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ELECTROCHEMICAL DEGRADATION OF
METHYL TERT-BUTYL ETHER (MTBE) USING
ALTERNATING AND DIRECT CURRENTS

presented by

CHEON YONG SEO

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of the requirements for the

M.S degree in CIVIL ENGINEERING

Major Professor's Signature

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Date

ELECTROCHEMICAL DEGRADATION OF METHYL TERT-BUTYL ETHER (MTBE) USING ALTERNATING AND DIRECT CURRENTS

By

Cheon Yong Seo

A THESIS

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ABSTRACT

ELECTROCHEMICAL DEGRADATION OF METHYL TERT-BUTYL ETHER (MTBE) USING ALTERNATING AND DIRECT CURRENTS

By

Cheon Yong Seo

Electrochemical degradation of methyl tert-butyl ether (MTBE) was investigated to evaluate the effect of current type and density, electrode material, deionized (DI) water and tap water as electrolytes and initial concentration of MTBE. MTBE is an organic compound, which is highly soluble in water and is common ground water (GW) contaminant that is typically released to the GW from gasoline spills. MTBE dissolved in DI water at initial concentrations equal to 25, 250 and 2,500 mg/L was subjected to alternating and direct currents (AC and DC) at current density ranging from 0.5 to 2 mA/cm^2. The volume of the electrochemical cell was 1 L and titanium, graphite, and boron doped diamond electrodes were tested. Sodium sulfate (Na_2SO_4) was used as the supporting electrolyte during tests at a concentration of 300 mg/L. The key results are: (1) both AC and DC resulted in electrochemical degradation of MTBE but the rate of degradation for DC was greater than that for AC at an equivalent current density; (2) rate of degradation increased as the current density increased for DC as well as for AC; (3) rate of degradation defined as change in normalized concentration decreased as the initial concentration of MTBE was increased; (4) rate of degradation for the graphite electrode was the least among the three materials tested; and (5) Nernst-Planck equation was able to accurately model the decrease in the MTBE concentration for low initial concentrations. At higher initial concentrations, the model results were not consistent.

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LIST OF ABBREVIATIONS

AC = Alternating Current

AOP = Advanced Oxidation Process

BCF = Bioaccumulation Factor

BDD = Boron Doped Diamond

BTEX = Benzene, Toluene, Ethyl benzene and Xylenes

DC = Direct Current

DI = De-ionized

EFOA = the European Fuel Oxygenates Association

EIA = Energy Information Administration

GAC = Granular Activated Carbon

GC = Gas Chromatography

MCLG = Maximum Contaminant Level Goal

MS = Mass Spectrometry

MTBE = Methyl tert-Butyl Ether

TBA = Tertiary Butyl Alcohol

TCB = Trichlorobenzenes

US EPA = the United States Environmental Protection Agency

LIST OF SYMBOLS

A = Current

C_t = Concentration with time

C_f = Final concentration

C_o = Initial concentration

C = Coulomb

D =Diffusion coefficient

F = Faraday's constant (96,487 C/mol)

J = Mass flux

K_{OC} = Soil-water partitioning coefficient

R = Gas Constant (8.314 kJ/mol.K)

T = Temperature

V = Voltage

W = Power

f = AC frequency

j = Current density

j_{eqv} = Equivalent current density

k = Pseudo-first-order degradation rate constant

$t_{1/2}$ = Half-life

v = Velocity of solution

z = Net charge of carrier

Ω = ohm

η = Viscosity of solution

CHAPTER 1

INTRODUCTION

1.1 MTBE AS GROUNDWATER CONTAMINANT

Methyl tertiary-butyl ether (MTBE) is a chemical compound that is manufactured by the chemical reaction of methanol and isobutylene. MTBE was produced in relatively large quantities (over 200,000 barrels per day) in the U.S. in 1999 and is almost exclusively used as a fuel additive in motor gasoline. It is a group of chemicals commonly known as "oxygenates" because it raises the oxygen content of gasoline. At room temperature, MTBE is volatile, flammable and colorless liquid that dissolves rather easily in water. MTBE could improve fuel combustion and reduce carbon monoxide but it is a risk to human health as a possible carcinogen and is classified by the United States Environmental Protection Agency (USEPA) (Song Hong *et al.*, 2007) as a toxic chemical. MTBE has relatively high solubility (~ 42 g/L), low soil-water partitioning coefficient (K_{OC} = 11; $\log_{10} K_{OC}$ = 1.04), and relatively low retardation factors when compared with other gasoline additive such as benzene (EFOA, 2002) (Table 1.1). Therefore, MTBE is highly mobile, and is relatively difficult to remove. USEPA drinking water advisory (USEPA, 2000) recommended concentration of MTBE not to exceed 20 to 40 µg/L. More than 40 U.S. states developed drinking water/groundwater standards with action levels that range from 6.4 to 240 µg/L. While there are thousands of MTBE impacted groundwater sites in the U.S, a spill in Monica, CA is one of the major spills where

MTBE concentration in groundwater ranged from 116 to 824 µg/L (US Water news, 1996).

1.2 BACKGROUND

1.2.1 Degradation Mechanism

Organic compounds can be degraded and transformed by electrochemical degradation (Pepprah and Khire, 2008; Pepprah, 2007; Alshawabkeh *et al.*, 2005). Electrochemical degradation of organic compounds in aqueous phase occurs due to direct oxidation and/or indirect oxidation or reduction. During the indirect oxidation processes, the agents that oxidize organic compounds are generated. Previous research has reported hydrogen peroxide (Brillas *et al.*, 1995), metal mediators (Farmer *et al.*, 1992), hypochlorite (Rajkumar *et al.*, 2005), ozone (Stucki *et al.*, 1987) and hydroxyl radicals (Yangqing *et al.*, 2007) as strong reactive agents during electrochemical degradation.

Equations 1.1 and 1.2 show breakdown of water at anode and cathode and resulting formation of oxygen at anode and hydrogen at cathode (Acar and Alshawabkeh, 1996).

$$\text{Anode: } 2H_2 \rightarrow O_2 + 4H^+ + 4e^- \qquad (1.1)$$

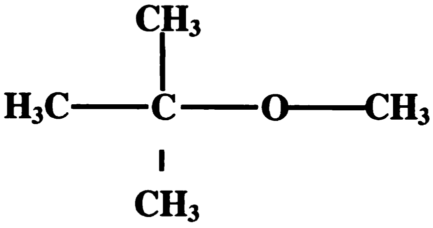
$$\text{Cathode: } 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (1.2)$$

During electrochemical conversion, hydroxyl radicals are also formed at the anode (Equation 1.3 and 1.4).

$$H_2O + e^- \rightarrow H^{\cdot} + OH^- \qquad (1.3)$$

$$OH^- \rightarrow OH^{\cdot} + e^- \qquad (1.4)$$

Table 1.1: Key physical properties of MTBE

Identifiers	IUPAC Name (International Union of Pure and Applied Chemistry)	2-Methoxy-2-methylpropane
	CAS No.	1634-04-4
Physical and Chemical Properties	Molecular Formula	$C_5H_{12}O$
	Molecular Weight (g/mol)	88.15
	Density (g/cm^3)	0.7404
	Melting Point	-109°C / -164°F / 164K
	Boling Point	55.2°C / 131°F / 328K
	Flash Point	-10°C / 14°F / 263K
	Auto ignition	425°C / 797°F / 698K
	Vapor Pressure (kPa)	33.4
	Water Solubility	42 g/L
	Partitioning Coefficient n-octanol/water (K_{OC}) (log10)	1.04 (estimated)
	Henry's Constant (Pa/m^3/mol)	65.4
	Bioaccumulation factor (BCF)	1.6 (estimated) / 1.5 (measured for fish)
Structure	 $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_3$	**CH_3-O-C(CH_3)$_3$**

Note: 1. Source: European Fuel Oxygenates Association (EFOA)
2. MTBE at 25°C and 100 kPa

Hydroxyl radicals are strong oxidizing agents that can breakdown many organic compounds including MTBE.

1.2.2 Electrical Efficiency

Electrical efficiency is one of the considerations for operation of electrochemical systems. Among other parameters, electrical power usage is important consideration for electrochemical systems. The electrical power consumption can be computed using Eq. 1.5.

$$Power\ (W) = Current\ (A) \times Voltage\ (V) \tag{1.5}$$

Electrical efficiency (Eq. 1.6) is another important parameter which relates degradation of the pollutant to the power usage (Alshawabkeh and Sarahney, 2005).

$$EE/O = \frac{P \times t}{V \times \log(C_o / C_f)} \tag{1.6}$$

where EE/O is electrical efficiency (kWh/m^3); P is power usage (kW); t is operational time (hours); V is electrochemical reactor volume (m^3); and C_i and C_f are initial and final concentration of the pollutants, respectively.

Pollutant breakdown rate is the ratio of rate of change in the concentration (i.e., degradation) of the pollutant to current density (Alshawabkeh and Sarahney, 2005), (Eq. 1.7) is as follow:

$$\eta_k = \frac{\Delta C / \Delta t}{j} \tag{1.7}$$

where η_k is the efficiency of pollutant breakdown (mg/C); ΔC is change in pollutant concentration (mg/L); Δt is electrolysis time (seconds); and j is the current density (A/L).

1.2.3 Current Type

1.2.3.1 Direct Current (DC)

Direct Current (DC) is a form of electrical current which does not change the directions of its flow. Usually constant DC means a DC which has zero frequency. A majority of published work on electrochemical breakdown of organic compounds has been focused on the use of direct current (DC). Wu and Lin (2007) used DC electrolysis for degradation of MTBE using iridium electrodes with supporting electrolytes that included sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and nitric acid (HNO_3). They used initial concentration of MTBE equal to 20 mg/L. Removal rate of MTBE ranged from 27% to 92% after electrolysis for 3 hr for various values of input voltage, which ranged from 0.5 to 3.0 V for the various electrolytes. Degradation rate of MTBE increased as a function of applied voltage.

While the use of DC in the lab-scale studies have demonstrated acceptable rates of breakdown of many organic chemicals, use of DC for field application poses many challenges (Khire and Pepprah 2008). Khire and Pepprah (2008) and Lee (2008) have indicated that power usage during DC is relatively high because the resistance of the electrolyte increases as the time of application of DC increases. Increased resistance requires proportionately greater voltage to maintain the current which, among other parameters, dictates the rate of breakdown of organic molecules in the solution. In addition, application of DC results in decrease in the pH near the anode and increase in the pH near the cathode. This results in relatively rapid fouling of the electrode which causes decrease in the rate of breakdown and affects the physical integrity of the electrode.

1.2.3.2 Alternating Current (AC)

Alternating Current (AC) is an electrical current which changes its direction periodically. AC wave form can have well defined shapes such as sinusoidal, triangular, square, or it can follow an arbitrary shape. While the frequency of sinusoidal AC available in north American power grid is 60 Hz, AC function generators typically can produce AC at frequencies ranging from 0.1 Hz to 1 MHz. Relatively few published studies where AC has been used for electrochemical breakdown of organic compounds exist. Nakamura *et al* (2005) presents degradation of Trichlorobenzene (TCB) using AC electrolysis in aqueous solution. Decomposition rate of TCB was 29.6% after electrolysis for 0.5 hr due to hydrogen and hydroxyl radicals produced during AC electrolysis.

Pepprah (2007), Pepprah and Khire (2008), and Khire and Pepprah (2008) have compared the use of DC and AC for electrochemical breakdown of naphthalene, pyrene, phenanthrene, and salicylic acid in aqueous solutions. For a given current density, these studies concluded that the rate of breakdown of the organic compounds was greater for DC compared to AC. For AC, the rate of breakdown decreased as the frequency of the AC was increased from 0.1 Hz to 1,000 Hz. However, the extent of electrode fouling and electrode mass loss was greater for DC compared to when AC was applied.

Lee (2008) evaluated the power consumption for AC versus DC when naphthalene was degraded in electrochemical cells having volumes equal to 1 L and 3.5 L. Lee (2008) concluded that the power consumption per unit volume of the electrochemical cell was about 2 to 5 greater when DC was used. Lee (2008) also found that as long as the current density (defined as total current divided by the total area of the electrodes that faces each other) was constant, the size of the cell did not influence the rate of degradation of naphthalene in aqueous solution.

1.2.4 Current Density

Pepprah (2007), Pepprah and Khire (2008), Khire and Pepprah (2008), and Lee (2008) studied decomposition of naphthalene with AC and DC at current densities ranging from 0.5 to 6 mA/cm^2. The degradation rate increased when current density was increased during AC as well as DC electrolysis.

1.2.5 Mass Transfer Process: The Nernst-Planck Equation

Mass transfer of charged species (i.e. ions) in solution subjected to electrical current involves migration, diffusion and convection (Bard *et al.*, 2001). Migration is the movement of a charged specie due to electrical potential difference. Diffusion is movement of chemical (i.e., contaminant in this study) under concentration gradient. Last, convection is from stirring or hydrodynamic movement. Equation 1.8 is the Nernst-Planck equation, which presents mass transfer due to migration, diffusion and convection between the two electrodes subjected to DC.

$$J_i(x) = -D_i(x)\frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \qquad (1.8)$$

Where $J_i(x)$is the flux of contaminant *i* (mol s^{-1} cm^{-2}) at distance x from the electrode surface; D_is the diffusion coefficient (cm^{-2} s^{-1}); $\frac{\partial C_i(x)}{\partial x}$ is the convection gradient at distance x from the electrode surface; z is valency of the net charge carrier (dimensionless); F is the number of coulombs of charge per mole of ion (C); C_i is the concentration of contaminant *i* (mol cm^{-3}); R and T are gas constants (j mol^{-1} K^{-1}) and absolute temperature (K), respectively; $\frac{\partial\phi(x)}{\partial x}$ is the potential gradient; $v(x)$ is the velocity (cm s^{-1}) of hydrodynamic flow between electrodes; and D is the diffusion coefficient of the specie. D of MTBE was estimated from the Hayduk-Laudie equation (1974) as shown in Eq. 1.9:

$$D = \frac{13.26\times10^{-5}}{\eta^{1.14}\times \overline{V}^{\,0.589}} \tag{1.9}$$

where D is diffusion coefficient (cm^{-2} s^{-1}); η is the solution viscosity (10^{-2} g cm^{-1} s^{-1}) at specific temperature; and V is the molar volume of contaminant (cm^3 mol^{-1}).

