



Electrochemical degradation of ethylene glycol in antifreeze liquids using boron doped diamond anode



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ABSTRACT

Large amounts of ethylene glycol (EG) based antifreeze liquids are daily discharge into the receiving waters. The chemical oxygen demand (COD) detected in most of the lakes and rivers close to the discharge points (industries, airports, etc.) exceeded 100,000 mg O₂/L. With such an amount, biological and chemical processes are inefficient to completely remove EG. In order to achieve better results, electrochemical oxidation (ECO) of EG was carried out on a laboratory scale. Niobium Boron Doped Diamond (Nb/BDD) was used as anode whereas carbon felt was used as cathode in a rectangular electrolytic cell. Different operating parameters including current intensity, treatment time, anode material, electrolyte type, electrolyte concentration and pollutant concentration were tested. The application of 0.077 A/cm² of current density during 120 min of treatment time in the presence of 7.0 g/L of Na₂SO₄ allowed 89.6 ± 0.2% of COD removal with 490 mg O₂/L of residual COD. This result was far below the legislation standard set by the province of Quebec that allows the discharge of 800 mg O₂/L of EG used for industrial purposes. The efficiency of ECO process was attributed to both direct and indirect oxidation that generate strong oxidizing species (ex: OH[•], S₂O₈²⁻, H₂O₂, etc.) capable of oxidizing organic matters on the surface of the anode and in the bulk of the solution.

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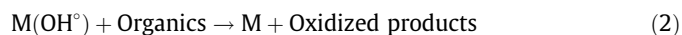
1. Introduction

Ethylene-Glycol (EG) (1,2-ethanediol) is an important basic organic compound frequently used as antifreeze agent in cooling systems and as de-icer liquid in airports [35]. Large concentrations of EG ranging between 1000 and 25,000 mg/L are generally detected in lakes and rivers close to airports [3]. Such quantities can easily increase the chemical oxygen demand (COD) in waters thereby creating hazards to aquatic and terrestrial organisms [13]. Over the last few years, biological and chemical treatments have been used for EG removal. However, EG at large concentrations limit the efficiency of biological processes [25] whereas with chemical processes such as Photo-Fenton, large amounts of sludge could be generated leading to an increase in the treatment cost [33].

Different strategies including electrochemical oxidation processes have been proposed and identified as an attractive

alternative for wastewater treatments [4,12,14,15,20,27,28]. It is well known that this advanced technique combines chemistry (generation *in situ* of oxidants) and electricity (electronic transfer) which makes it an ecofriendly technology [1,4,16]. Furthermore, the presence of direct and indirect oxidation mechanisms has made electrochemical oxidation an effective tool in the degradation of organic compounds [20].

Direct oxidation consists in producing hydroxyl radicals (E°(OH[•]/H₂O) = 2.80 V vs. SHE) from the anodic oxidation of water molecules (Eq. (1)). Hydroxyl radicals OH[•] are a very powerful oxidants able to oxidize a wide range of organic compounds (Eq. (2)) [12,14]. The second most important mechanism is the indirect oxidation through which other radical systems such as H₂O₂, HClO and S₂O₈²⁻ produced in the bulk are capable of destroying organic pollutants [2,20].



In this study, we investigated the electrochemical oxidation of Ethylene-Glycol used as an antifreeze liquid in industrial cooling systems. For that matter, different operating parameters including

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Nomenclature

ECO	electrochemical oxidation	Ti/IrO ₂	titanium coated with iridium oxide
EG	ethylene glycol	Ti/IrO ₂ /RuO ₂	titanium coated with iridium oxide and ruthenium oxide (MMO)
COD	chemical oxygen demand	MMO	multi-metal oxide
Nb/BDD	niobium boron doped diamond	RNO	p-nitrosodimethylaniline
Ti/Pt	titanium coated with platinum		
Ti/PbO ₂	titanium coated with lead oxide		

current intensity, treatment time, anode material, electrolyte type, electrolyte concentration and pollutant concentration have been tested in order to determine the optimal conditions for EG removal.

2. Materials and methods

2.1. EG effluent

The EG solution used in this study was an anti-freezing sample provided by Produits Chimiques Magnus Ltd. Company (Boucherville, QC, Canada) and used in industrial cooling systems. It was comprised of 530 g/L of ethylene glycol (C₂H₆O₂), 0.60 g/L of azole and 8.72 g/L of phosphate (PO₄³⁻). The EG solution had an initial COD content of more than 100 g/L and a pH around 9.5. Synthetic EG effluents having different concentrations of EG (2.5–5 g/L) were prepared using distilled water. Sodium salt (Na₂SO₄) was added to increase the electrical conductivity. Mixing and stirring time of 5 min was required to completely dissolve sodium salt by means of a Teflon-covered stirring bar (750 rpm) installed in the bottom of the 4.0 L beaker.

