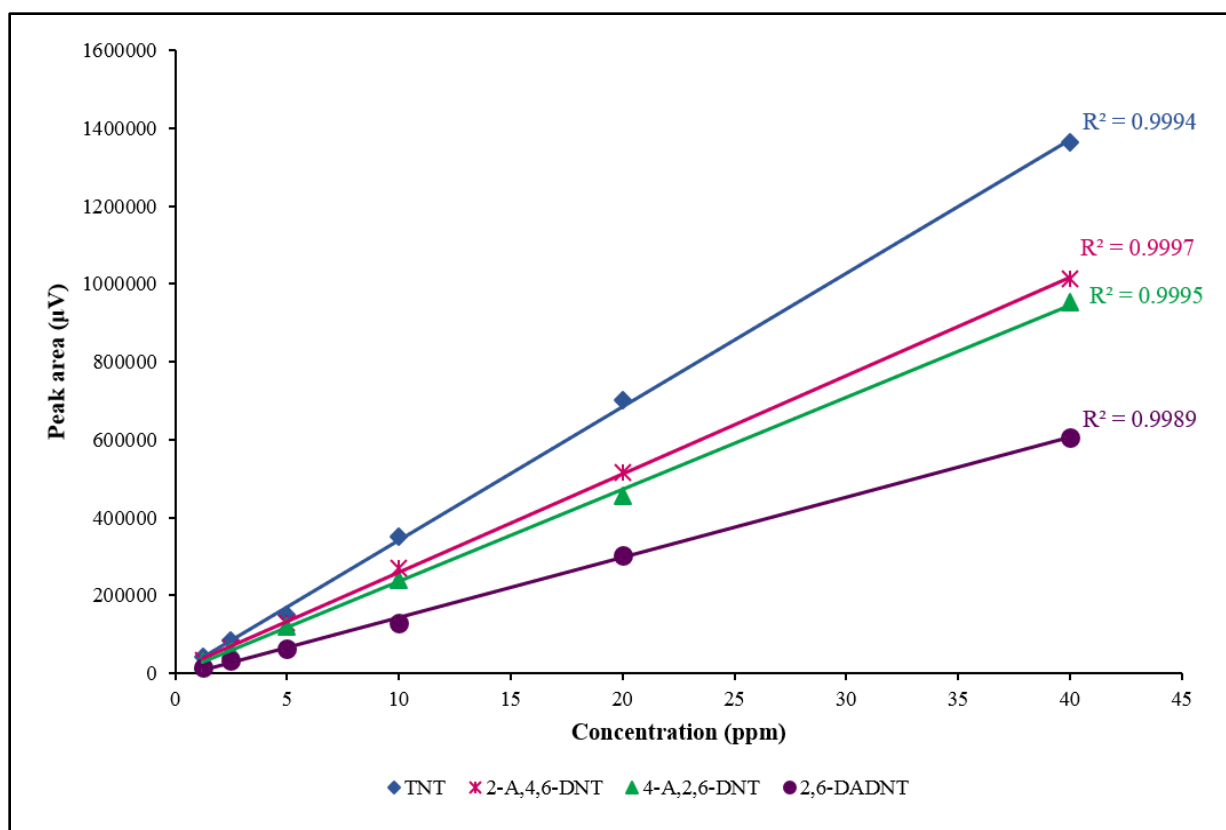


Figure 65: GC-MS peak area as a function of TNT and its byproduct concentrations.

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