1.3 CONVENTIONAL REMEDIATION TECHNIQUES

1.3.1 Air Sparging

Air sparging involves pumping air in the shallow plume of organic contaminants that are present in the ground water that are volatile. The air bubbles created by the pumped air allow the dissolved volatile organic compounds to volatilize at a faster rate. The vapors are removed by vacuum applied using an extraction system.

Many sites contaminated with benzene, toluene, ethyl benzene and xylenes (BTEX) compounds in shallow ground water have been successfully remediated by air sparging (Suthersan, 1997; USEPA, 1996). However, this technology is not effective for dense non-aqueous phase liquids such as the chlorinated solvents and also MTBE which has relatively low liquid-gas partitioning coefficient.

1.3.2 Chemical Oxidation Processes

The chemical Oxidation Processes are used to convert contaminant to end products, which are non toxic. Typically, the degradation or conversion occurs due to hydroxyl radicals which are produced. Hydroxyl radicals are strong oxidizing agents. A few examples of this application include the use of Fenton's reagent, hydrogen peroxide, and ozonation.

1.3.3 Natural Attenuation

Natural Attenuation involves several processes: (1) adsorption to aquifer materials leading to contaminant retardation; (2) dilution of contaminants through advection, dispersion and diffusion; and (3) volatilization. However, half-life period of MTBE is 0.1 year. Hence, it will require relatively long for MTBE to degrade using natural degradation (Hert *et al.*, 1999)

1.3.4 Bioremediation

Bioremediation uses microorganisms to degrade or immobilize contaminants. In order to optimize the rate of degradation or immobilization, several options are required. These options include injection of oxygen or electron acceptor, nutrients, and growth simulating materials (National Academy Press, 1993). In addition, temperature and pH have effect on decomposition efficiency (LaGrega *et al.*, 1994).

1.4 OBJECTIVES

1.4.1 Key Challenges

MTBE has relatively high solubility and low adsorption ability. Hence, air sparging or granular activated carbon adsorption does not work well (Sutherland *et al.*, 2004; Shih *et al.*, 2003). Advanced oxidation methods do work. However, they are relatively expensive. (Hseih *et al.*, 2004; Watt, 1998; Anderson, 1994; Wagler and Malley, 1994).

Electrochemical methods have a potential for source zone remediation. Electrochemical methods are yet not proven to be technically sound and cheap. Hence, additional research is needed to explore the use of AC versus DC and electrode materials on the efficiency of degradation of MTBE. Published studies have tested various materials for electrodes including: platinum (Ernst and Knoll, 2001); nickel (Wu, 2007); and iridium (Wu and Lin, 2007). These electrodes are expensive and undergo physical decay. There is lack of data on efficiency of electrochemical techniques.

1.4.2 Key Objectives

The key objectives of this study are to investigate:

1. Effect of current types and density on the degradation rate;
2. The effect of electrode material on the rate of electrochemical degradation of MTBE in aqueous solution;
3. The effect of initial concentration of MTBE on the rate of degradation; and
4. The effect of DI water versus MSU tap water on the rate of degradation and energy consumptions.

CHAPTER 2

MATERIALS

2.1 CHEMICALS

The chemicals used for this project included MTBE (target contaminant), acetone (cleaning solvent), sodium sulfate (Na_2SO_4) which was the supporting electrolyte, and deionized (DI) water which was the primary medium in which MTBE and Na_2SO_4 were dissolved.

MTBE was purchased from Sigma-Aldrich Company (Serial No. 306975). Acetone was purchased from J.T. Baker Company (Serial No. 9002-03). Acetone was 99.8% pure. DI water is obtained from the lab DI water system which produces DI water that has an electrical conductivity that exceeds 1 M. All chemicals were environmental grade.

2.2 ELECTRODES

Three material types for the electrodes were evaluated in this study. These materials included titanium, graphite, and boron doped diamond (BDD). BDD is also referred to as diamler.

2.2.1 Titanium

The titanium electrodes used in this study were uncoated titanium. This material was selected because it is cheaper than platinum, nickel, and mixed metal electrodes used in published electrochemical studies. Furthermore, it is corrosion-resistant, lustrous and strong so can be potentially used for long-term field use (Chen et al, 2003). Zaggout and Hallway (2008) used titanium electrodes for degradation of o-nitro phenol and observed relatively high removal rate. In this study, titanium electrodes were 12 cm high (H) x 5 cm wide (W) 0.1 cm thick (area ~ 60 cm^2). Immersed area of the electrodes in 1 L aqueous solution was about 55 cm^2. Photographs of the titanium electrodes are presented in Figure 2.1 and dimensions of all electrodes are summarized in Table 2.1.

2.2.2 Graphite

Graphite is one of the allotropes of carbon and is an electrical conductor. Graphite is relatively cheap. Sathish and Viswanath (2005) used graphite electrodes for degradation of phenol in aqueous solution and reported 85% degradation within 30 hrs using DC at a 5 V. The dimensions of the graphite electrodes used in this project were 12.8 cm (H) by 5.3 cm (W) by 0.6 cm (immersed area ~ 68 cm^2). A photograph of the electrodes and their dimensions are presented in Figure 2.2 and Table 2.1, respectively.

Table 2.1: Dimensions of titanium, graphite and BDD electrodes

Electrode Type	Shape of Electrode	Diameter of screw (D_{screw})	Length or Diameter (H, cm)	Width or Diameter (W, cm)	Immersed Area of the two Electrode (cm^2)	Thickness (B, cm)
Titanium	Rectangle	0.5	12	5	55	0.1
Graphite	Rectangle	0.5	12.8	5.3	68	0.6
BDD	Circle	0.5	7.4		35.9	0.1

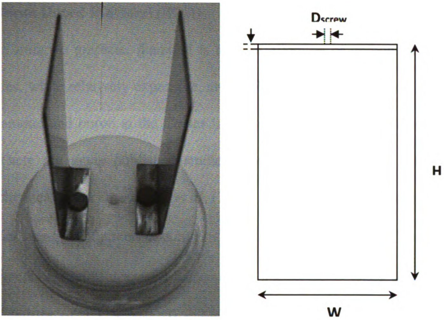


Figure 2.1 Photograph and schematic diagram of titanium electrodes attached to the top cap

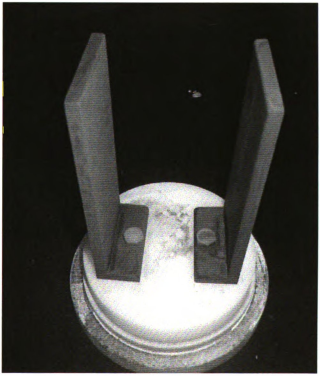


Figure 2.2: Photograph of graphite electrodes attached to the top cap

2.2.3 Boron Doped Diamond (BDD)

Similar to graphite, diamond is also an allotrope of carbon. However, diamond electrodes, while relatively expensive, are stable. In this study, silicon wafer was coated with diamond and boron at the Center for Coatings and Laser Applications, Fraunhofer USA. There are many published studies where BDD electrodes have been used for electrochemical research. Ammar *et al.* (2006) studied degradation of indigo dye at BDD electrodes using DC applied at a current density of 100 mA/cm^2. Oliveira *et al.* (2007) and Zhao *et al.* (2008) degraded benzene and phenol using BDD with DC applied at a current density of 2.5 V and 20 mA/cm^2, respectively. In this study, circular BDD electrodes were fabricated. The total and immersed areas of the electrodes were 43 cm^2 and 35.9 cm^2, respectively. A photograph of the electrodes is presented in Figure 2.3 and dimensions are listed in Table 2.1.

2.3 SUPPORTING ELECTROLYTE

Sodium sulfate (Na_2SO_4) was used as the supporting electrolyte in this study. Lee *et al.* (2003) selected Na_2SO_4 as the electrolyte for decontamination of radioactive metal waste. Pepprah and Khire (2008) compared the use of Na_2SO_4 and NaCl as supporting electrolytes during electrochemical degradation of naphthalene and concluded that NaCl caused rapid decay of uncoated titanium electrodes due to the formation of hypochloric acid.

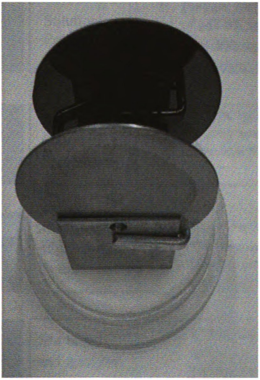


Figure 2.3: Photograph of Boron Doped Diamond (BDD) electrodes attached to the top cap

CHAPTER 3

EXPERIMENTAL METHODOLOGY

An outline of the experimental procedure is presented in Figure 3.1.

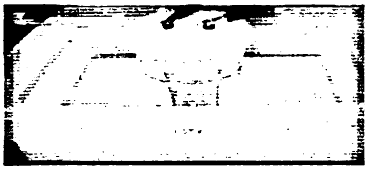
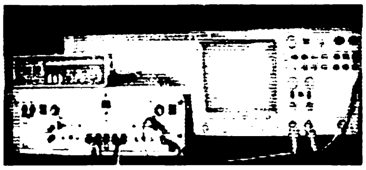
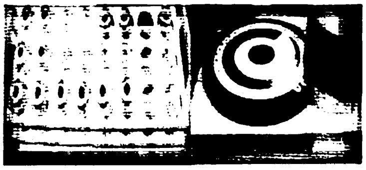
Photo	Steps	Description
	Solution Preparation	1. Prepare for 25, 250 and 2,500 mg/L of MTBE solution 2. Add 300 mg of Na_2SO_4 as supporting electrolyte
	Reaction Chamber Preparation	1. Add the spiked solution to the reaction vessel 2. Place reaction vessel in water bath
	Electrical Equipment Setup	1. Apply the pre-determined electrical current to the cell 2. Measure temperature, current and voltage at specific time
	Sampling and Analysis	1. Collect liquid samples at specific times 2. Run GC to analyze MTBE concentration
	Cleaning	1. Wash and polish the Ti and Graphite electrodes 2. Wash the BDD electrodes, all beakers and vials using acetone and DI water

Figure 3.1: Outline of experimental procedure

3.1 EXPERIMENTAL SETUP

The Experimental setup consisted of electrochemical reactor and electrical equipment as displayed in Figure 3.2.

3.1.1 Electrolytic Reactor

The electrochemical cell consisted of 1 L Pyrex beaker, Teflon cap, and electrodes. Pyrex beaker and Teflon cap minimize sorption and volatilization of MTBE. A water bath was used to minimize temperature increase and fluctuation. The room temperature was maintained between 20 to 22 °C. Figure 3.3 shows the reaction chamber placed inside a water bath.

3.1.2 Electrical Equipment

The electrical equipment consisted of: DC power supply/AC amplifier, function generator, and oscilloscope (Figure 3.4). The function generator was able to generate triangular, sinusoidal, or square wave AC signals having 0 to 2 MHz frequency. Square wave AC having 0.1 Hz frequency was selected because Pepprah (2007) has shown that when AC is used, lower the frequency, greater the rate of degradation rate due to more time given for the reactions to occur at each instantaneous anode and cathode. The power supply used for this project was manufactured by Kepco, model BOP 200W. It consisted of bipolar operational amplifier and power supply with maximum 200 V and 1 A of AC/DC. Oscilloscope, which is Agilent model No. 54621A, was used to measure the current passing through the reaction chamber and the voltage applied to the chamber. It has two channels to measure voltage. The Kepco amplifier has a special setup that allows measurement of the current supplied by the amplifier in the form of an equipment voltage signal.

3.1.3 MTBE in Aqueous Solution

MTBE in aqueous solution was prepared by adding 300 mg of Na_2SO_4 (in crystal form, EMD chemicals Inc.) to 1 L of DI water and 0.0337, 0.337 and 3.37 mL of MTBE in liquid form to the solution to prepare 25, 250 and 2500 mg/L, respectively of MTBE spiked test solutions. Volume of MTBE was converted to weight using the density of MTBE which is equal to 0.74 g/cm^3. 300 mg of Na_2SO_4 was selected based on Maximum Contaminant Level Goal (MCLG) (1990, 55 FR 30370), which EPA has proposed for Na_2SO_4.

3.2 TESTING, SAMPLING AND ANALYSIS

3.2.1 Testing

In order to measure the concentration of MTBE, six standard solution samples were prepared as Gas Chromatograph (GC) standards. The identification of MTBE and quantification of its concentration was achieved by comparison of retention times and area under the chromatograms for standard solutions. R-square values in calibration curves obtained for the standard solution ranged from 0.9399 to 0.999. When 2,500 mg/L MTBE solution was analyzed, all samples were diluted to 2/3rd or 1/3rd to keep the measurement within the most accurate range of the GC.

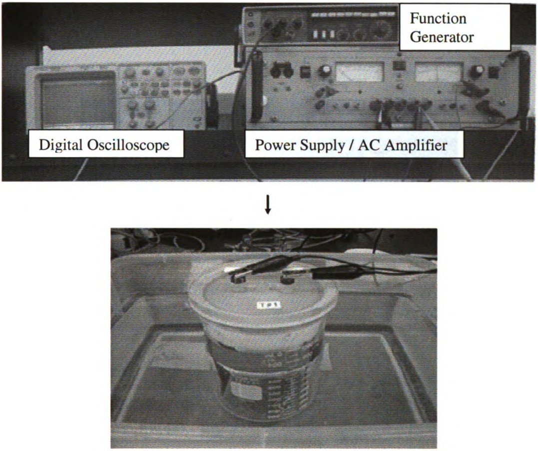


Figure 3.2: Experimental setup

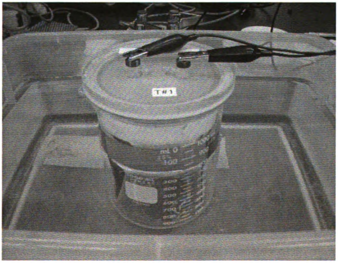


Figure 3.3: Reaction chamber placed inside water bath

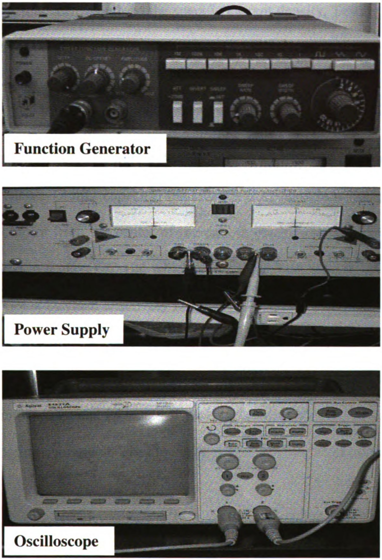


Figure 3.4: Photographs of electrical equipment used in the study

Table 3.1 presents volumes of specific concentration of MTBE solution and DI water for making standard solutions for 25, 250 and 2,500 mg/L of MTBE. Current density tested in this project ranged from 0.5 to 2 mA/cm^2 for DC and 1 to 5 mA/cm^2 for AC. Table 3.2 shows the current that corresponds to the specific current density. Testing time was fixed at 24 hr for all tests.

