



# Electrochemical removal of MTBE from water using the iridium dioxide coated electrode

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## ARTICLE INFO

### Keywords:

Methyl tert-butyl ether (MTBE)  
Iridium dioxide (IrO<sub>2</sub>)  
Direct oxidation  
Indirect oxidation  
Redox mediator

## ABSTRACT

Methyl tert-butyl ether (MTBE) is always the most likely found compound at the front of a gasoline plume due to its chemical characteristics. In this study, an iridium dioxide (IrO<sub>2</sub>) coated electrode was utilized to perform electrochemical removal of MTBE in a lab-scale bath electrolyzer. Depending on the constant-potential controls, electrochemical removal of MTBE can be conducted either through direct oxidation, water electrolysis competition, or indirect oxidation. Direct oxidation mechanism performed MTBE removal up to 39% as electrolyzing below 1.2 V, and the occurrence of water electrolysis competition dropped MTBE removal as increasing the operative potential up to 2.0 V. The continual increase of operative potential above 2.0 V brought about indirect oxidation of MTBE through the chain reactions of the redox mediator S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/SO<sub>4</sub><sup>2-</sup>. The matrix effect of iron enhances electrochemical oxidation of MTBE to provide about 2 times improvement on MTBE removal. The products of MTBE degradation were identified as tert-butyl alcohol (TBA), acetone, and CO<sub>2</sub> by GC/MS, and the distributions of carbon atoms in TBA, acetone, CO<sub>2</sub>, and MTBE were found 18, 12, 62, and 8% through the optimum control of electrochemical oxidation.

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## 1. Introduction

Methyl tertiary butyl ether (MTBE, C<sub>5</sub>H<sub>12</sub>O) is the most prevalent gasoline additive used for meeting the requirement of octane rating because of its blending characteristics and economic benefit over other oxygenates such as ethyl tertiary butyl ether and tertiary amyl methyl ether. Typically, reformulated gasoline blends with 10–15% MTBE before sale in order to reduce carbon monoxide and hydrocarbon emissions from vehicle exhaust. MTBE is soluble in gasoline as well as water (about 48,000 mg/L), and thus it will partition itself quickly between both phases in case of fuel spills. Some field study has pointed out that MTBE is always the most likely found compound at the front of a gasoline plume than other gasoline constituents [1], and it is ascribed to its high water solubility, low air–water partition, low organic carbon sorption, and less biodegradability. Annual use of MTBE was estimated around half million t in Taiwan, and the leaking of underground storage tanks has been found in numerous aged gas stations according to a countrywide survey. The concentration of MTBE in groundwater attenuates with plume transport; levels of 0.2–0.6 mg/L and a ceiling value of 477 mg/L MTBE in groundwater have been reported around leaky gas stations in Taiwan

[2,3]. MTBE was classified as a suspect human carcinogen by the USEPA, and a public health level of 13 µg/L MTBE in drinking water was suggested in California based on its low taste threshold [4].

Numerous treatment processes proposed for removing MTBE from water include aerobic biodegradation, air stripping, adsorption, and advanced oxidation. The presence of the tert-butyl group in its molecular structure impedes environmental degradation of MTBE under natural conditions. Microbial mediated MTBE degradation takes more than 189 d to degrade MTBE to below detection under an aerobic condition [5]. Air stripping is difficult and needs a high air-to-water ratio to treat MTBE according to its tiny Henry's law constant, and it is less efficient at low temperatures [6]. MTBE, which has a 0.62 nm kinetic diameter [7], can be sorbed into certain materials: granular activated carbon [8] and zeolite [9] in particular. However, activated carbon adsorption is significantly more expensive than air stripping and advanced oxidation technologies [6]. As a consequence, these conventional MTBE removal methods are either inefficient or expensive. Advanced oxidation technologies can generate hydroxyl radicals to degrade or even mineralize MTBE with a high reaction rate such as ozone/hydrogen peroxide [10], Fenton's reagent [11], UV/peroxide [12], potassium permanganate [13], persulfate [14], gamma radiolysis [15], and electrochemical oxidation [16–18]. Compared with chemical oxidation, electrochemical oxidation has little or no adverse impact on the environment without using harmful reagents. On a bench-scale reactor, electrochemical

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oxidation appears to be a promising method for removing aqueous MTBE [19].