2.2. Electrolytic reactor set up

The electrolytic cell used was made of Plexiglas material with a dimension of 17 cm (depth) × 5 cm (width) × 15 cm (length). It was comprised of one anode and one cathode with an inter-electrode gap of 1 cm. The anode has a solid surface area of 65 cm² and a void surface area of 45 cm². The circular anode electrode (12 cm of diameter × 0.1 cm thick) was either made of niobium coated with boron doped diamond (Nb/BDD) or made of titanium coated with transition metal such as Ti/PbO₂, MMO (Ti/IrO₂/RuO₂), Ti/IrO₂ and Ti/Pt. On the other hand, the cathode was a carbon felt having a surface area of 127 cm². The electrodes were vertically installed on a perforated Plexiglas plate at 2 cm from the bottom of the cell.

All experiments were carried out in a closed loop as shown in Fig. 1. The loop consisted of 2.0 L of a Plexiglas tank (1), a peristaltic

recycling pump (2) and the electrolytic cell (3). During the treatment, the solution in the electrolytic cell was recirculated through the pump. A recycle flow rate of 170 ml/min was maintained using the peristaltic recycling pump (Master flex, Model 77200-50, USA). A current intensity ranging between 1.0 and 10 A was imposed during 30–120 min of treatment time. The current intensity was delivered by means of DC power supply Xantrex XFR 40-70 (Aca Tmetrix, Mississauga, Ontario, Canada) with a maximum current intensity of 70 A and a maximum voltage of 40 V. All experiments were carried out at room temperature (25 ± 0.1 °C) with a total volume of 1.0 L.

2.3. Electrochemical treatment of EG effluent

In order to evaluate the effect of operating parameters on EG removal during ECO, an Iterative method (IM) was elaborated. Optimum parameters were then chosen based on the efficiency and the treatment cost of the process. Firstly, current intensity was varied between 1.0 and 10 A during a treatment time ranging from 30 to 120 min. Different types of anode such as Nb/BDD, Ti/PbO₂, MMO (Ti/IrO₂/RuO₂), Ti/Pt and Ti/IrO₂ were tested. The type (Na₂SO₄, NaCl, NaBr and NaNO₃) and the concentration (1.0–10 g/L) of electrolyte were also taking into account. Subsequently, the concentration of EG was varied between 2500 and 5000 mg/L in order to complete the study. During these essays, the effectiveness of the electrochemical oxidation process was evaluated by measuring the residual concentration of COD and by calculating the energy consumption. All of the tests performed during this study were repeated in duplicate.

Furthermore, an iodide method was investigated in order to quantify the total oxidants (S₂O₈²⁻ and H₂O₂) produced during the electrochemical oxidation process. At the end of the treatment, 1 g of iodide potassium (KI) and 5 ml of acetic acid (buffer) were added to 50 ml of the treated solution. In the presence of oxidants, the color of the treated solution changes and turns yellow indicating the oxidation of iodide ion (I⁻) to iodine (I₂). The quantification of oxidants is then performed by the addition of thiosulfate solution (C = 0.1 mol/L) until the equilibrium (the disappearance of color).

Another method allowing the quantification of hydroxyl radicals OH° and ozone O₃ by bleaching p-nitrosodimethylaniline (RNO) was also investigated. For that matter, 6.0 mg of RNO was prepared in a glass tank containing 1.0 L of buffer. Buffer solutions were prepared using anhydrous dibasic sodium phosphate (99% purity) and crystalline monobasic potassium phosphate (99% purity) with a pH around 7.0. The final solution (C = 4 × 10⁻⁵ mol/L) was then stirred at a speed of 900 rpm for 120 min in the absence of light. In order to enhance the electrical conductivity of the solution, sulfate sodium was added.

2.4. Analytical details

The pH was determined using a pH-meter (Fisher Acumet model 915) equipped with a double junction Cole-Palmer electrode with Ag/AgCl reference cell. The conductivity was also measured

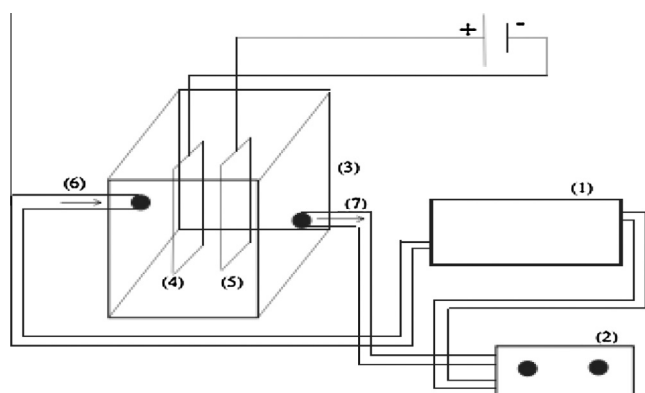


Fig. 1. Electrolytic reactor design; Plexiglas tank (1), peristaltic recycling pump (2), electrolytic cell (3), anode (4), cathode (5), inlet (6), outlet (7).

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