3.2.2 Sampling

Samples of test solution were collected at 0, 1, 2, 4, 8, and 24 hours after the test began. Micro syringes (2 mL, capacity) manufactured by Hamilton Company were used to collect the samples from the center of the cell, halfway between the electrodes. The sample was stored in a glass GC vial which was capped with silicon Teflon and 20 mm standard seals (Grace Davison Discovery Deerfield) and stored in refrigerator until it was analyzed using GC within 24 hours. Photographs of the vials and the micro syringe are shown in Figure 3.5. The sampling syringe was decontaminated and cleaned after every sampling by using acetone and DI water. Figure 3.6 shows a photograph of the setup used to clean the sampling equipment. The chemical current was not stopped during sampling.

3.2.3 Gas Chromatography (GC) Analysis

GC manufactured by Perkin Elmer (model EK-3441) was used to analyze the concentrations of MTBE in the test solution. The GC was connected to a head space sampler (Perkin Elmer, HS-40). The GC run was set up for MTBE. The specific details related to the setup are as follows:

Table 3.1: Volumes of MTBE and DI water used for preparation of standard solutions

Target Concentration → (mg/L)	0	5	10	15	20	25
Volume of 25 mg/L of MTBE solution (mL)	0.0	0.4	0.8	1.2	1.6	2.0
Volume of DI water (mL)	2.0	1.6	1.2	0.8	0.4	0.0

Target Concentration → (mg/L)	0	50	100	150	200	250
Volume of 250 mg/L of MTBE solution (mL)	0.0	0.4	0.8	1.2	1.6	2.0
Volume of DI water (mL)	2.0	1.6	1.2	0.8	0.4	0.0

Target Concentration → (mg/L)	0	500	1,000	1,500	2,000	2,500
Volume of 2,500 mg/L of MTBE solution (mL)	0.0	0.4	0.8	1.2	1.6	2.0
Volume of DI water (mL)	2.0	1.6	1.2	0.8	0.4	0.0

Table 3.2: Current densities and equivalent currents

Electrode	**Measured Current (mA) Corresponding the Current Density**				
	$j_{eqv.}$ = 0.5 mA/cm^2	$j_{eqv.}$ = 1 mA/cm^2	$j_{eqv.}$ = 2 mA/cm^2	$j_{eqv.}$ = 4 mA/cm^2	$j_{eqv.}$ = 5 mA/cm^2
Titanium	55	110	220	440	550
Graphite	68	136	272	544	680
BDD	35	70	140	280	350

1. GC cycle time: 10 min
2. Heating time per vial: 30 min
3. Pressurizing time per vial: 2 min
4. Injection and withdrawal time of needle to vials: 0.2 min, respectively
5. Sampler, needle and transfer temperature: 80°C, 120°C and 120°C, respectively
6. Helium, hydrogen and air gas cylinder controlled pressure: 525 kPa (77 psi), 340 kPa (50 psi) and 500 kPa (72 psi), respectively.

Figure 3.7 shows a photograph of the GC setup. Fig. 3.8 shows a schematic of the connections used for the GC setup.

3.3 MONITORED PARAMETERS

During the test, the parameters that were monitored included pH, temperature, voltage, and electrical resistance, R (for DC) and impedance, Z (for AC). Temperature and voltage were measured at the sampling time, which was 0, 1, 2, 4, 8, and 24 hours using microprocessor thermometer (ΩE Omega) and digital oscilloscope, respectively. Electrical resistance and pH were monitored just before the test started and just after the test ended using LCR ESR meter (BK Precision) and pH meter (IQ scientific instruments), respectively. The resistance was also calculated from the voltage readings that were taken throughout the test and the fixed current which was maintained throughout the test. These measurement devices are shown in Figure 3.9.

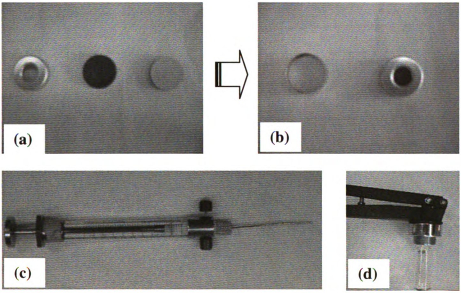


Figure 3.5: Photographs: (a) aluminum cap; (b) silicon septa and combined cap; (c) micro needle (2 mL capacity); and (d) capped vial

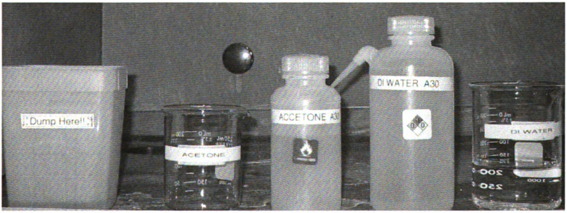


Figure 3.6: Photograph of setup to clean the sampling equipment

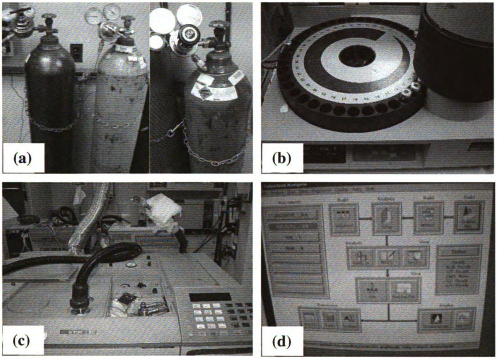


Figure 3.7: Photographs: (a) carrier gas (H_2, Air and He); (b) head space sampler; (c) GC; and (d) connected computer for data access

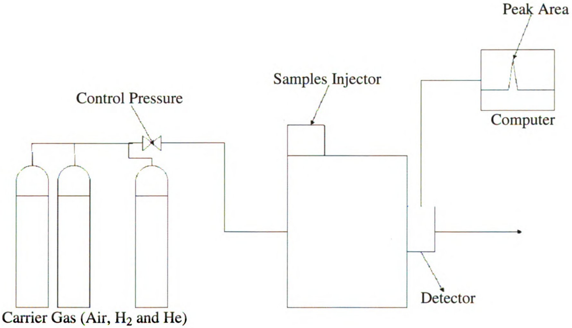


Figure 3.8: Schematic of carrier gas (H_2, Air and He), head space sampler, GC, and connected computer

3.4 DECONTAMINATION AND CLEANING

3.4.1 Electrode

Cleaning electrodes was critical for many reasons including deposits on the electrode surface have effect on the reaction rate that results in the degradation of the target chemical and the electrodes were reused. The used titanium electrodes were polished using a pneumatic metal brush scrubber followed by cleaning it using detergent (Alcox) and rinsing with DI water. The process of cleaning titanium electrodes is depicted in Figure 3.10. Graphite electrodes were cleaned by scrubbing with a sand paper followed by cleaning and rinsing with the detergent and DI water.

3.4.2 Microneedle, Beaker and Miscellanea

Microneedle was washed using one part acetone and 2 parts DI water. A photograph of how the micro needle was cleaned is presented in Figure 3.11. Beaker and vials were washed using detergent (Alcox) and rinsed using DI water and oven dried for 24 hours. Immersed components of all measuring devices also were cleaned using the same procedure as discussed above after every sampling/monitoring event.

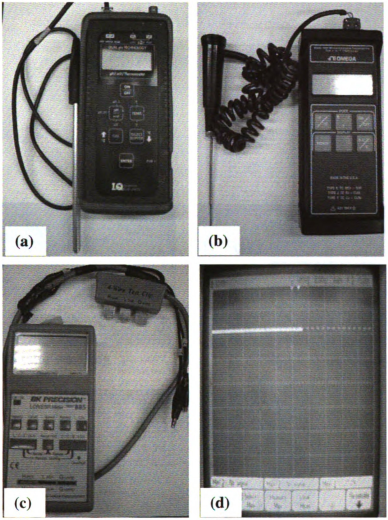


Figure 3.9: Photographs: (a) pH meter; (b) Thermometer; (c) LCR meter; and (d) Oscilloscope

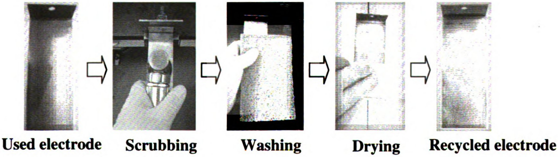
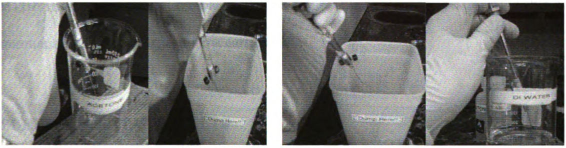
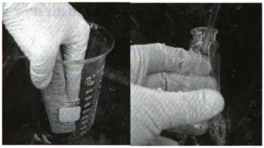


Figure 3.10: Procedure followed for cleaning titanium electrodes



Acetone washing

DI water washing for 2 times



Cleaning beakers and vials

Figure 3.11: Photographs of decontamination and cleaning of micro needle, beakers, and sampling vials

CHAPTER 4

RESULTS AND DISCUSSION

The effect of current type and current density, electrode materials, use of tap water versus DI water, and initial concentration of MTBE on the rate of degradation of MTBE in an aqueous solution was evaluated from total 37, 24-hr experiments. Table 4.1 summarizes the list of experiments carried out.

4.1 EXPERIMENTAL RESULTS

Figures 4.1 to 4.3 show normalized MTBE concentration (C_t/C_o) versus elapsed time during electrolysis with titanium electrodes where DC and AC at current densities equal to 0.5, 1, 2, 4 mA/cm^2 were applied with initial concentration of MTBE equal to 25, 250 and 2,500 mg/L. The error bars shown in all graphs are maximum and minimum values of the ordinate measured from duplicate tests. Table 4.2 presents the final concentration versus initial concentration ratio (C_f/C_O) for all current densities, current types, and initial concentrations.

4.1.1 Control Cell

Control tests were carried out for each of the initial concentrations using an identical setup as that where current was applied. However, for the control tests, no current was passed. When current passes through an electrochemical cell, hydrogen and oxygen gases bubble out at the cathode and anode, respectively.

Table 4.1: Summary of experiments carried out

Initial Concentration (mg/L)	**Electrode Material**	**Current Type**	**Current density j (mA/cm^2)**	**Total Current (mA)**	**Number of Tests**
0	Titanium	AC	1 / 2	110 / 220	2
		DC	0.5 / 1	55 / 110	2
25/250 /2500	Titanium	Control	-	-	3
25	Titanium	AC	1	110	1
			2	220	1
		DC	0.5	55	2
			1	110	1
25[1]	Titanium	DC	0.5	55	1
	Unpolished Titanium	DC	0.5	55	1
250	Titanium	AC	1	110	1
			2	220	2
		DC	0.5	55	2
			1	110	1
	Graphite	AC	5	696	1
		DC	0.5	58	2
			1	174	1
			2.5	348	1
	BDD	AC	1	70	1
	BDD	DC	1	70	2
2500	Titanium	AC	1	110	2
			2	220	1
			4	440	1
		DC	0.5	55	2
			1	110	1
			2	220	1
	Unpolished Titanium	DC	0.5	55	1

Total number of tests : 37

Notes: 1. Electrolyte prepared using MSU tap water. For all other tests, DI waster used

2. AC Frequency was 0.1 Hz for all AC tests

Table 4.2: Effect of current densities at C_0 = 25, 250 and 2,500 mg/L

Type	**Initial Concentration (mg/L) of MTBE**	$\dot{j}_{eqv.}$ **(mA/cm^2)**	**C_f/C_o**
DC	25	0.5	0.02
		1	0.03
	250	0.5	0.33
		1	0.1
	2,500	0.5	0.72
		1	0.51
		2	0.12
AC	25	1	0.3
		2	0.14
	250	1	0.64
		2	0.56
	2,500	1	0.82
		2	0.68
		4	0.7

Hence, these gases can remove the volatile organic chemical (e.g., MTBE) via sparging or aeration. For the current densities used in this study, the amount of oxygen and hydrogen produced at the electrodes ranged from 0.45 l/d to 3.6 L/d based on estimates using the Faraday's equation (Eq. 4.1)

$$\frac{\dot{j}}{nF} = N_{H_2 or O_2} \tag{4.1}$$

where j is current density (mA/cm^2); n is number of electrons; F is faraday constant (C/mol); and N is gas flux (mol/cm^2.s).

Goel et al (2003) evaluated the effect of aeration by sparging 1.6 L/d of nitrogen gas in a cell containing 10 mg/L of naphthalene. The authors reported insignificant stripping of naphthalene due to the aeration. Drogos and Diaz (2000) evaluated removal of MTBE (concentration ~ 10 mg/L) added to gasoline in a large-scale lab model (~ 500 m^3) filled with saturated sand by pumping air at a rate of about 1.9×10^5 L/d for five days and 7.8×10^5 L/d for 10 additional days. After 20 days of continuous pumping of air, MTBE removed from the tank was about 4% while toluene and xylene removals were about 11% and 14%, respectively. The authors attributed the relatively low removal of MTBE to its relatively low Henry's Law liquid/gas partitioning coefficient equal to 5.87×10^{-4} atm-m^3/g-mole. The Henry's Law liquid/gas partitioning coefficient for naphthalene (4.5×10^{-3} atm-m^3/g-mole) is about one order greater than MTBE and Goel et al. (2003) observed negligible removal of naphthalene at the rate of aeration which is similar to the rate of gas production in the experiments carried out in this project. Hence, the control cell in this study did not include aeration. Removal of MTBE due to aeration is expected to be relatively small.