The IrO<sub>2</sub> electrode with a long lifetime is one of the most representative dimensionally stable anodes, which have a wide application to wastewater treatment. This study utilized an IrO<sub>2</sub> electrode as working electrode to perform electrochemical removal of MTBE from contaminated water. Our previous study pointed out that MTBE removal can be ascribed to direct oxidation or indirect oxidation mechanisms depending upon the operational potentials [17]. This study was also aimed at exploring the behavior of MTBE degradation and examining the influence of main operation factors including potential, electrolyte, pH, and matrix effect of iron as using the IrO<sub>2</sub> electrode. In addition, the degradation pathway of MTBE was identified to ascertain the effectiveness of electrochemical oxidation mechanisms. In this study, experimental data of a bench-scale electrolytic system was provided for developing practical application of the IrO<sub>2</sub> electrode to remediate the potential problem of MTBE contamination linked to leaky gas stations.

## 2. Materials and methods

### 2.1. Chemicals

Analytical-grade MTBE (99.5%) was purchased from Merck Ltd. (Taiwan, ROC). Nitric acid (65%) obtained from Merck Ltd. (Taiwan, ROC), hydrochloric acid (37%) and sulfuric acid (96%) from Nihon Shiyaku Industries Ltd. (Japan) were reagent grade used as electrolytes. Acetone (99.7%) obtained from Uni-Ward Co. (Taiwan, ROC) and tert-butyl alcohol (TBA) from TEDIA (USA) were used for the quantification of degradation by-products. All reagents were prepared with de-ionized water, which was made by Milli-Q system (Millipore TK-10, USA).

### 2.2. Reactor setup

The bench-scale reactor system was used for electrochemical experiments and mainly consisted of an electrolytic cell, an electrochemical analyzer, an electrical multimeter, and a thermostatically controlled water bath. A double-jacketed glass vial with a Teflon cap was used as the electrolytic reactor, which was equipped with an IrO<sub>2</sub>-coated working electrode, a Pt wire as counter electrode, and a saturated Ag/AgCl electrode as reference electrode. The IrO<sub>2</sub> electrode was a plate-type commercial product with a 2 cm<sup>2</sup> surface area. Constant voltammetric potential was supplied and precisely controlled using an electrochemical analyzer (Model 100B; Bio Analytical Systems, Inc., USA), and the alteration of passing current between the working electrode and the counter electrode was monitored using a multimeter (Model 2000; Keithley Instruments, Inc., USA). During the experiment, the liquid in the reactor was completely mixed with a mini magnetic stirrer, and the temperature of the electrolytic reactor was controlled at 18 °C by recycling cool water from a thermostatically controlled water bath.

### 2.3. Electrochemical experiments

All batch experiments were conducted in a bench-scale electrolytic reactor, which was sealed with a Teflon cap to prevent the loss of MTBE through volatilization during the experiments. Before each experiment, the IrO<sub>2</sub>-coated electrode was ultrasonically cleaned for 5 min and then rinsed with deionized water. The reference electrode was immersed in a 3 M KCl solution to maintain its saturated status while not in use. The initial concentration of 20 mg/L of MTBE (about 0.227 mM) was prepared in the reaction solute that typically contained 1 M electrolyte to facilitate electrochemical reactions. Nitric acid (HNO<sub>3</sub>), hydrochloric acid (HCl), and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were selected as electrolytes

and examined for the suitability in the IrO<sub>2</sub>-electrolytic system. The cyclic voltammetric behavior of the IrO<sub>2</sub>-coated electrode was investigated using the electrochemical analyzer. Each oxidation experiment was done at a specified constant potential, which fell in the range of 0.50–3.00 V. Each run was lasted for 180 min and sampled with a syringe every 30 min. The sampled liquor (25 μL) was immediately diluted to 5 mL in a purging vessel. Following the purge-and-trap procedure, the extract was instantly subjected to the analysis of gas chromatography/mass spectrometry (GC/MS) for the determination of remaining MTBE and its intermediates or by-products. The pH of the reaction solute was measured at the beginning and the end of the experiments. The online monitoring of passing current was recorded to calculate the passage of charge in the IrO<sub>2</sub>-electrolytic system every 30 min.

