

전기화학적으로 재생되는 Ag(II)를 사용한 유기제염폐액의 분해

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Destruction of Organic Decontamination Liquid Wastes Using Electro-Regenerative Ag (II)

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Introduction

Relatively large quantity of organic liquid wastes containing complexing agents such as EDTA and citric acid is generated from the chemical decontamination campaigns. In order to increase the utility of chemical decontamination, safe and effective treatment for waste reduction and final disposal is required. Destruction of organic decontamination liquid wastes can lead to significant reduction in the final waste volume and improvement in long term stability of encapsulated organic radioactive wastes for disposal. Various oxidation processes which involve chemical, electrochemical and photochemical treatments have been investigated in many countries for the destruction of organic radioactive liquid wastes[1].

Mediated electrochemical oxidation(MEO) process, which operates at low temperature and low pressure, has been intensively developed in the UK and USA for the safe destruction of toxic or hazardous organic wastes because of its powerful destroying capability, applicability on a mixed wastes as well as a wide range of organic compounds, and controllability of the reaction. Ag(II) has been widely used as a mediator in the anodic oxidation of both inorganic and organic substrates[2, 3]. Numerous studies have been reported on the MEO of organic substrates such as TBP, formic acid, ethylene glycol, and benzene by electro-regenerative Ag(II).

In this study, MEO of organic component of chemical decontamination agents such as ethylenediaminetetraacetic acid(EDTA), oxalic acid(OA), and citric acid(CA) was carried out using electro-regenerative Ag(II) as a mediator under constant current in order to develop a radioactive waste treatment process for the safe destruction of organic compounds at ambient temperature.

Work Description

The MEO of EDTA, OA, and CA was carried out using continually regenerated Ag(II) by applying a constant current between the anode and the cathode of a flow type electrolysis cell which has two compartments, one anodic and one cathodic of dimensions 0.03x0.12x0.002 m, divided by Nafion 117 cation selective membrane. Platinum plate electrodes, of which dimensions are 0.03 m in width and 0.065 m in length, were used as an anode and a cathode, respectively. The constant temperature was maintained in the anolyte and the catholyte by putting the electrolyte feed chamber in the constant temperature water bath. Air was continuously sparged into the catholyte to convert nitrous acid to nitric acid and suppress the generation of NO_x.

The experimental parameters studied were cell current, temperature, and anolyte concentration. The cell current was varied from 250 to 1000 mA, the temperature of electrolyte was ranged between 30 and 70 °C. The acid concentration varied from 1.5 to 7 mol dm⁻³ and the concentration of AgNO₃ as a mediator in all the experiments was 0.5 mol dm⁻³. The anodic compartment was always charged with 0.25 dm³ consisted of desired concentration of organic substrates, nitric acid, and AgNO₃. Initial concentrations of EDTA, citric acid, and oxalic acid were 4x10⁻³ mol dm⁻³, 1x10⁻² mol dm⁻³, and 2x10⁻² mol dm⁻³, respectively.

Concentration of carbon dioxide were measured continuously with infrared gas analyzer(ZRF type, Fuji Electric) to observe the destruction behavior of EDTA, OA, and CA during the MEO. At the end of the experiments, samples of the anolyte and the catholyte were taken to analyze TOC.

Results

1. MEO of EDTA

MEO of EDTA were carried out with varying the applied current from 250 mA to 1000 mA in $5 \text{ mol dm}^{-3} \text{ HNO}_3$ with $0.5 \text{ mol dm}^{-3} \text{ AgNO}_3$ at 30°C . The measurements of EDTA conversion to CO_2 , based upon the EDTA remaining in the anolyte are plotted against oxidation time as shown in Fig. 1. The oxidation rate of EDTA increased with increasing the applied current in experimental current range and the coulombic efficiency was 66% at 250 mA, but decreased to 45% at 500 mA and 28% at 1000 mA. The retardation of destruction rate after about 40% conversion as shown in Fig. 1 is assumed to be due to the decomposition of the reaction intermediates produced by oxidation of four carboxyl group.

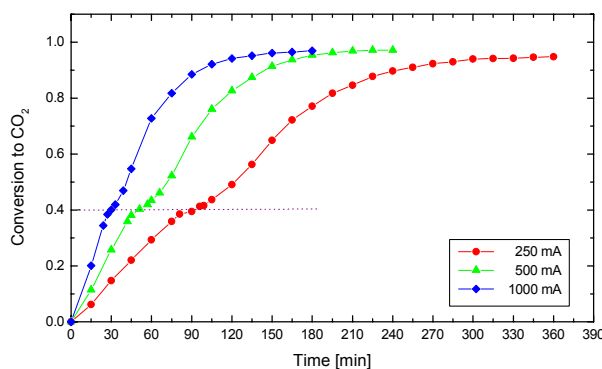


Fig. 1. Mediated electrochemical oxidation behavior of EDTA.

The effects of temperature and the anolyte (nitric acid) concentration on the MEO behavior of EDTA with varying the temperature from 30 to 70°C and the nitric acid concentration from 1.5 to 7 M , respectively, were studied as well. A slight increase in the destruction rate of EDTA was observed with increasing temperature. On the effect of acid concentration, there was no effect on the destruction rate of EDTA except below 3 M HNO_3 in the anolyte in which Ag oxide was precipitated. Especially, only 85% conversion of EDTA to CO_2 , based upon the EDTA remaining in the anolyte, observed in the experimental condition under 1.5 M HNO_3 in the anolyte is attributed to significant reduction of Ag^+ concentration in the anolyte due to the precipitation by formation of silver sesquioxide (Ag_2O_3) according to the Pourbaix atlas of electrochemical equilibria.