4.1.2 Effect of Current Density and Current Type

Figures 4.1 to 4.3 and Table 4.2 show that as the current density increases, the rate of degradation also increases. However, for a fixed current density and initial concentration, the rate of degradation for DC was greater than that for AC. Pepprah and Khire (2008) and Alshawabkeh and Sarahney (2005) also reported similar results during electrolysis of naphthalene in an aqueous phase. Greater the current density, higher the rate of production of hydroxyl radicals (Panizza and Cerisola 2009). Because hydroxyl radicals are strong oxidizing agents, they react with MTBE and breakdown MTBE.

Pepprah and Khire (2008) report the reason for lower degradation rate for AC compared to DC is because during an AC electrolysis, the current direction is reversed at time period equal to the reciprocal of the AC frequency (equal to 5 sec when $f = 0.1$ Hz) and this results in : (1) delay in mass transfer of the organic chemical to the electrode where it is degraded; and (2) both electrodes act as instantaneous anode and cathode where oxidation and reduction reactions occur, respectively, but some of these reactions are reversed when the electrode changes from anode to cathode or vice versa. While the rate of degradation for AC was lower than that for DC, Pepprah and Khire (2008) report that the electrode decay in the presence of NaCl as the supporting electrolyte for AC was relatively small compared to that for DC.

4.1.3 Effect of Electrode Material

Three electrode materials were tested: (1) uncoated 99% purity titanium; (2) solid graphite; and (3) BDD. The initial concentration of MTBE and the current density (DC) were fixed at 250 mg/L and 1 mA/cm^2, respectively. Fig. 4.4 shows the normalized concentration versus time for the three types of electrodes tested in the 1 L cells when DC was applied. The rate of degradation of MTBE when titanium or BDD electrodes were used was significantly greater than that for graphite (~ 13%). Titanium and BDD showed very similar rates of degradation (about 82 to 89%). These results indicate that the rate of degradation is a function of electrode material. It may be because the rate of production of hydroxyl radicals is a function of the electrode material.

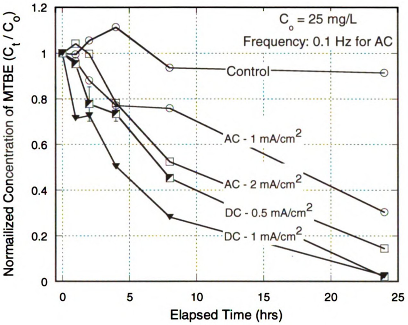


Figure 4.1: Normalized concentration (C_t/C_O) for MTBE for C_O = 25 mg/L with titanium electrodes

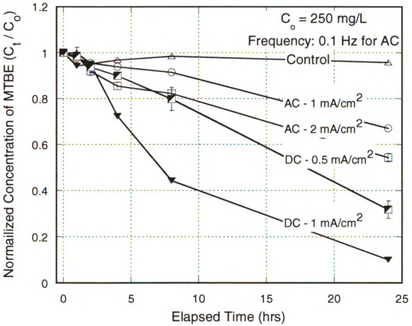


Figure 4.2: Normalized concentration (C_t/C_O) for MTBE for C_O = 250 mg/L with titanium electrodes

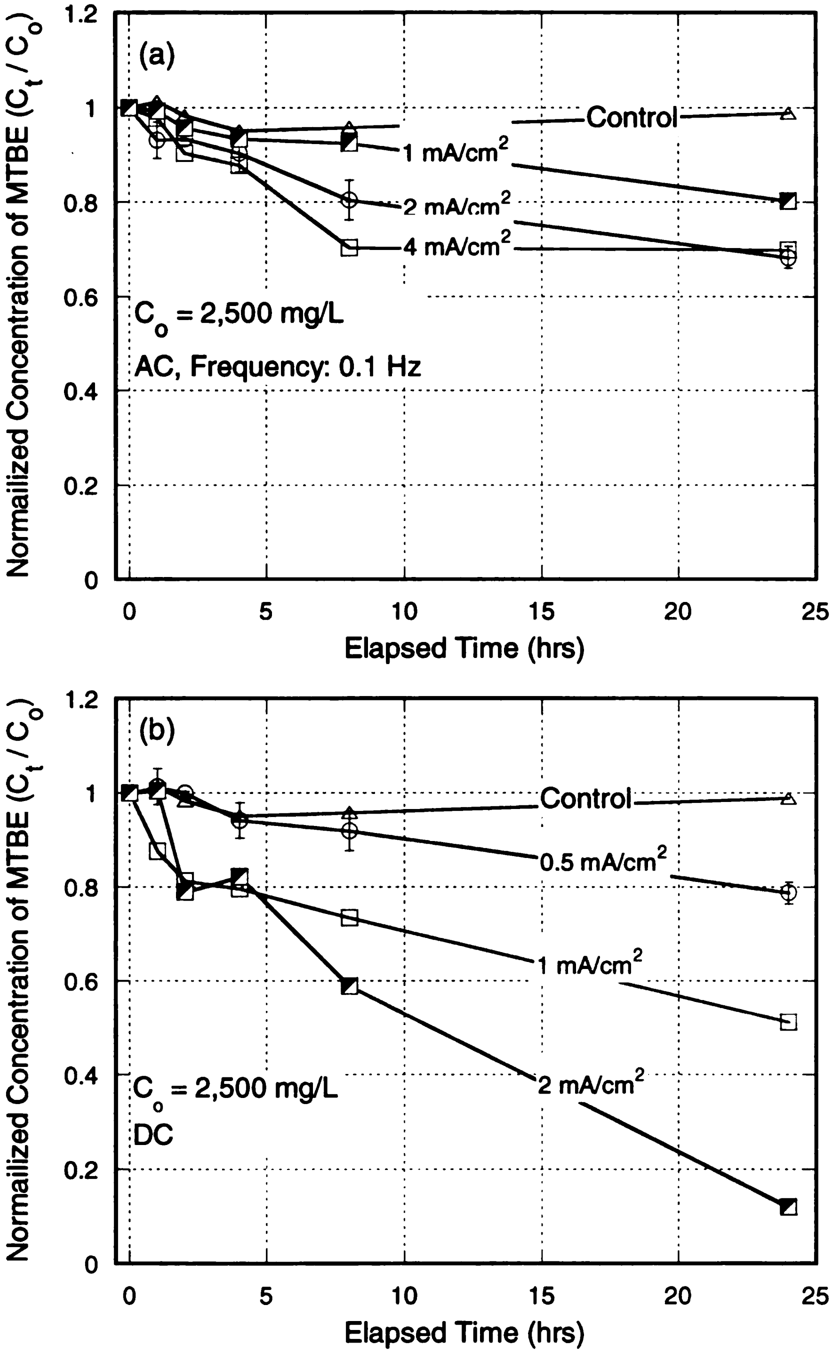


Figure 4.3: Normalized concentration (C_t/C_O) for MTBE for C_O = 2,500 mg/L with titanium electrodes: (a) AC; and (b) DC

Because hydroxyl radicals are primarily responsible for degradation of organic molecules such as MTBE (Pepprah 2007), the rate of degradation varies for various electrode materials. Graphite electrodes most likely produced the least amount of hydroxyl radials. Hence, while graphite is relatively cheap, it is not as effective in electrochemical degradation of MTBE.

After the tests were completed, the electrode surfaces were observed and noted. Titanium electrodes had deposits whereas BDD and graphite electrodes looked unaltered. Figure 4.5 shows the surface of each of the electrodes before and after electrolysis.

Fig. 4.6 shows the normalized concentration versus time for titanium and BDD when AC having current density equal to 1mA/cm^{2}was applied. The rates of degradation for both electrodes were about the same. However, these rates were significantly less than those for DC. This finding is consistent with the AC and DC comparisons presented in Figs. 4.1 to 4.3.

4.1.4 Effect of Initial Concentration of MTBE

Figs 4.7, 4.8, 4.9 and 4.10 show the normalized concentration versus time for experiments where the initial concentration of MTBE was 25 mg/L, 250 mg/L, and 2,500 mg/L. Greater the initial concentration, lower was the rate of degradation. However, the cumulative mass of MTBE degraded increased with increase in the initial concentration of MTBE (Figs. 4.11 to 4.14). Wang *et al.* (2009) also reported similar results for degradation of 4-chlorophenol during electrolysis.

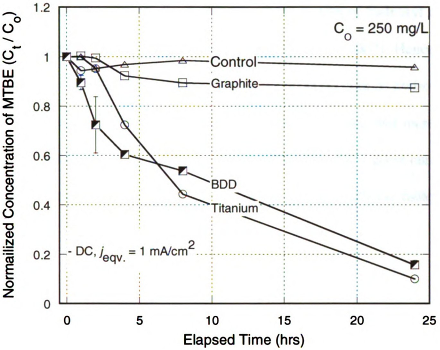


Figure 4.4: Normalized concentration of MTBE with graphite, BDD and titanium electrodes during DC Electrolysis

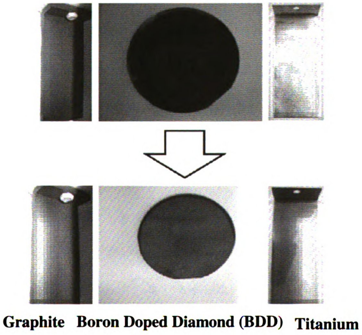


Figure 4.5: The electrode surface of graphite, BDD and titanium before (upper) and after (below) electrolysis

Assuming all other parameters are fixed, the rate of production of hydroxyl radicals is a function of the current density (Pepprah 2005; Yanqing *et al.*, 2007). Hence, while the initial concentration of MTBE was increased, the rate of production of hydroxyl radicals was unchanged. The cumulative mass of MTBE degraded or converted increased (Figs. 4.11 to 4.14) as the initial concentration was increased because for a given current density, more MTBE molecules were available in the solution for the hydroxyl radicals to react with.

4.1.5 Effect of DI Water vs. Tap Water

Most experiments in this study were carried out using DI water as the electrolyte with electrodes having polished surfaces to maintain the surface properties of the electrodes consistent throughout the experimental program. The effect of using of tap water as the electrolyte and potential electrode fouling during electrolysis were evaluated by carrying out these tests where: (1) the electrolyte was tap water from the lab; and (2) the titanium electrode surfaces from a previous test with tap water were not polished to simulate the effect of electrode fouling. Initial concentrations equal to 25 mg/L and 2,500 mg/L and current density for DC equal to 0.5 mA/cm^2 were used for these tests. The results are presented in Figs. 4.15 and 4.16. The results show that the use of tap water instead of DI water as the electrolyte and by not polishing the electrode surface after a test had insignificant impact on the rate of degradation.

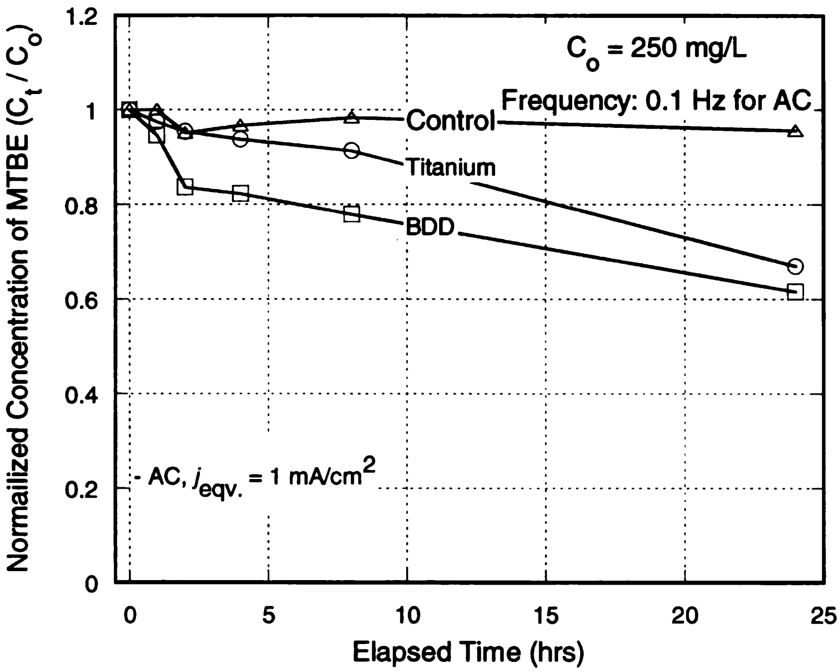


Figure 4.6: Normalized concentration of MTBE solution for C_O = 250 mg/L with BDD and titanium electrodes during AC electrolysis

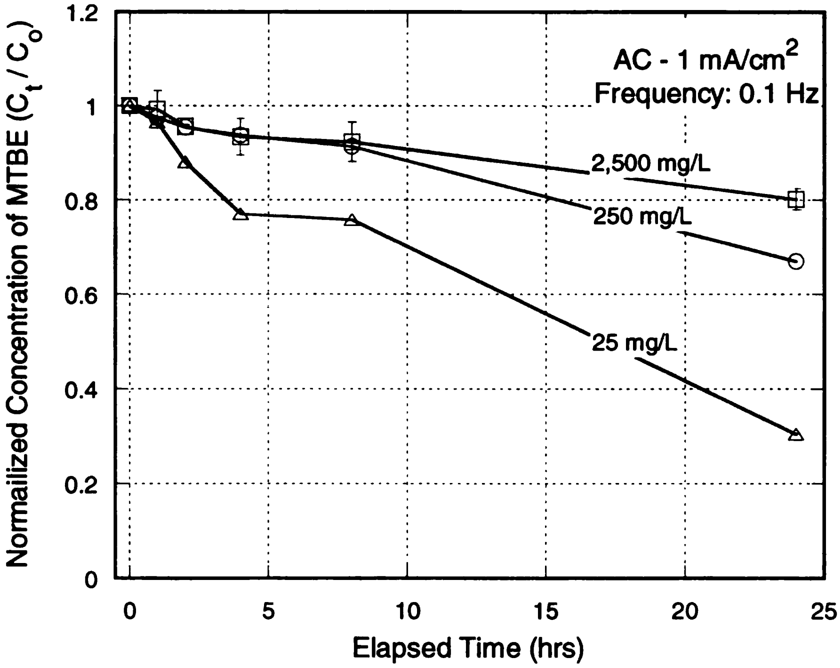


Figure 4.7: Effect of initial concentration of MTBE at AC density of 1mA/cm^2 for C_O = 25, 250 and 2,500 mg/L with titanium electrodes