### 2.4. Sample analysis

Concentrations of MTBE and its degradation intermediates were measured by the purge-and-trap method coupled to a GC/MS system (Model Clarus 500; Perkin Elmer, Inc., USA) equipped with a capillary column (60 m L × 0.25 mm ID × 0.25 μm thick) (Inno-Wax; Hewlett Packard, Inc., USA). The operating conditions for the purge-and-trap unit (Eclipse 4660 Purge-and-Trap Sample Concentrator; O.I. Analytical, Inc., USA) were: purging at 20 °C for 11 min, desorbing at 190 °C for 1 min, and baking at 210 °C for 15 min. The operating conditions for the GC/MS system were: N<sub>2</sub> carrier gas at 1 mL/min, split ratio at 10:1, injector temperature at 40 °C, and detector temperature at 200 °C. The column was isothermal at 40 °C for 4 min, ramped at 10 °C/min to 100 °C, held for 2 min, continually ramped at 30 °C/min to 180 °C, and held for 2 min.

## 3. Results and discussion

### 3.1. Selection of supporting electrolytes

The addition of supporting electrolyte to the reactor is required in order to provide a conducting medium and minimize the iR drop through the electrodes. The IrO<sub>2</sub> electrode might cause surface cracking or lose catalytic capability as working in a basic condition, and thus only acidic electrolytes were allowed for test. Three common species of acidic electrolytes including HNO<sub>3</sub>, HCl, and H<sub>2</sub>SO<sub>4</sub> were examined at 1 M concentration by comparing the efficiency of MTBE degradation at a constant potential 3.00 V. As shown in Fig. 1, the plots of ln[C<sub>0</sub>/C] versus time were linear with the R<sup>2</sup> values between 0.861 and 0.985, and it suggested that MTBE degradation follows the first-order kinetics. The rate constants of MTBE

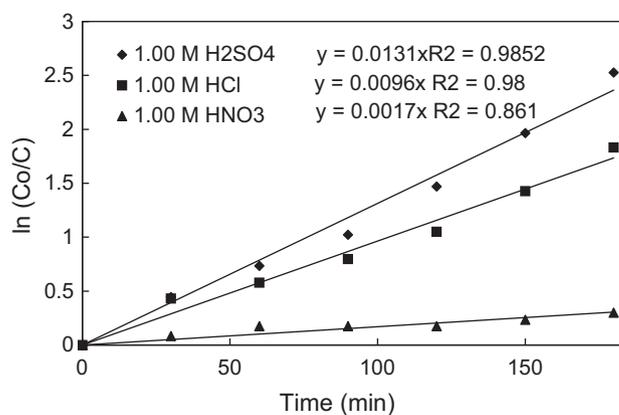
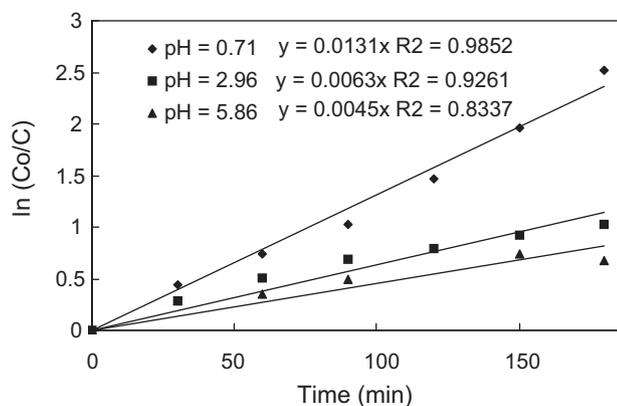
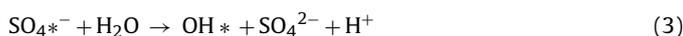


Fig. 1. First-order kinetic plots of ln[MTBE] versus time through electrochemical oxidation in a 1 M HNO<sub>3</sub>, HCl, or H<sub>2</sub>SO<sub>4</sub> solution (conditions: [MTBE]<sub>initial</sub> = 20 mg/L and potential = 3.00 V).



