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Electrocatalytic oxidation of methyl *tert*-butyl ether (MTBE) in aqueous solution at a nickel electrode

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Abstract

This study utilized the electrocatalytic characteristics of nickel electrode to perform degradation of methyl *tert*-butyl ether (MTBE) in aqueous solution. Lab experiments were conducted in a spiltless bath type cell equipped with a nickel electrode as working electrode, a platinum wire as counter electrode, and an Ag/AgCl electrode as reference electrode. Effects of controlled potential, supporting electrolyte, and solution pH on the efficiency of MTBE removal were examined under the control of the constant-potential conditions. Experiment results showed that the optimum electrolytic condition was operated at 0.35 V in a 1 M KOH electrolyte solution, and the initial 20 mg l^{-1} MTBE was reduced by 73% within 180 min under the optimum control. As using 1 M Na_2SO_4 and 1 M KCl as electrolyte, the efficiency of MTBE removal dropped to 60% and 50% under the similar controls. Comparing with various pH controls, the strong basic condition is favorable for electrocatalytic oxidation of MTBE in the Ni-electrolytic system. The efficiency of MTBE removal showed a rising trend with increasing initial pH of the solution. The formation of a redox $NiOOH/Ni(OH)_2$ layer on the anode surface, which was observed on the SEM image, can explain that nickel plays a mediator role on improving electrocatalytic oxidation of MTBE at 0.35 V in a strong basic condition. The by-products of MTBE degradation were identified as acetone and CO_2 by GC/MS, and the distributions of carbon atoms in acetone, CO_2, and MTBE were found 22%, 51%, and 27% through the optimum control of electrochemical oxidation.

Keywords: Electrochemical oxidation; Nickel; Methyl *tert*-butyl ether (MTBE); Redox couple; Electrolysis; Degradation

1. Introduction

Since the late 1970s, methyl tertiary butyl ether (MTBE, $C_5H_{12}O$) has replaced alkyl lead additives as the most widely used gasoline additive for maintaining the adequate octane rating. The use of MTBE in reformulated gasoline has brought about remarkable improvements on air quality in many urban areas; however, MTBE appears to have imposed significant adverse impacts on groundwater supply (Rong, 2001). The presence of MTBE in groundwater was typically derived from leaking of underground fuel tanks and pipelines, tank overfilling and faulty construction at gas stations (Johnson et al., 2000). In Taiwan, the annual use of MTBE was estimated around half million tons, and the leaking of underground fuel tanks has been subsequently found in numerous aged gas stations according to countrywide survey. The detected level of 0.3–0.5 mg l^{-1} and a ceiling value of 766 mg l^{-1} MTBE in groundwater were reported around leaky gas stations.

MTBE has higher water solubility, lower air–water partition, lower organic carbon sorption, and less biodegradability than other gasoline constituents. Because of its chemical characteristics, MTBE is always the most likely found compound at the front of a gasoline plume (Day et al., 2001). The presence of the *tert*-butyl group in its molecular structure impedes environmental degradation of MTBE under natural conditions. Several remedial schemes have been proposed for removing MTBE from water such as aerobic biodegradation, air stripping, adsorption, and advanced oxidation. Microbially mediated MTBE degradation has been demonstrated under aerobic

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condition, even though it takes more than 189 d to degrade MTBE to below detection (Schirmer et al., 2003). Air stripping is less efficient for the removal of MTBE at low temperatures (Sutherland et al., 2004), and it may not be a readily applicable treatment due to its low volatility and high water solubility. MTBE with a 0.62 nm kinetic diameter (Giaya and Thompson, 2002) can be sorbed into certain materials, in particular granular activated carbon (Shih et al., 2003) and all-silica β-zeolite (Li et al., 2003). However, activated carbon adsorption showed the highest treatment costs as comparing with air stripping and advanced oxidation technologies (AOTs) (Sutherland et al., 2004). AOTs including ozone (Vel et al., 1994), hydrogen peroxide (Yeh and Novak, 1995), Fenton's reagent (Xu et al., 2004), UV/peroxide (Wagler and Malley, 1994), potassium permanganate (Damm et al., 2002), persulfate (Huang et al., 2002), and gamma radiolysis (Hsieh et al., 2004) have been testified as promising treatment methods for MTBE. Electrochemical oxidation method also demonstrated a satisfactory performance on the removal of MTBE from water (Lin, 2005), plus it has been applied as a remedy scheme for many refractory compounds such as pesticides (Brillas et al., 2000; Ventura et al., 2002) and chlorinated phenols (Brillas et al., 2003; Torres et al., 2003). Comparing with chemical oxidation, electrochemical oxidation has little or no adverse impacts on the environment without using harmful reagents.