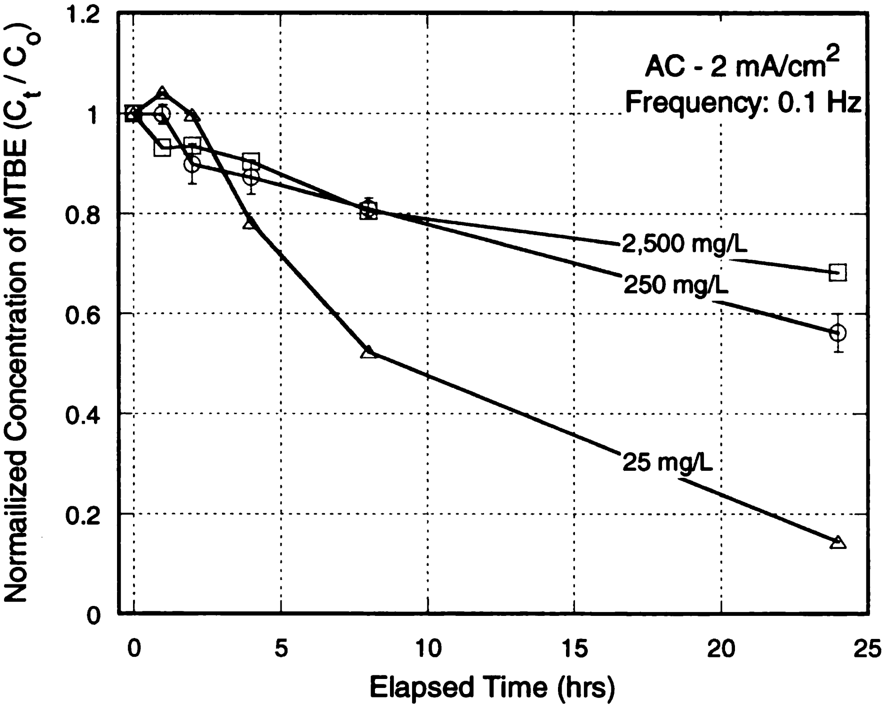


Figure 4.8: Effect of initial concentration of MTBE at AC density of 2 mA/cm^2 for C_O = 25, 250 and 2,500 mg/L with titanium electrodes

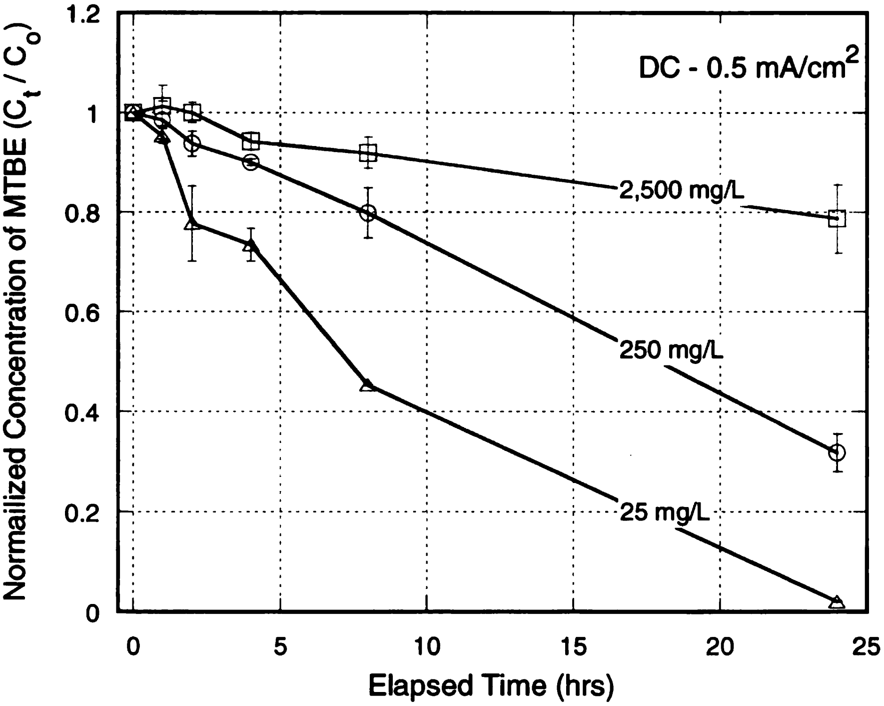


Figure 4.9: Effect of initial concentration of MTBE at DC density of 0.5 mA/cm^2 for C_O = 25, 250 and 2,500 mg/L with titanium electrodes

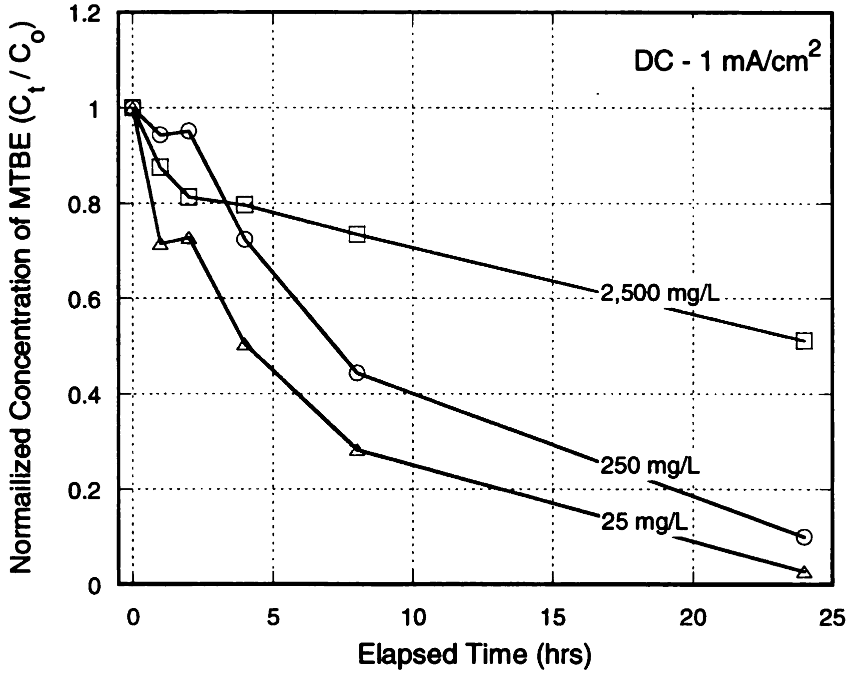


Figure 4.10: Effect of initial concentration of MTBE at DC density of 1 mA/cm^2 for C_O = 25, 250 and 2,500 mg/L with titanium electrodes

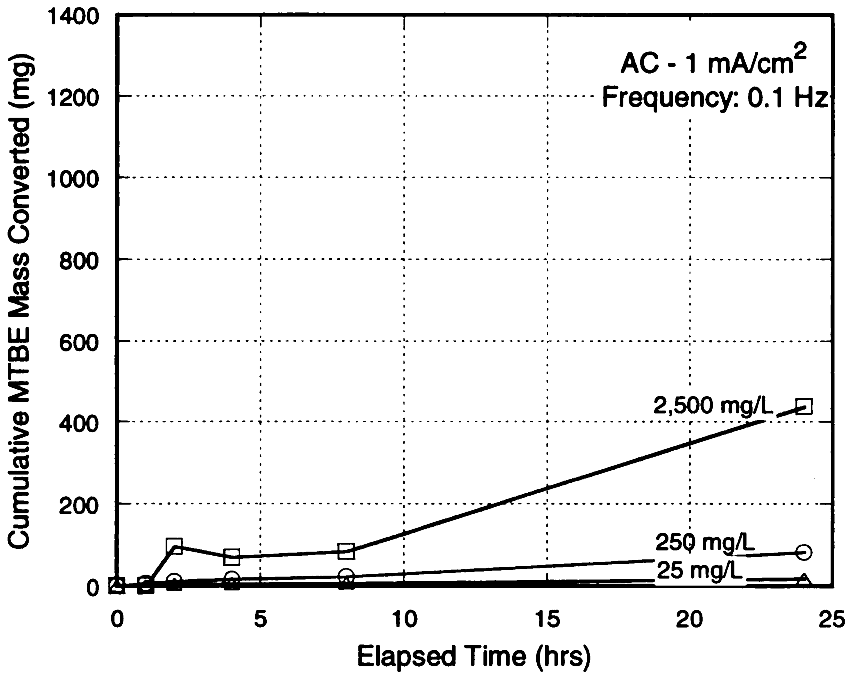


Figure 4.11: Cumulative MTBE mass converted at AC density of 1 mA/cm^2 for C_O = 25, 250 and 2,500 mg/L with titanium electrodes

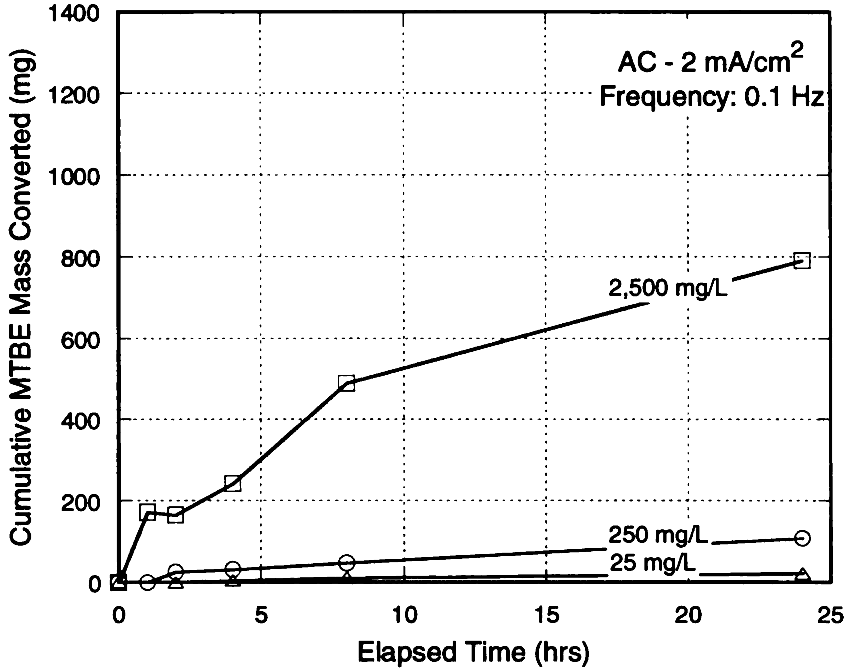


Figure 4.12: Cumulative MTBE mass converted at AC density of 2 mA/cm^2 for C_O = 25, 250 and 2,500 mg/L with titanium electrodes

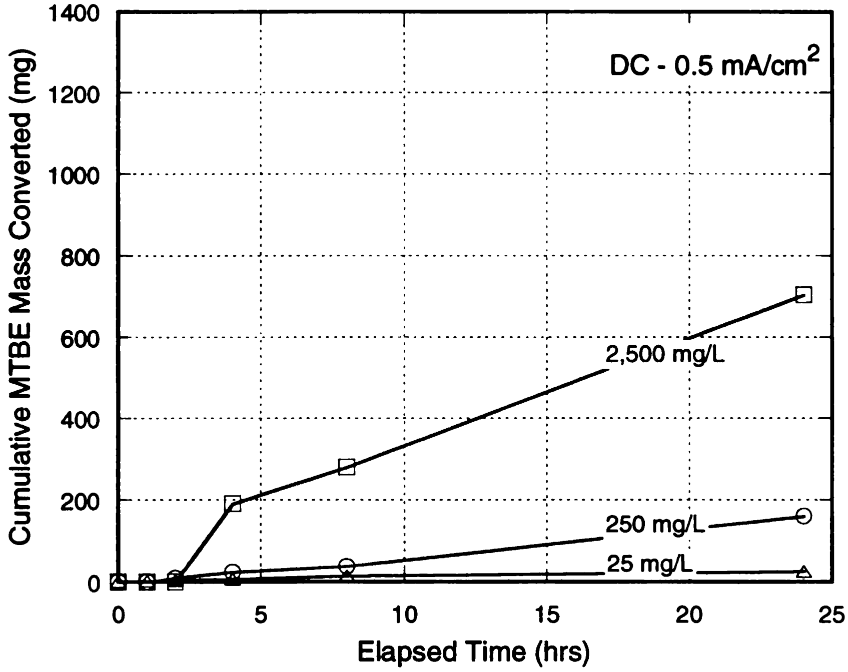


Figure 4.13: Cumulative MTBE mass converted at DC density of 0.5 mA/cm^2 for C_O = 25, 250 and 2,500 mg/L with titanium electrodes

