Evoluation of Electrochemical Cell Characteristics in Cerium-MEO Process

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Introduction

The Mediated electrochemical oxidation (MEO) technique offers several advantages which are inherently safe system. This process is non - thermal that is it does not as thermal energy to break down and destroy organic waste [1-3]. The mediators as strong oxidant allow oxidizing the organic waste completely converted into carbon dioxide and water.

$$\text{Organic} + Ce^{4+} \rightarrow CO_2 + H_2O + Ce^{3+}$$

The mediator is a multivalent metal ion which cleanly recycled in the process [2]. The most commonly used mediator like Mn^{2+}/Mn^{3+}, Co^{2+}/Co^{3+}, Cr^{2+}/Cr^{3+}, Cr^{3+}/Cr^{6+}, Ce^{3+}/Ce^{4+}, Ag^{2+}/Ag^{+} in the form of liquid reagent are available for carrying out the electrochemical regeneration.[4] In the MEO process, the electrochemical cell is an important component of the operation. MEO is a cyclic process involving electrochemical generation of a redox agent and use of that agent to effect a chemical reaction for the oxidation of organic waste.

The electrochemical cell consists of an anode and cathode separated by a membrane. In the electrochemical cell, oxidation of Ce(III) to Ce(IV) in electrolyte occurs at the anode. Therefore, degradation of organics depends up on performance of electrochemical cell. And corresponding reduction of nitric acid to nitrous acid will occurs at the cathode, then recovery of nitric acid by the oxidation of NO and capture in water.

At the anode, the primary reaction is the oxidation of Cerium(III) to Cerium(IV). The reaction is limited by mass transfer at increased potentials. The secondary reaction is the oxygen evolution reaction which is kinetically controlled.

$$Ce^{3+} \rightarrow Ce^{4+} + e^-$$

$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$$

At the cathode, the primary reaction is the reduction of nitric acid to nitrous acid

$$2H^+ + 2e^- + HNO_3 \rightarrow H_2O + HNO_2$$

$$2HNO_2 \rightarrow H_2O + NO + NO_2$$

The high yield of Cerium(IV), conversion ratio, selectivity and current efficiency were affect by the electrochemical parameters like applied voltage, current, concentration and temperature during the electrochemical reaction. This study was performed with the aim of evaluating the performance of electrochemical cell, which comprised different voltage and current.

Experimental

In this experiment, the electrochemical cell consisted of anode and cathode of dimensions 2×2×0.5cm, which separated by selective floropolymer membrane. This membrane was excellent chemical resistance in a highly oxidizing, strong acid environment. Fig. 1 shows the schematic diagram of the experimental setup. The anolyte solution consisted of 1M $Ce(NO3)_3$ and 3M HNO_3 mixture. 4M HNO_3 solution used in the catholyte for this study. The temperature of the anolyte and the catholyte solution was maintained constantly by heating mantles at 80°C. Air was continuously sent into the catholyte solution to convert nitrous acid to nitric acid during this reaction. During the oxidation of cerium experiment, volume of the cerium solution was taken in the anolyte tank was 200ml. The concentration of Cerium(IV) was measure with respect to time and also oxygen flow rate was measure by flow meter.

In order to measure concentration of Ce(IV), redox potential of anolyte solution was measured by pH/ISE meter(Orion Co. Ltd., Model 720A) using Pt-Ag/AgCl combined electrode.

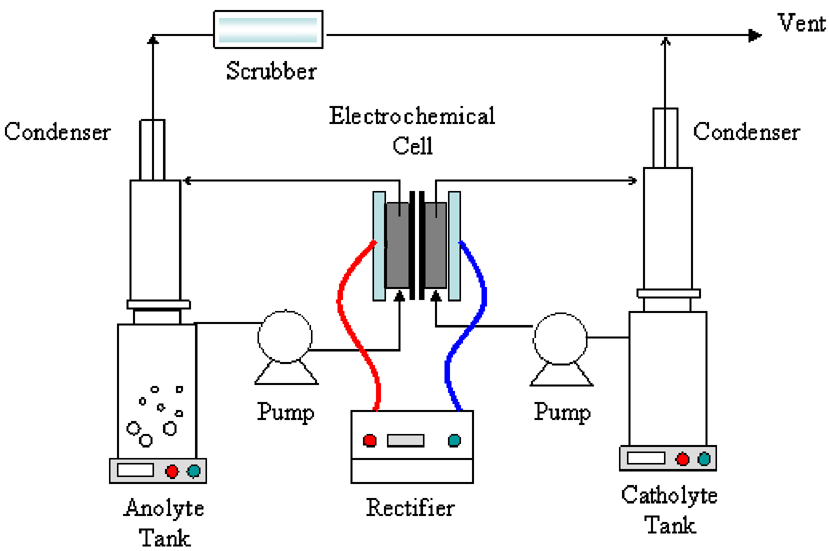

Fig. 1. Schematic diagram of experimental setup

Result and Discussion

Fig. 2 and 3 shown the conversion ratio of Cerium(III) to Cerium(IV) during the electrochemical oxidation at constant current and constant applied voltage. The conversion of cerium was studied at various current and applied Voltage. The Conversion ratio of cerium was increase with increasing current. From the results, calculate the energy consumption and columbic efficiency for cerium oxidation by electrochemical cell. Further experiment was carried for calculating the energy consumption, current efficiency and for finding optimum current for cerium oxidation.