2. MEO of oxalic acid

MEO of OA were conducted at the applied current from 250 mA to 1000 mA in $5 \text{ mol dm}^{-3} \text{ HNO}_3$ with $0.5 \text{ mol dm}^{-3} \text{ AgNO}_3$ at 30°C . The measurements of OA conversion to CO_2 , based upon the OA remaining in the anolyte are plotted against oxidation time as shown in Fig. 2. The destruction rate of OA increased with increasing the applied current and the coulombic efficiency was 60% at 250 mA, but decreased to 29~30% at 500~1000 mA.

The effects of temperature on the MEO behavior of OA with varying the temperature from 30 to 70°C were studied as well. The destruction and coulombic efficiency did not change regardless of temperature.

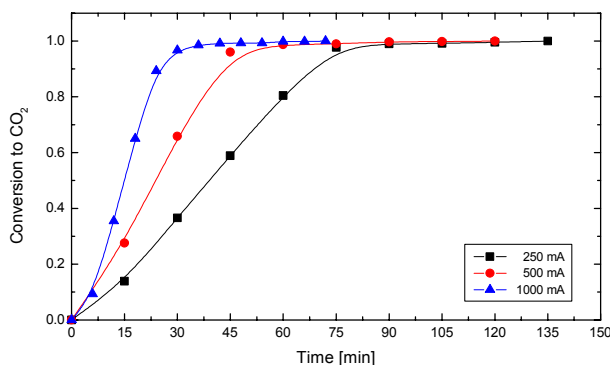


Fig. 2. Mediated electrochemical oxidation behavior of oxalic acid.

3. MEO of citric acid

MEO of CA were performed at the applied current from 250 mA to 1000 mA in $5 \text{ mol dm}^{-3} \text{ HNO}_3$ with $0.5 \text{ mol dm}^{-3} \text{ AgNO}_3$ at 30°C . The measurements of CA conversion to CO_2 , based upon the CA remaining in the anolyte are plotted against oxidation time as shown in Fig. 3. The destruction rate of CA increased with increasing the applied current and the coulombic efficiency was 85% at 250 mA, but decreased to 50~58% at 500 mA to 1000 mA.

The effects of temperature on the MEO behavior of CA with varying the temperature from 30 to 70°C were studied as well and the coulombic efficiency increased slightly with increasing temperature.

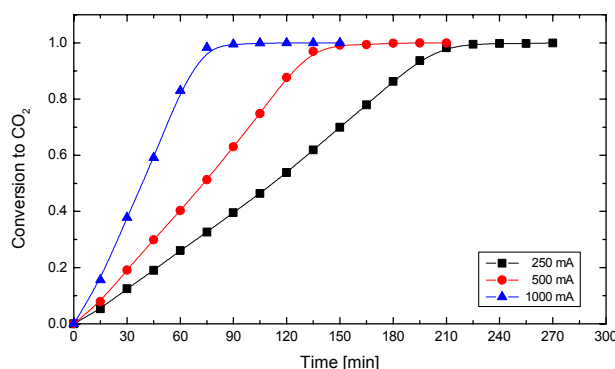


Fig. 3. Mediated electrochemical oxidation behavior of citric acid.

Conclusions and Discussions

Mediated electrochemical oxidation of organic components of the chemical decontamination liquid wastes using Ag(II) as a mediator was investigated to develop a radioactive waste treatment process for the safe destruction of organic compounds at ambient temperature. Ultimate conversion efficiencies of 93~97% were obtained with EDTA, citric acid, and oxalic acid due to the transportation of some of organic substrates to the catholyte across the cation selective membrane and the volatilization of intermediates produced during the MEO. Organic substrates remaining in the anolyte, however, could be completely destroyed to form carbon dioxide and water by reaction with electro-regenerative Ag(II) .

In the MEO of EDTA, the retardation of destruction rate to CO_2 in a short time interval after around 40 % conversion is assumed to be due to the decomposition of $-\text{CH}_2\text{OH}$ produced as a result of oxidation of four $-\text{CH}_2\text{COOH}$. In the MEO of citric acid, we expected the change of the destruction

rate around 50 % conversion to CO₂. It could not be shown any changes in destruction rate over the whole MEO period. Probably, it can be explained that the oxidation of side-chain -OH to =O through -O[·] easily leads the extraction of -COOH.

In case of EDTA destruction, significant reduction in conversion efficiency was observed under the concentration of 1.5 mol dm⁻³ HNO₃ due to the precipitation of Ag oxide. Below the concentration of 3 mol dm⁻³ HNO₃, silver sesquioxide, which is verified by reaction with Ag⁺ in acid solution, is formed by the electrochemical reaction, $2\text{Ag}^+ + 3\text{H}_2\text{O} = \text{Ag}_2\text{O}_3 + 6\text{H}^+ + 4\text{e}^-$, according to the Pourbaix atals of electrochemical equilibria. Therefore the acid concentration should be maintained above 3 mol dm⁻³ to prevent the formation of silver sesquioxide and the reduction of conversion efficiency of the organic substrates.

With increasing temperature, the coulombic efficiency on the MEO of each chemical decontamination agent was slight increased in case of EDTA and citric acid but did not change in case of oxalic acid. Relatively small effect of temperature implies that the MEO process using electro-regenerative Ag(II) can be used effectively for the safe destruction of toxic or hazardous organic liquid wastes at ambient temperature.

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Reference

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