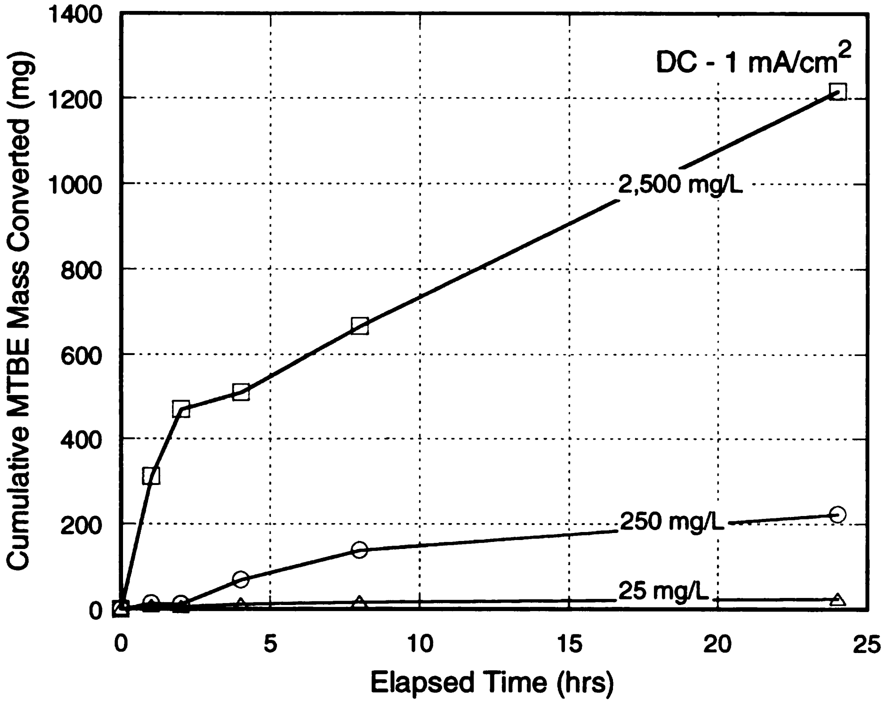


Figure 4.14: Cumulative MTBE mass converted at DC density of 1mA/cm^2 for C_O = 25, 250 and 2,500 mg/L with titanium electrodes

Pepprah and Khire (2008) achieved significantly lower removal rate of phenathrene and pyrene when they used unpolished titanium electrodes with AC density equal to 18.5 mA/cm^2. Greater current density may result in greater electrode fouling which impacts the rate of degradation. While there was no significant difference in the rate of degradation, the applied voltage increased more rapidly when tap water and unpolished electrodes were used. Electrical conductivities of DI water, the tap water, and 300 mg of Na_2SO_4 dissolved in 1 L of DI water were 0.9, 754, and 866 μs, respectively. Hence, more rapid increase in the voltage during the tests when tap water and unpolished electrodes were used was most likely due to deposit formation or fouling of the electrodes that resulted in a rapid increase in the resistance of the cell. In order to maintain the current density, the constant current amplifier increased the voltage proportionate to the resistance. White precipitates were observed after the test when tap water was used as the electrolyte (Figs. 4.17 and 4.18).

Final voltage of 2,500 mg/L and 25 mg/L of MTBE solution in DI water was 45 and 48 V, respectively. For unpolished electrode for C_O = 2,500 mg/L, 25 mg/L (tap water) and 25 mg/L (DI water), the final voltages were 52.5, 67 and 83 V.

4.1.6 Degradation Kinetics

The degradation rate of MTBE solution during electrolysis can be described as a pseudo-first-order decay reaction, which is presented in Eq. 4.2:

$$\frac{dC}{dt} = -k[C] \tag{4.2}$$

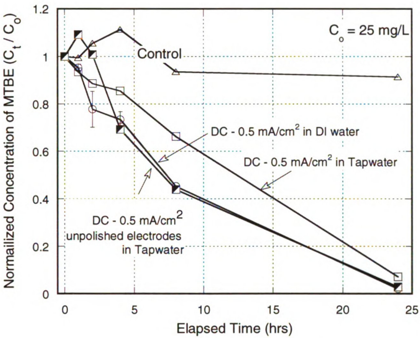


Figure 4.15: Effect of electrolyte on the rate of degradation of MTBE for C_O = 25 mg/L at DC density = 0.5 mA/cm^2 with titanium electrodes

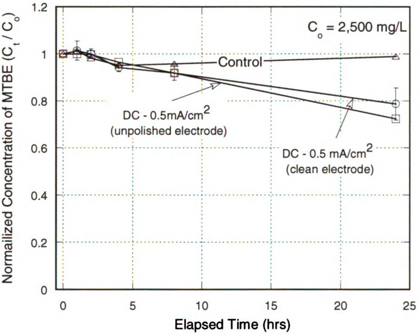


Figure 4.16: Effect of electrolyte on the rate of degradation of MTBE for C_O = 2,500 mg/L at DC density = 0.5 mA/cm^2 with titanium electrodes

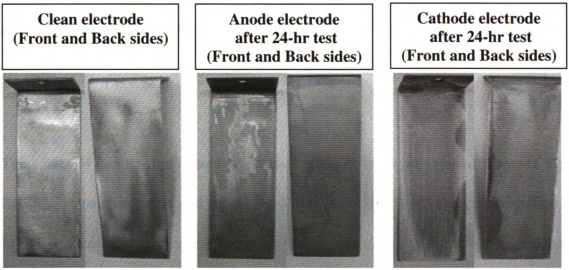


Figure 4.17: Photographs of titanium electrode surface after a 24-hr test when $C_O = 25$ mg/L for MTBE in Tap water

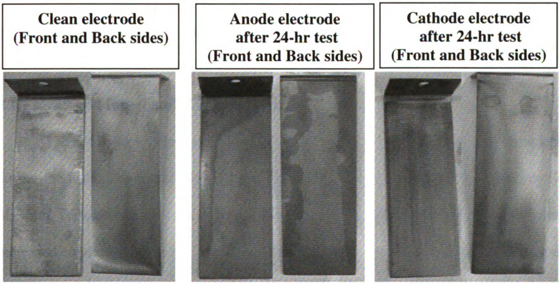


Figure 4.18: Photographs of titanium electrode surface after a 24-hr test when $C_O = 2,500$ mg/L for MTBE in 300 mg of Na_2SO_4 dissolved in 1 L of DI water

where C is the concentration of MTBE (mg/L); dC/dt is the rate of change of contaminant concentration; and k is the pseudo-first-order rate constant (T^{-1}). Half life of MTBE is estimated from Equation 4.3

$$t_{1/2} = \frac{0.693}{k} \qquad (4.3)$$

The values of pseudo-first-order rate constant for each test were calculated by making a $\ln[C_t/C_0]$ versus time plot and measuring the slope of the line. Initial concentration of MTBE, current type and current density, electrolyte, and electrode materials influenced the k values (Table 4.3; Figs 4.19 and 4.20). Fig. 4.19 shows that the degradation rate constant increases as the: (1) current density increases; (2) DC is used rather than AC; and (3) initial concentration is lowered. The rate constant was highest for titanium electrodes (0.09/hr) and was smallest for graphite (0.005/hr) (Fig. 4.20).

4.1.7 Measured Initial and Final Parameters

Table 4.4 summarizes measured initial and final (after the 24-hr test) parameters during the tests. These parameters were: Voltage (V), Resistance (R) or Impedance (Z), pH, and Temperature (°C). During a majority of the experiments, the applied voltage increased continuously during the electrolysis because the resistance of the cell increased. Voltage went up more rapidly at greater current densities especially when DC was used.

For the DC tests, the initial resistance of the electrochemical cell ranged from 116 Ω to 161 Ω and the final resistance ranged from 122 Ω to 191 Ω. For the AC tests, the initial impedance of the electrochemical cell ranged from 146 Ω to 188 Ω and the final impedance ranged from 131 Ω to 172 Ω.

For the DC tests, initial pH ranged from 6 to 7.4 and final pH ranged from 6.4 to 8.1. For AC tests, initial pH ranged from 6 to 7.3 and final pH ranged from 5.5 to 8.4. Wu (2007) also observed increase in pH when DC was used during electrolysis of MTBE using nickel electrodes. Pepprah and Khire (2008) reported increase in pH during DC and a decrease during AC electrolyses. Thus, oxidation of water molecule was prominent during AC and reduction of water was more dominant during DC electrolysis.

Room temperature during the tests ranged from 19 ~ 24 °C. However, during a specific test, the room temperature usually fluctuated within 2 °C. The temperature of the electrochemical cell followed the room temperature because it was immersed in a relatively large water bath. However, when the current densities were 2 mA/cm^2 and 4 mA/cm^2, temperature of the cell increased to 29 to 32 °C due to joule heating. This increase in temperature will have effect on volatilization and diffusion coefficient of MTBE. As temperature increases, the rate of volatilization and diffusion coefficient increased too. Hence, the control sample was placed in the same water bath adjacent to the cell that was subjected to electricity to experience the elevated temperature.

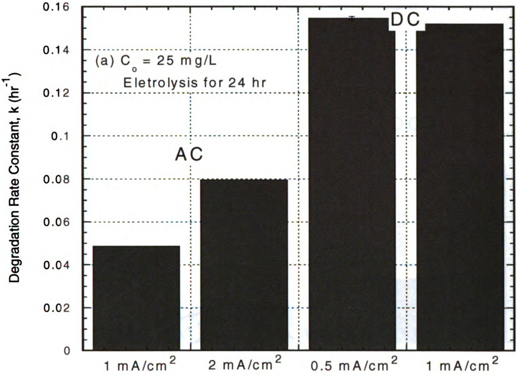
4.2 ELECTRICAL ENERGY CONSUMPTION

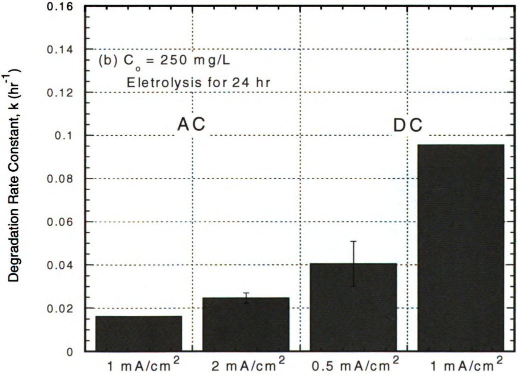
Table 4.5 summarizes the total electrical energy consumed during the 24-hr electrolysis for all tests. The electrical energy in kJ and kWh was calculated from equation (1.3) and kWh/L was computed from equation (1.4).

Table 4.3: Degradation of rate constant (k) and half-life of MTBE

C_O (mg/L)	**Current Type**	**i (mA)**	**j_{eqv} (mA/ cm^2)**	**Electrode materials**	**Immersed Electrode Area (cm^2)**	**k Constant (hr^{-1})**	**R^2**	**$t_{1/2}$ (hr)**
25	AC	110	1.0	Titanium	55	0.049	0.98	14.3
		220	2.0		55	0.079	0.98	8.7
	DC	55	0.5		55	0.155	0.96	4.5
		110	1.0		55	0.152	0.99	4.6
		55	0.5	Titanium in tapwater	55	0.102	0.95	6.8
		55	0.5	Unpolished Titanium	55	0.141	0.97	4.9
250	AC	110	1.0	Titanium	55	0.016	0.98	43.0
		220	2.0		55	0.025	0.98	28.2
		680	5.0	Graphite	68	0.005	0.32	144.4
	DC	55	0.5	Titanium	55	0.040	0.95	17.2
		110	1.0		55	0.096	0.99	7.3
		70	1.0	BDD	35	0.023	0.74	30.1
		70	1.0		35	0.075	0.97	9.2
		58	0.5	Graphite	68	0.003	0.77	256.7
		136	1.0		68	0.007	0.63	101.9
		170	2.5		68	0.011	0.99	64.2
2,500	AC	110	1.0	Titanium	55	0.008	0.90	91.2
		220	2.0		55	0.017	0.87	39.8
		440	4.0		55	0.018	0.55	37.7
		55	0.5		55	0.007	0.95	105.0
	DC	110	1.0		55	0.030	0.80	22.9
		220	2.0		55	0.085	0.98	8.1
		55	0.5	Unpolished Titanium	55	0.013	0.98	53.3

Note: 1. Unless specified, all tests were carried out using DI water
2. AC Frequency = 0.1 Hz for all AC tests


0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Degradation Rate Constant, k (hr^{-1})
(a) C$_o$ = 25 mg/L
Eletrolysis for 24 hr
AC
DC
1 mA/cm^2
2 mA/cm^2
0.5 mA/cm^2
1 mA/cm^2


0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Degradation Rate Constant, k (hr^{-1})
(b) C$_o$ = 250 mg/L
Eletrolysis for 24 hr
AC
DC
1 mA/cm^2
2 mA/cm^2
0.5 mA/cm^2
1 mA/cm^2

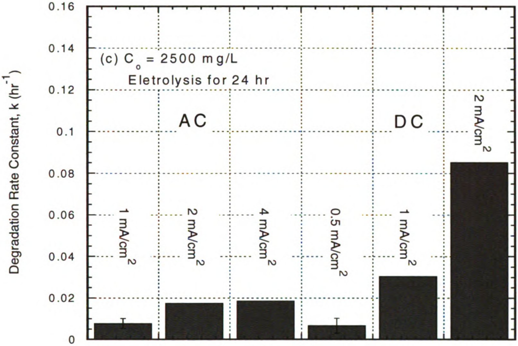


Figure 4.19: Estimated k (hr^{-1}) for MTBE C_O = 25 mg/L (a); 250 mg/L (b); and 2,500 mg/L (c) using AC and DC during 24 hr electrolysis with titanium electrodes