The amount of Cerium(IV) generated is dependent on the quantity of electricity passed through the electrolytic solution. For the amount of Cerium(IV) generated, to calculated the current efficiency. Current efficiency is the ratio of amount of Cerium(IV) generated to the theoretical amount of Cerium(IV) by Faradys law. The current efficiency was mainly depends on the quantity of charge pass to the electrochemical cell. The current efficiency for cerium ion generation was increased with increasing in the current and decreased at an high current.

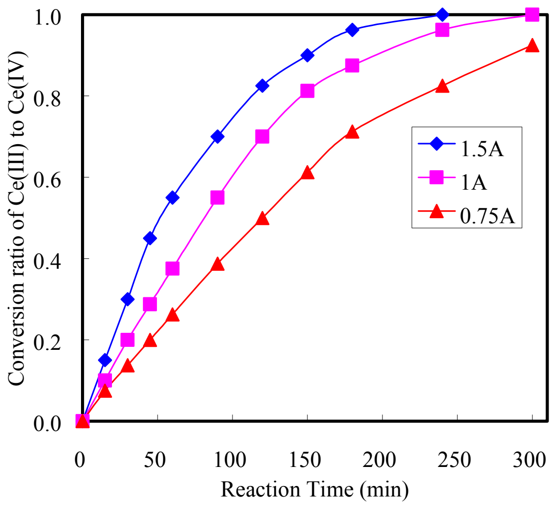

Fig. 2. Conversion ratio of Ce(Ⅲ) to Ce(Ⅳ) with reaction time at different current in the electrochemical cell, 80℃(1M Ce(Ⅲ), 3M HNO_3).

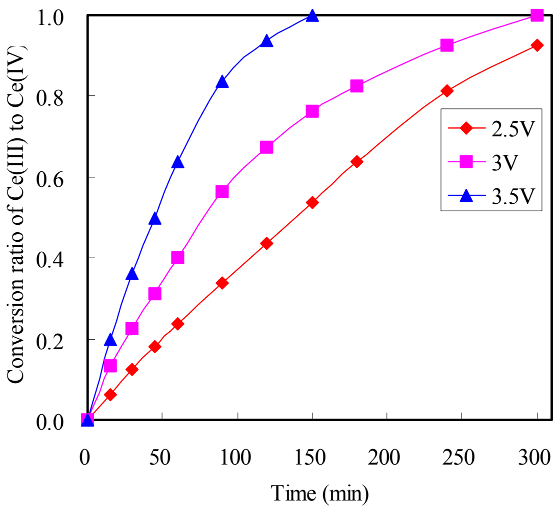

Fig. 3. Conversion ratio of Ce(Ⅲ) to Ce(Ⅳ) with reaction time at different applied voltage in the electrochemical cell, 80℃(1M Ce(Ⅲ), 3M HNO_3).

Energy consumption was an important factor for the electrochemical process. The energy consumption of the electrochemical process was mainly depending on the cell voltage applied during the generation of Cerium(IV).

In the electrochemical oxidation process, oxygen evolution is the important process in the electrochemical reaction. Further experiment was carried for measure the flow rate of oxygen evolution. From the experiment results, to calculate the amount of current used for the oxidation of cerium during the experiment.

Conclusion

For Mediated Electrochemical oxidation, the electrochemical cell is the main component of the process. The conversion ratio of Cerium(III) to Cerium(IV) was increase with increasing the current. A high current efficiency for Cerium(IV) generation at high anode current densities reduces the electro chemical cost and subsequently the product cost of quinines. Based on the above results, to optimum condition of Ce(III)/Ce(IV) redox system were determined. In the Ce(III)/Ce(IV) oxidation reaction was evaluated in the nitric acid medium in current efficiency, yield and low energy consumption.

Acknowledgement

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References

1. D.F. Steele, D. Richardson, J.D. Campbell, D.R. Craig and J.D. Quinn, "The Low temperature Destruction of Organic waste by Electrochemical Oxidation", Trans IChemE, Vol 68, part B,115-121(1990).
2. Martyn G. Adamson, Zoher Chiba,Erica H. von Holtz and Ronald D. streit, "Development of Advanced Waste Treatment Technologies for Demonstration in the Mixed Waste Management Facility", presented at the Third Biennial Mixed Waste Symposium, Baltimore, MD August 7-11(1995).
3. Norvell Nelson. "Electrochemical Destruction of Organic Hazardous Wastes. The Cerium oxidation CerOx Process Electrochemical Cell", Platinum Metals Rev., 46, (1), 13-23(2002).
4. T. Raju and C. Ahmed Bashe, "Electrochemical cell design and development for mediated electrochemical oxidation – Ce(III)/Ce(IV) system", *Chemical Engineering Journal,* 114, 55-65, (2005).