**Fig. 2.** First-order kinetic plots of  $\ln[\text{MTBE}]$  versus time through electrochemical oxidation in various pH solutions (conditions:  $[\text{MTBE}]_{\text{initial}} = 20 \text{ mg/L}$ , potential = 3.00 V, and electrolyte = 1 M  $\text{H}_2\text{SO}_4$ ).

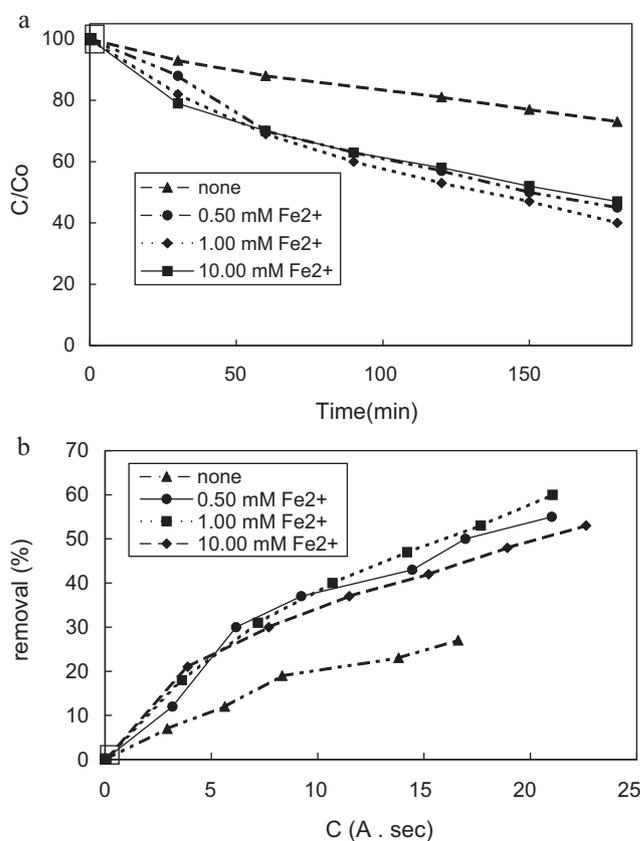
degradation were 0.0017, 0.0096, and  $0.0131 \text{ min}^{-1}$  in a 1 M solution of  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{H}_2\text{SO}_4$ , respectively. The results indicated that  $\text{H}_2\text{SO}_4$  is a better selection to act as electrolyte than  $\text{HCl}$  and  $\text{HNO}_3$  in the  $\text{IrO}_2$ -electrolytic system due to its favorable formation of the  $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$  redox couple. According to reaction 1 through 3, the produced persulfate ion can initiate serial radical reactions to form hydroxyl radicals that can easily break down MTBE molecules [14].  $\text{HCl}$  is another suitable electrolyte in the  $\text{IrO}_2$ -electrolytic system that electrochemical generation of active chloride compounds such as hypochlorite ion, hypochlorous acid, and chlorate ion can effectively attack MTBE molecules like the active hydroxyl radical [20]. As a result,  $\text{H}_2\text{SO}_4$  is used as electrolyte for electrochemical experiments.



In a 1 M  $\text{H}_2\text{SO}_4$  solution, three different initial pH conditions were examined for their effect on MTBE removal. Fig. 2 illustrates that MTBE removal increased with decreasing initial solute pH, and the first-order rate constants of MTBE degradation were 0.0131, 0.0063, and  $0.0045 \text{ min}^{-1}$  in a 1 M  $\text{H}_2\text{SO}_4$  solution at pH 0.71, 2.96, and 5.86, respectively. A trend of increasing solute pH was noticed after electrolyzing 180 min, especially in a weak acidic condition. The pH increase in the solution may result from the consumption of  $\text{H}^+$  ions in the reductive half-reaction during the experiments. A strong acidic condition was found favorable for the  $\text{IrO}_2$  electrode to work efficiently, and a satisfied efficiency of MTBE removal (92%) can be achieved under such an acidic condition.

**Table 1**  
MTBE removals and first-order rate constants of MTBE degradation through electrochemical oxidation at various potentials (Conditions:  $[\text{MTBE}]_{\text{initial}} = 20 \text{ mg/L}$ , electrolyte = 1.0 M  $\text{H}_2\text{SO}_4$ ).