Electrochemical oxidation, one of the innovative AOTs, has been the focus of much research on wastewater treatment because of its high oxidation efficiency, fast reaction rate, and ease of operation. Our previous works have reported the bench-scale application of electrochemical oxidation scheme to treat MTBE contaminated water through the employment of a platinum electrode (Wu et al., 2006) and an iridium dioxide-coated electrode (Wu and Lin, 2007), and the breakdown of MTBE was primarily counted on electro-generated hydroxyl radicals or other chemical oxidants. Nickel electrode is widely used as an electrocatalyst in water electrolysis processes and employed as a positive electrode for rechargeable batteries; nonetheless, cases of its application to organic destruction are very rare. In this study, a Ni electrode was employed as working electrode to demonstrate its electrocatalytic performance on removing MTBE from its dissolved phase. This study was also aimed at exploring the behavior of MTBE degradation and examining the influence of main operation factors such as voltammetric charge, electrolyte, and pH in the Ni-electrolytic system.

2. Materials and methods

2.1. Chemicals

MTBE (99.5%) was purchased from Merck Ltd. (Taiwan, ROC). Potassium chloride (99%) obtained from Shimakyu Chemical Co. (Japan), sodium sulfate (99%) from Kanto Chemical Co. (Japan) and potassium hydroxide (85%) from Wako Chemical Co. (Japan) were reagent grade used as electrolytes. Acetone (99.7%) was obtained from Uni-Ward Co. (Taiwan, ROC) for the quantification of degradation intermediate. All reagents were prepared with de-ionized water, which was made by Mili-Q system (Millipore TK-10, USA).

2.2. Experimental setup

Experimental setup of the bench-scale electro-oxidation system was comprised with an electrolytic reactor, an electrochemical analyzer, an electrical multimeter, and a thermostatic water bath. A 14 ml glass vial with a Teflon cap was used as the splitless electrolytic reactor, which was equipped with a Ni electrode as working electrode (WE), a Pt wire as counter electrode (CE) and a saturated Ag/AgCl electrode as reference electrode (RE). The Ni electrode was plate-type with a 1.28 cm^2 surface area. A constant voltammetric potential was supplied and precisely controlled by a Bio Analytical System (BAS) 100B electrochemical analyzer, and the alteration of passing current between WE and CE was monitored by a Keithley 2000 multimeter. During the experiment, the liquor of the reactor was completely mixed with a mini magnetic stirrer, and the temperature of the electrolytic reactor was controlled at 18 °C by the recycle of cooling water from a thermostatic water bath.

2.3. Electrocatalytic oxidation 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. The initial concentration of 20 $mg\,l^{-1}$ MTBE (about 0.227 mM) was prepared in the reaction solute that typically contained 1 M electrolyte for the ease of electro-oxidation reactions. Potassium hydroxide, potassium chloride, and sodium sulfate were selected as electrolyte and examined for the suitability in the Ni-electrolytic system. Before each oxidation experiment, the Ni electrode was polished with a fine polishing paper, immersed 1 min in a 0.5 M nitric acid solution, cleaned 5 min by an ultrasonic cleaner, and rinsed with de-ionized water to remove adsorbed deposits on the surface. RE was immersed in a 3 M KCl solution to maintain its saturated status while not in use. The cyclic voltammetric behavior for the Ni electrode was investigated using a BAS 100B electrochemical analyzer. Each oxidation experiment was carried out at a specified constant potential, which fell in the range of 0.25–0.75 V. Each run was lasted for 180 min and sampled with a syringe every 30 min. The sampled liquor (25 μl) was diluted to 5 ml in the purging vessel immediately. Following the procedure of purge and trap, 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 begin-