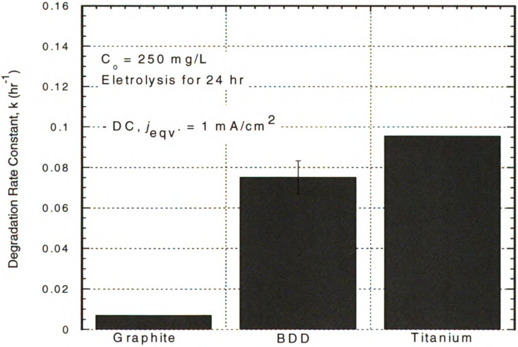


Figure 4.20: Effect of electrode material on k during DC electrolysis

Table4.4: Summary of voltage, pH and temperature of the electrolytic cell

Co (mg/L)	AC /DC	i (mA)	j_{eqv}• (mA/cm^2)	Electrode materials	Voltage (V)		Impedance (Ω)		pH		Temperature(ºC)	
					Initial	Final	Initial	Final	Initial	Final	Initial	Final
25	AC	110	1.0	Titanium	28.00	48.00	188.00	153.30	6.88	6.15	24.1	23.3
		220	2.0		48.00	67.00	159.40	172.00	6.58	8.36	25.2	26.7
	DC	55	0.5		18.00	48.00	137.20	169.00	6.53	7.40	23.8	18.3
		110	1.0		25.00	75.00	153.60	153.40	6.65	6.60	24.6	21.6
25[1]	DC	55	0.5		12.50	67.50	137.60	299.90	6.72	7.78	21.0	21
25[1]	DC	55	0.5	Titanium[2]	13.10	83.00	122.20	423.10	7.30	8.24	22.0	22
250	AC	110	1.0	Titanium	18.50	30.00	146.00	155.10	6.92	6.50	25.1	21.5
		220	2.0		49.00	61.00	160.60	155.60	6.62	7.18	22.6	22.4
	DC	55	0.5		18.00	44.00	149.30	190.90	6.73	7.04	23.7	22.1
		110	1.0		28.00	70.00	150.60	225.50	6.80	6.73	24.5	25.8
	AC	680	5.0	Graphite	63.60	56.10	182.50	87.67	6.88	3.94	22.0	32.0
	DC	58	0.5		10.50	15.00	206.80	745.00	7.38	8.11	22.8	19.4
	AC	70	1.0	BDD	16.00	17.50	228.57	250.00	6.56	6.25	23.0	24.0
	DC	70	1.0		14.00	15.90	205.00	220.00	6.71	6.64	20.0	20.0
2,500	AC	110	1.0	Titanium	28.50	23.00	169.50	157.50	6.11	5.50	24.4	22.3
		220	2.0		40.00	33.00	153.10	143.10	6.05	5.96	24.2	24.2
		440	4.0		74.00	109.00	169.70	130.20	6.80	4.99	22.0	29.0
	DC	55	0.5		18.00	33.00	115.60	121.80	6.70	6.40	24.4	22.6
		110	1.0		25.00	80.00	129.00	157.80	6.90	8.30	22.1	22.0
		220	2.0		50.00	115.00	160.90	152.00	6.03	6.65	21.0	30.0
	DC	55	0.5	Titanium[2]	15.60	52.50	152.50	194.50	6.87	7.37	19.0	21.0

Note: 1. Electrolyte prepared using MSU tap water. For all other tests, DI water used.
2. Unpolished electrode.
3. AC Frequency was 0.1 Hz for all AC tests.

The electrical energy cost was assumed equal to 6.867 cents/kWh as presented in Energy Information Administration (2008).

4.2.1 Effect of Current Density and Type

Figure 4.21 presents the cumulative energy consumed per unit volume of the electrolyte during AC and DC electrolysis carried out for C_O = 250 mg/L. For a given current density, DC consumed more electrical energy compared to AC during the 24-hr testing period. However, the rate of degradation as well as the MTBE mass degraded or converted by DC was greater than that by AC for a given current density during the 24-hr testing period. Hence, the cumulative MTBE mass converted during electrolysis was normalized with respect to the cumulative electrical energy (Fig. 4.22). Fig. 4.22 shows that DC was more energy efficient for degrading MTBE because it resulted in greater mass converted per unit energy consumed.

4.2.2 Effect of Electrode Material

Figure 4.23 presents the cumulative energy consumed per unit volume of the electrolyte during DC electrolysis carried out using titanium, graphite, and BDD electrodes for MTBE C_O = 250 mg/L and current density = 1 mA/cm^2. While the rate of MTBE degradation was highest for titanium, BDD consumed the least total electrical energy.

4.2.3 Effect of Initial Concentration of MTBE

Figure 4.24 presents the cumulative electrical energy consumed per unit volume of the electrolyte during AC electrolysis carried out for C_O = 0, 25, 250, and 2,500 mg/L at current density = 1 mA/cm^2. Fig. 4.24 shows that as C_O increases, the total electrical energy consumption during the 24-hr period decreases. Comparison of initial and final voltages measured during the tests (Fig. 4.24) indicates that the final voltage decreased as the initial concentration was increased. This may be because greater initial concentration of MTBE resulted in greater concentration of ions formed as intermediate byproducts of degradation of MTBE. Greater mass of ions reduced the impedance of the electrolyte and hence the energy consumption was less.

Fig. 4.25 shows the cumulative MTBE mass converted during electrolysis normalized with respect to the cumulative electrical energy. It can be observed from Fig. 4.25 that degradation of MTBE was more energy efficient at higher initial concentrations of MTBE because it resulted in greater MTBE mass converted per unit energy consumed.

4.2.4 Effect of DI vs. Tap Water as Electrolytes

Figure 4.26 presents the cumulative electrical energy consumed per unit volume of the electrolyte during DC electrolysis carried out for C_O = 25 mg/L at current density = 0.5 mA/cm^2 using tap water and DI water as the electrolytes for polished and unpolished titanium electrodes. The polished electrode in DI water consumed the least amount of electrical energy during the 24-hr test duration. Unpolished electrode in tap water consumed the most electrical energy.

Table 4.5 Electrical energy consumption during the tests

Co (mg/L)	**AC / DC**	**i (mA)**	**j_{eqv} (mA/cm^2)**	**Electrode materials**	**24hr (kJ/L)**	**kWh/m^3**	**kWh**	**Cost (USD) per 24hr**
25	AC	110	1.0	Titanium	321	30	13	22
	AC	220	2.0	Titanium	1105	104	46	75
	DC	55	0.5	Titanium	172	16	7	11
	DC	110	1.0	Titanium	579	54	24	39
25[1]	DC	55	0.5	Titanium	226	21	9	15
	DC	55	0.5	Titanium[2]	281	26	11	19
250	AC	110	1.0	Titanium	277	26	11	19
	AC	220	2.0	Titanium	1056	100	44	72
	AC	680	5.0	Graphite	3488	330	145	239
	DC	55	0.5	Titanium	161	15	6	11
	DC	110	1.0	Titanium	523	49	21	35
	DC	70	1.0	BDD	95	14	4	6
	DC	68	0.5	Graphite	67	6	3	4
	DC	136	1.0	Graphite	282	26	11	19
	DC	170	2.5	Graphite	973	92	40	66
2,500	AC	110	1.0	Titanium	207	19	8	14
	AC	220	2.0	Titanium	803	76	33	55
	AC	440	4.0	Titanium	3419	323	142	234
	DC	55	0.50	Titanium	141	13	5	9
	DC	110	1.0	Titanium	552	52	23	37
	DC	220	2.0	Titanium	1848	175	77	126
	DC	55	0.5	Titanium[2]	197	18	8	13

Note: 1. Electrolyte prepared using MSU tap water. For all other tests, DI water used.
2. Unpolished electrode.
3. AC Frequency is 0.1 Hz for all AC tests

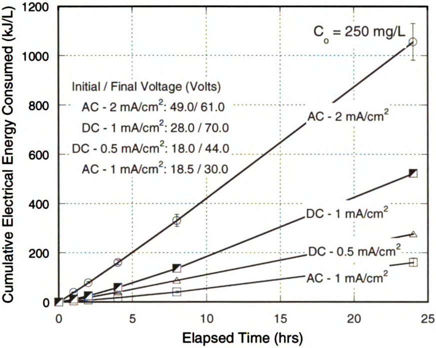


Figure 4.21: Cumulative electrical energy consumption (kJ/L) at AC – 2 mA/cm^2, DC – 1 mA/cm^2, DC – 0.5 mA/cm^2 and AC – 1 mA/cm^2 with titanium electrodes

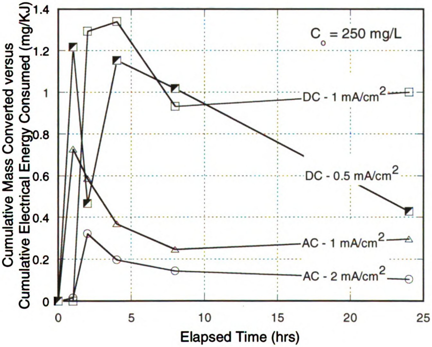


Figure 4.22: Cumulative mass converted per unit electrical energy consumed for C_O = 250 mg/L during AC and DC electrolysis using titanium electrodes

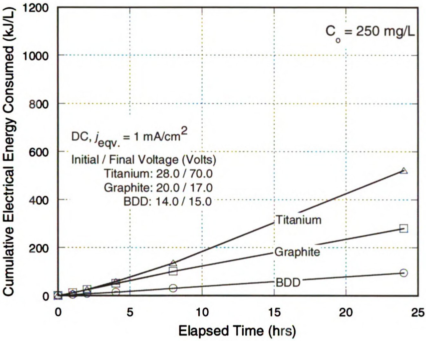


Figure 4.23: Cumulative electrical energy consumption (kJ/L) for titanium, graphite and BDD electrodes

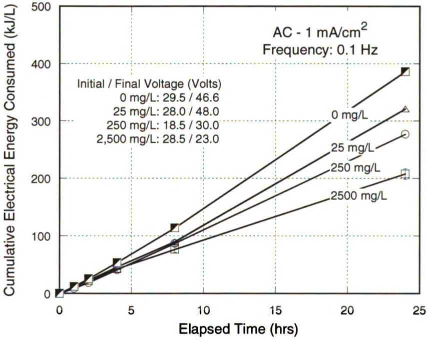


Figure 4.24: Cumulative electrical energy consumption (kJ/L) at AC -1 mA/cm^2 with titanium electrodes

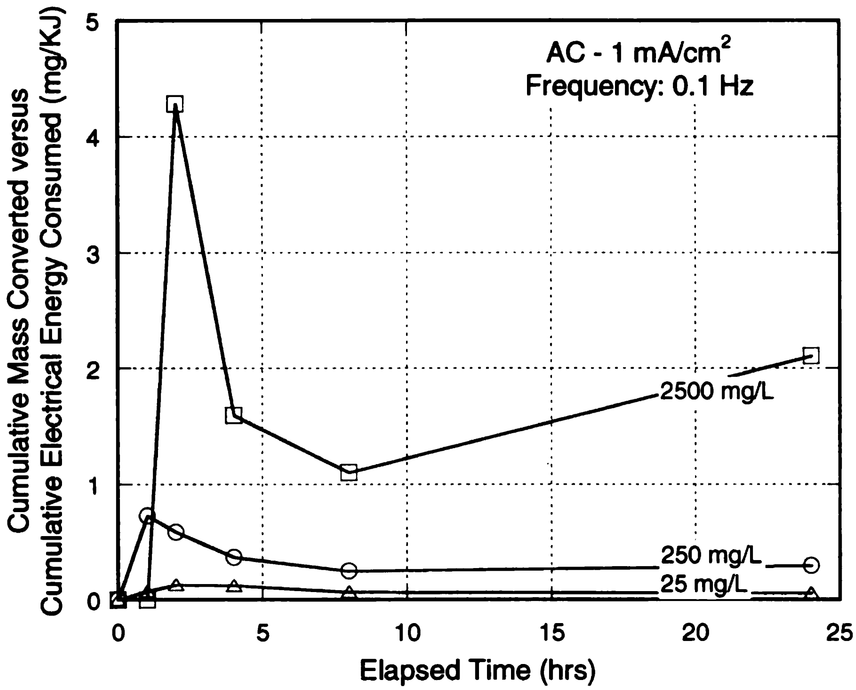


Figure 4.25: Cumulative mass converted per unit electrical energy consumed for AC electrolysis at current density = 1 mA/cm^2 for C_O = 25, 250, and 2,500 mg/L using titanium electrodes

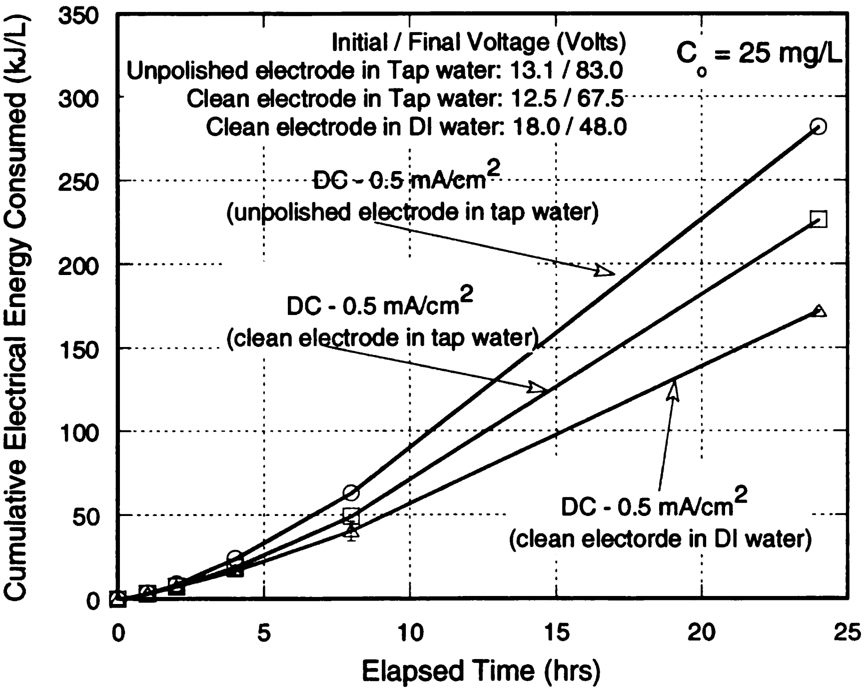


Figure 4.26: Cumulative electrical energy consumption for tap water versus DI water as electrolyte for C_O = 25 mg/L using polished and unpolished titanium electrodes

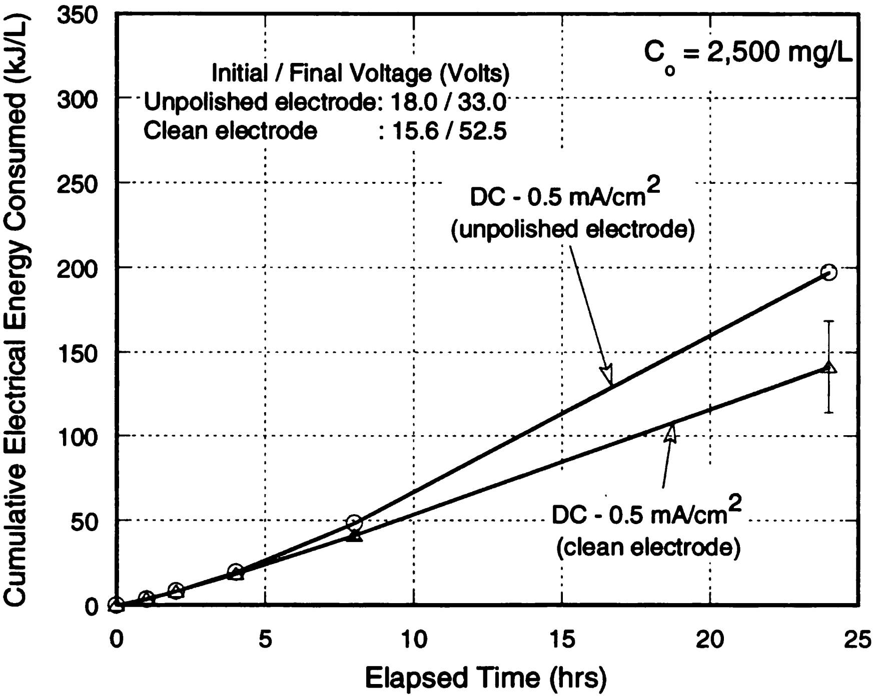


Figure 4.27: Cumulative electrical energy consumption for C_O = 2,500 mg/L using polished and unpolished titanium electrodes in DI water

The rate of increase in the voltage as the experiment progressed indicates that when unpolished electrodes were used in tap water, the fouling of the electrode surface resulted in a more rapid increase in the resistance of the cell which resulted in greater power consumption. Similar trend in energy consumption was observed when the initial concentration of MTBE was 2,500 mg/L (Fig. 4.27).