Mechanism	Potential (V)	pH		MTBE removal in 180 min (%)	First-order rate constant ( $\text{min}^{-1}$ )	$R^2$
		Initial	Final			
Direct oxidation	0.50	0.75	0.75	30	0.0020	0.975
	0.75	0.85	0.81	38	0.0029	0.826
	1.00	0.71	0.79	39	0.0033	0.846
Competition of water electrolysis	1.50	0.56	0.66	32	0.0023	0.984
	1.80	0.56	0.61	30	0.0022	0.851
	2.00	0.75	0.79	27	0.0018	0.988
Indirect oxidation	2.30	0.66	0.77	37	0.0029	0.967
	3.00	0.71	0.75	92	0.0131	0.985



**Fig. 3.** (a) Progress of residual MTBE, (b) coulometric efficiency of MTBE removal through electrochemical oxidation with the addition of 0.00 mM, 0.50 mM, 1.00 mM, and 10.00 mM ferrous ions (conditions:  $[\text{MTBE}]_{\text{initial}} = 20 \text{ mg/L}$ , potential = 3.00 V, and electrolyte = 1 M  $\text{H}_2\text{SO}_4$ ).

### 3.2. Effect of potential on MTBE removal

Cyclic voltammetry (CV) is a widely used technique to obtain information about fairly complicated electrode reactions. MTBE was found inert to the  $\text{IrO}_2$  electrode due to the lack of clear peaks on the cyclic voltammogram. In a 1 M  $\text{H}_2\text{SO}_4$  solution, the occurrence of oxygen evolution was observed above 1.20 V, and hydrogen evolved below  $-0.40 \text{ V}$ . Controlled-potential electrolysis was applied in this study, and the electrochemical oxidation of MTBE in a 1 M  $\text{H}_2\text{SO}_4$  solution was investigated at a specified potential ranging between 0.50 and 3.00 V. It is observed from Table 1 that the first-order kinetics of MTBE degradation exists at various potential levels based on the linear relationships of  $\ln[C_0/C]$  and time ( $0.826 < R^2 < 0.988$ ). In Table 1, the efficiency of MTBE removal after

electrolyzing 180 min is not always increasing with the operating potential as expected. As electrolyzing below 1.2 V, MTBE removals and the first-order rate constants are found growing with the operating potential. However, this growing trend no longer exists as the operating potential keeps increasing to 2.0 V, and the efficiency of MTBE removal is found to decrease adversely in a potential range of 1.0 and 2.0 V. The efficiency of MTBE removal is found increasing with the operating potential again as electrolyzing above 2.0 V.

There is no significant difference on removal efficiency through electrochemical oxidation as applying a specified potential below 1.0 V. The catalytic mechanism for organic oxidation on the IrO<sub>2</sub> electrode was performed as reaction (4). Water is first discharged to form hydroxyl radicals, which interact with the IrO<sub>2</sub> electrode and grow the higher oxide IrO<sub>3</sub> as reactive intermediate [21]. MTBE must be first adsorbed on the surface of the electrode and then oxidized by reactive IrO<sub>3</sub> through direct oxidation. Thus, the rate of direct oxidation is determined by the adsorption-control process. Electrolyzing at a potential ranging between 1.2 and 2.0 V, the reduction of MTBE removal is ascribed to the competition of water electrolysis as reaction (5). Oxygen evolution through water electrolysis certainly consumes energy, and the formed oxygen, a weak oxidant, might attack MTBE molecule but not degrade it quickly. Electrolyzing above 2.0 V, the improvement on MTBE removal especially resulted from the formation of radicals to initiate indirect oxidation. As illustrated in reactions (1)–(3), the formation of persulfate can be initiated above 2.01 V, and a series of mediator reactions subsequently produce OH radicals [14]. Besides, the electrochemical oxidation processes can perform water electrolysis above 2.85 V to produce OH radicals as reaction (6), and the formed OH radical was subsequently released to oxidize MTBE in solute. The mechanisms of forming OH radicals give a good explanation of a great improvement on MTBE removal as electrolyzing at 3.0 V. Therefore, MTBE can be degraded through direct oxidation or indirect oxidation depending upon the strength of the operating potential in the IrO<sub>2</sub>-electrolytic system.



### 3.3. Matrix effect of iron on MTBE removal

Groundwater has very different chemical compositions that might make the electrochemical system more complicated. Some groundwater is abundant in iron content that the reported ceiling concentration is 10.2 mg/L (about 0.18 mM) among 34 local monitoring wells [22]. The matrix effect of iron was tested in a 1 M H<sub>2</sub>SO<sub>4</sub> solution containing 0.50, 1.00, or 10.00 mM Fe<sup>2+</sup> ions. Fig. 3a shows that the addition of Fe<sup>2+</sup> ions does enhance the efficiency of MTBE removal no matter what levels being added, and about 2 times improvement on MTBE removal was noticed. It is well known that the formation of Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couple may enhance the Fenton reactions in the electrochemical system. The presence of Fe<sup>2+</sup> ions can act as mediator; the coulometric efficiency of MTBE degradation with different levels of mediator was compared in Fig. 3b. The consumed coulomb is calculated by integrating the recorded current with time, while the recorded current is mainly contributed by Faradic processes. The endpoint of the progressive curve in Fig. 3b records the ultimate efficiency of MTBE removal and the accumulated charge at each controlled condition, and the slope of the progressive curve explains the associated response of all Faradic processes, such as MTBE degradation, water electrolysis, and mediator reactions. Thus, the equivalent slopes for different levels of mediator addition in Fig. 3b imply that the identical mechanisms of MTBE removal occur in the IrO<sub>2</sub>-electrolytic system. Fig. 3b also

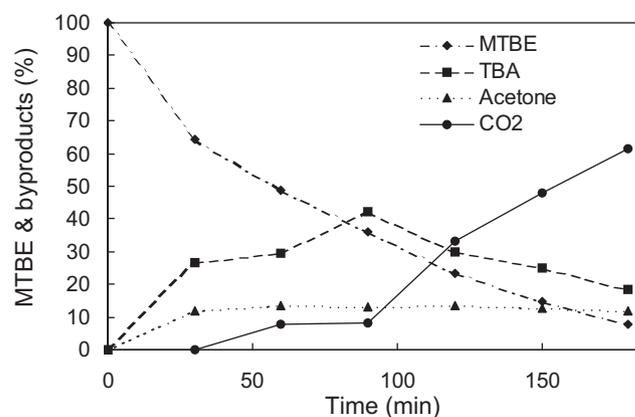
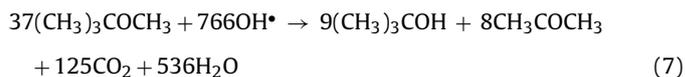


Fig. 4. The progressive curve of MTBE disappearance and degradation intermediate production through electrochemical oxidation (conditions: [MTBE]<sub>initial</sub> = 20 mg/L, potential = 3.00 V, and electrolyte = 1 M H<sub>2</sub>SO<sub>4</sub>).

gives the evidence that the occurrence of Fenton reactions may result in a better coulometric efficiency of MTBE removal than that without adding Fe<sup>2+</sup> ions.

### 3.4. Intermediate and pathway of MTBE degradation

Two possible routes of MTBE degradation by electrochemical oxidation were reported: one pathway to breakdown MTBE to tert-butyl formate (TBF), tert-butyl alcohol (TBA), and acetone before complete mineralization, and the other to form methyl acetate as degradation intermediate [16]. The breakdown of MTBE is initiated with hydrogen abstraction by the hydroxyl radicals, followed by oxygen addition to form peroxy radicals for continual decomposition to different intermediates [23,24]. In this study, all the sampled liquors were subjected to the analysis of GC/MS to identify the degradation intermediates and measure the disappearance of MTBE. The major identified intermediate of MTBE degradation is TBA and acetone as shown in Fig. 4, while TBF in the same degradation pathway are seldom found due to its low level of possible accumulation. For each experiment, carbon dioxide was also found based on the identification of MS ion fragments with mass-to-charge ratio during electrochemical oxidation. Based on the identification of intermediates and products, the overall reactions of MTBE degradation was elucidated as reaction (7).