4.3 ANALYTICAL MODELLING USING NERNST-PLANCK EQUATION

Nernst-Planck equation (Eq. 1.8) can be used to predict migration of charged specie subjected to electrical gradients in an aqueous solution. The equation calculates migration under diffusive gradients, electrical gradients, and due to mechanical mixing or convection. Convection is not considered for unstirred systems. Hence, the equation takes this form (Eq. 4.4):

$$J_i(x) = -D_i(x)\frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} \tag{4.4}$$

The variables are described in Eq. 1.8. Eq. 4.4 was applied to predict the observed changes in the MTBE concentrations during the tests carried out in this project.

The key assumptions that were made to use Eq. 4.4 for modeling the experimental data are as follows.

1. Contaminants react and completely convert (or degrade) to byproducts when they reach the electrode surface. Therefore, concentration of contaminant at both reactive electrodes remains zero;
2. A concentration gradient is established that drives reactants by diffusion to the surface of the electrodes;

3. Steady-state diffusion is assumed during the time step of 1 hr used to solve Eq. 4.4; and
4. Linear mass transfer and electric field exist in the cell between the electrodes.

MTBE diffusion coefficient (D ~ $8.63 \times 10^{-6} cm^2/s$) was calculated based on Hayduk-Laudie equation (Eq. 1.9) and also was compared with that presented online at EPA's website. The input parameters used for solving Eq. 4.4 are as follow:

1. Diffusion Coefficient, D: 8.63×10^{-6} cm^2/s
2. Gas constant, R: 8.31447 J/mol.K
3. Faraday's Constant, F: 9.65×10^4 Coulomb
4. Surface area of Titanium electrodes: 55 cm^2
5. Distance between the two titanium electrodes: 8 cm; graphite electrodes: 6.5 cm; and BDD: 4 cm.

MTBE Concentrations measured during the tests and those predicted using the Nernst-Planck equation (Eq. 4.4.) for initial concentration of MTBE equal to 25 mg/L for DC electrolysis at 0.5 and 1 mA/cm^2 current densities is presented in Fig. 4.28.

In order to apply Eq. 4.4 to predict the normalized concentration, the value of the effective charge (z) was empirically obtained from the best fit to the measured concentration profile. The best fit shown in Fig. 4.28 was achieved when z was assumed equal to -0.45. MTBE molecule does not have a net charge. However, it is hypothesized that the ions present in the supporting electrolyte (anhydrous sodium sulfate) as well as ions of intermediate or final byproducts that are formed during the electrolysis drag

MTBE molecules to the anode where it is oxidized. Fig. 4.28 shows that for $z = -0.45$, the predicted normalized of concentrations for the two tests carried out at current densities equal to 0.5 and 1 mA/cm^2 are fairly accurate.

Figs. 4.29 and 4.30 present the measured and simulated normalized concentrations of MTBE for $C_O = 250$ and 2,500 mg/L. The simulated normalized concentrations agree reasonably well with the measured normalized concentrations for $C_O = 250$ mg/L when the value of the effective charge is assumed equal to -0.2. For $C_O = 2{,}500$ mg/L, the best predicted fit with the measured data is obtained when z ranges from -0.06 to -0.12 for current densities equal to 0.5 to 2 mA/cm^2. One of the key trends observed here is that z decreases as the initial concentration of MTBE increases. This may be because the rate of production of hydroxyl radicals responsible for oxidation of MTBE are produced at about the same rate for a given current density irrespective of the initial concentration of MTBE in the solution. In addition, one of the assumptions made for simulating normalized concentration measured during the tests is that MTBE molecules, once they reach the electrode surface, are instantaneously converted. This assumption may be more realistic at lower concentrations of MTBE (or relatively high current densities) where the rate at which hydroxyl radicals are produced at the surface exceeds the stoichiometric demand of the radicals needed to breakdown the mass of MTBE migrated to the electrodes. This may be the reason why the z values were not consistent when the equation was applied for the tests carried out at relatively high initial concentration equal to 2,500 mg/L (Fig. 4.30).

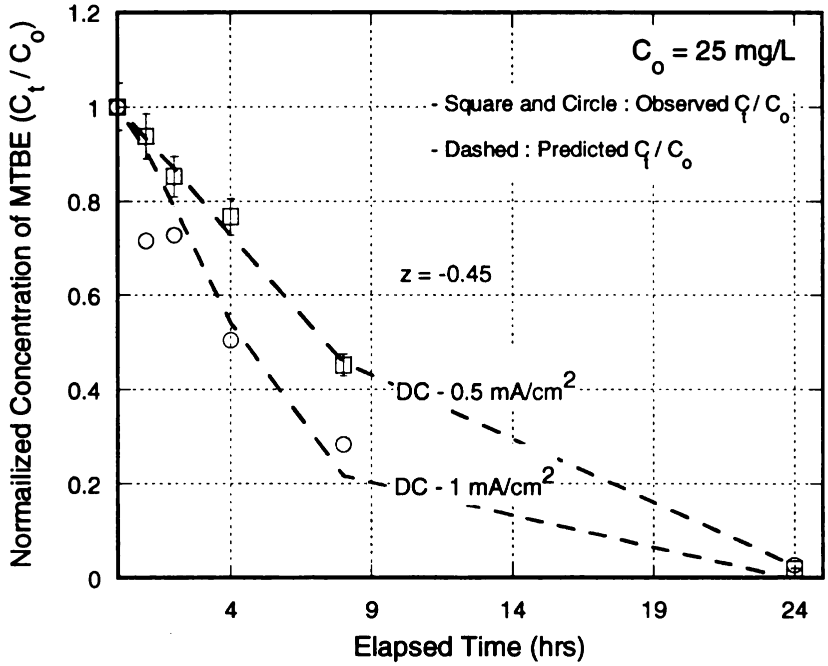


Figure 4.28: Experimental and predicted normalized concentrations of MTBE for C_O = 25 mg/L for DC electrolysis using current densities equal to 0.5 and 1 mA/cm^2

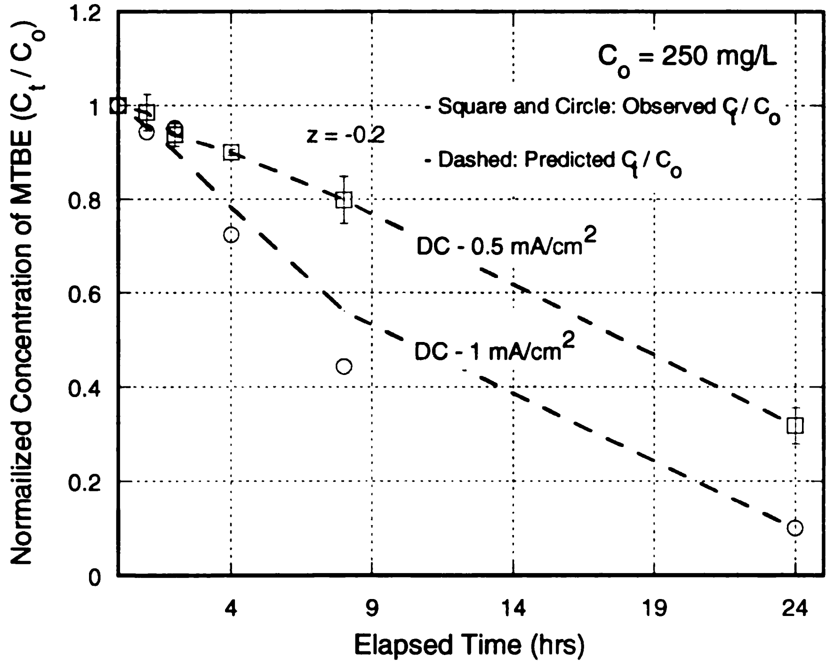


Figure 4.29: Experimental and predicted normalized concentrations of MTBE for C_O = 250 mg/L for DC electrolysis using current densities equal to 0.5 and 1 mA/cm^2

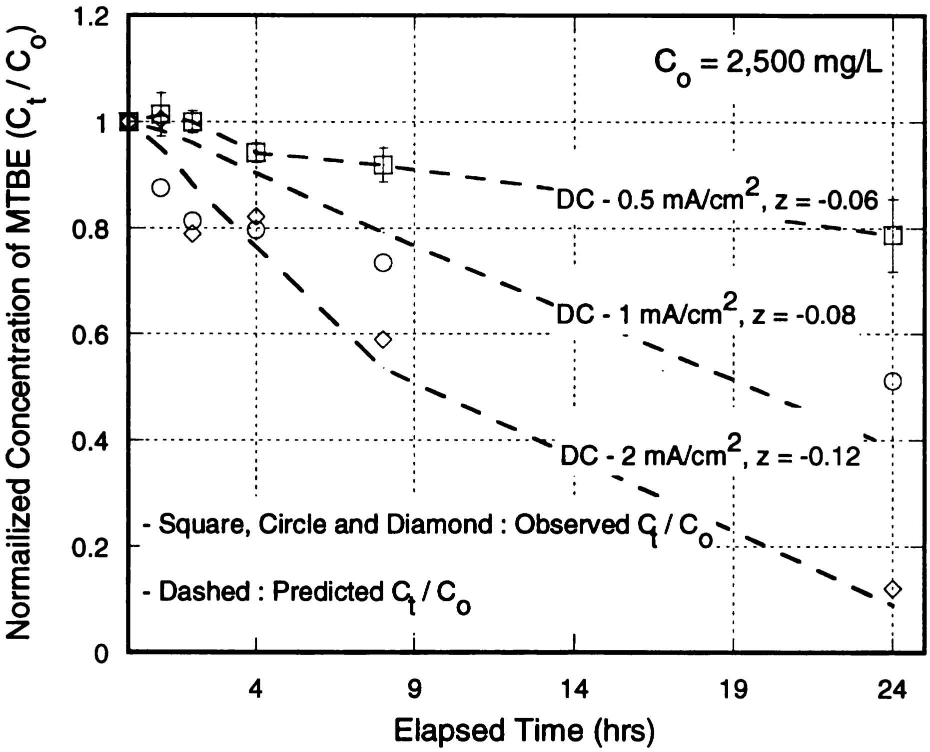


Figure 4.30: Experimental and predicted normalized concentrations of MTBE for C_O = 2,500 mg/L for DC electrolysis using current densities equal to 0.5 and 1 mA/cm^2.

CHAPTER 5

SUMMARY AND CONCLUSIONS

In this lab-scale study, electrochemical degradation of MTBE dissolved in DI water with Na_2SO_4 as the supporting electrolyte was evaluated. The effect of current type and current density, electrode materials, initial concentration of MTBE in the solution, DI water versus tap water as electrolyte, and effect of electrode fouling was evaluated by measuring the concentration of MTBE in a 1 L cell during 24-hr tests. The current densities ranged from 0.5 to 4 mA/cm^2; current types applied were DC and square-wave AC ($f = 0.1$ Hz); and the electrode materials tested were 99% pure titanium, solid graphite, and boron doped diamond on a silicon wafer. The key findings are as follows:

1. Rate of degradation of MTBE increased when the current density was increased from 0.5 to 4 mA/cm^2;

2. Degradation rates during DC electrolysis were greater than those when AC was used for a fixed current density;

3. Degradation rate when titanium electrodes were used was about the same as with BDD electrodes. However, graphite electrodes had the least degradation rate. Visual observation after the tests indicated deposits on the titanium electrodes. Such deposits were not seen on the BDD and the solid graphite electrodes;

4. Degradation rates decreased as initial MTBE concentration increased probably because the rate of production of hydroxyl radicals was not proportionately more

for reaction with MTBE and probably additional mass of byproducts also competed with MTBE for degradation with hydroxyl radicals at higher initial concentrations of MTBE;

5. Degradation rates were similar when the electrolytes were DI water or tap water and when the electrode surface was polished versus when it was left unpolished for relatively low current density. However, the consumption of electrical energy was not the same. Greater energy was consumed for unpolished electrodes used in tap water. The reason for this is faster fouling of the electrode surface;
6. Degradation kinetics of MTBE observed in the lab experiments followed pseudo-first order decay equation; and
7. Nernst-Planck equation was able to relatively accurately predict the concentration of MTBE during DC electrolysis for lower initial concentrations (25 and 250 mg/L). The predictions did not consistently match the measured values when the initial concentration was relatively high (2,500 mg/L). The discrepancy is because the equation is a transport equation that does not consider the rate of production of reactive species. The predictions would be more accurate when the concentration of the specie is relatively low or the applied current is relatively high. However, additional experiments are needed to confirm this hypothesis.

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