In reaction (7), MTBE is oxidized to acetone releasing 16 electrons and further mineralized to CO<sub>2</sub> releasing 750 electrons by the attack of OH radicals. In Fig. 4, the instrumental determination shows that 92% MTBE can be degraded to generate 18% TBA and 9% acetone after electrolyzing at 3.0 V, and the formation of CO<sub>2</sub> should be 62% based on the calculation of carbon balance.

Irrefutably, MTBE can be partially mineralized to carbon dioxide by the attack of OH radicals. As mentioned previously, the extent of MTBE degradation may show a rising or reducing trend within the different ranges of operating potential in the IrO<sub>2</sub>-electrolytic system. According to the controls of experiment conditions, the extent of MTBE degradation as well as the accumulation of the intermediates could be varied. Fig. 5 illustrates carbon distribution in formed TBA, acetone, CO<sub>2</sub>, and remaining MTBE at the end of experiments for various potentials. It is clearly seen from Fig. 5 that the mechanism of direct oxidation degraded 30–40% of MTBE and formed the only intermediate acetone. The competition of direct oxidation and water electrolysis slowed down the degradation pathway

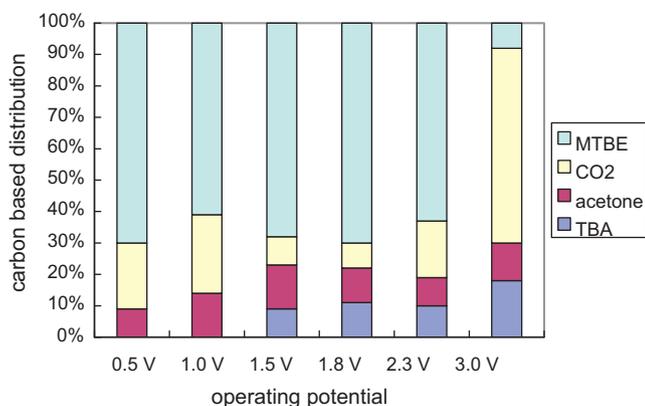


Fig. 5. Comparison of carbon distributions in TBA, acetone, CO<sub>2</sub>, and MTBE through electrochemical oxidation of MTBE at various potentials.

of MTBE to form TBA and acetone as intermediate, and also the production of CO<sub>2</sub> was minimized. The mechanism of indirect oxidation resulted in the optimum control at 3.0V that the extent of complete mineralization was greatly enhanced. Consequently, not only the extent of MTBE degradation but also the levels of intermediate accumulation are strongly affected by the operating potential in the IrO<sub>2</sub>-electrolytic system.

#### 4. Conclusions

This study successfully demonstrated electrochemical oxidation of MTBE in a bench-scale electrolyzer with the IrO<sub>2</sub> electrode. H<sub>2</sub>SO<sub>4</sub> is a suitable electrolyte due to its capability of forming S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/SO<sub>4</sub><sup>2-</sup> redox couple to generate OH radicals for further attacking MTBE molecules in the IrO<sub>2</sub>-electrolytic system. Initial 20 mg/L of MTBE can be efficiently removed 92% after electrolyzing 180 min at 3.0V in a 1 M H<sub>2</sub>SO<sub>4</sub> solution. Results showed that the mechanisms of MTBE removal could be direct oxidation, water electrolysis competition, and indirect oxidation depending upon the applied constant potentials. The breakdown of MTBE was mainly counted on the electrochemically generated OH radicals, and the presence of ferrous ions may result in Fenton reactions to provide 2 times improvement on MTBE removal. The major pathway of MTBE degradation was followed by the formation of TBA, acetone, and final mineralization to CO<sub>2</sub>. Based on the carbon balance, the estimated distributions of TBA accumulation, acetone accumulation, mineralization, and non-degraded MTBE were 18%, 12%, 62%, and 8% for the optimum control. Operating potential can definitely determine MTBE removal efficiency and also affect the levels of intermediate accumulation in the IrO<sub>2</sub>-electrolytic system.

#### Acknowledgements

This work was partially supported by the National Science Council (NSC), Taiwan, ROC under grant no. NSC-93-2211-E-168-001. The author would like to thank Zong-Chih Lin for his support on analytical work and Department of Environmental Engineering, Kun Shan University for the financial support on the establishment of analytical instruments.

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