

전기화학적 매개산화 공정에서 Ag와 Ce을 이용한 유기물 분해

정상준, M. 마테스와란, 문일식*
순천대학교 공과대학 화학공학과
(ismoon@sunchon.ac.kr*)

Organic Destruction by Ag and Ce in Mediated Electrochemical Oxidation

Sang Joon Chung, M. Matheswaran, Il Shik Moon*
Department of Chemical Engineering, Sunchon National University
(ismoon@sunchon.ac.kr*)

Introduction

The Mediated Electrochemical Oxidation (MEO) is an emerging new technology for the destruction of organic waste materials. In this process the hazardous or mixed organic waste streams can be destructed at ambient temperatures (less than 100°C) and atmospheric pressure. In the MEO process the mediator oxidant is continuously regenerated by an electrochemical cell to minimize the production of secondary wastes[1]. Steel et al[2] have reported that mediated electrochemical oxidation might provide a new alternative for the safe disposal of chemical wastes.

The commonly used mediator redox pairs in MEO process are $\text{Ag}^{2+}/\text{Ag}^+$, $\text{Mn}^{3+}/\text{Mn}^{2+}$, $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$. Among them Ag and Ce are the most powerful oxidizing agent in acid media owing to its high redox potential. It may react directly with the organic material to be destroyed or it may first react with water to form hydroxyl radicals, which in turn oxidize the organic compounds.

The objective of this paper is to present the results of generation of Ag(II) and Ce(IV) in a batch type electrochemical reactor with recirculation mode with various operating parameters like temperature, concentration of mediator under the constant potential mode. And to destruct phenol in continuous feeding modes under the optimum conditions for Ag(II) and Ce(IV) production.

Experiment

The Figure 1 shows the schematic diagram of mediated electrochemical oxidation process. The electrodes were placed parallel to each other in the flow type electrochemical reactor. A 50ml solution of Ag(I) and Ce(III) in nitric acid and only nitric acid were taken in the anolyte and catholyte reservoirs respectively. The electrolyte solutions continuously circulated through anolyte and catholyte compartments of the reactor at constant flow rate.

A constant potential was applied between the electrodes during the oxidation reaction. In both anolyte and catholyte reservoirs, the temperature was maintained constant throughout the reaction.

During the experiment, suitable analytical methods were developed to check the concentrations of reactants, and final products of oxidation reaction. Samples at different time intervals were taken in the reactors and the concentration of Ag(II) and Ce(IV) was checked by titration with ammonium iron (II) sulfate hexahydrate (Samchun Pure Chemical Co. Ltd. Korea).

Phenol destruction was carried out in continuous addition mode and also simultaneous addition of organic and mediator ion in batch mode in the anolyte. In case of continuous organic addition phenol was added into the anolyte after the concentration of Ag(II) and Ce(IV) attained steady state. The phenol solution was constantly fed at the rate of 0.05 ml/min up to 30 min. using a syringe pump.

The reduced mediator ions were continuously regenerated in the cell. The CO₂ formed during the organic destruction reaction was measured by passing carrier gas stream (500 ml/min of N₂) into the reservoir. From the accumulated CO₂ and CO volume, the destruction efficiency of phenol was calculated. The concentrations of CO₂, CO and oxygen produced were measured continuously as ppm by using an Infra red CO₂ analyzer (Anagas CD 98, Environmental Instruments) and converted in to volume at 25°C.

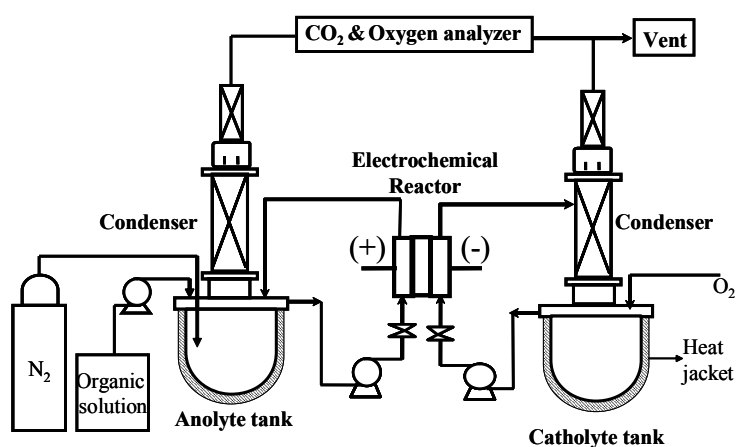


Figure 1. Schematic diagram of destruction of phenol in MEO process

Results

The effect of temperature on electrochemical oxidation of Ag(I) was studied in the range of 25 - 60°C at a fixed Ag(I) and nitric acid concentrations. Figure 2 shows the concentration of Ag(II) production with respect to the reaction time at different temperatures. It can be seen that as the temperature was increased, the formation of Ag(II) concentration decreased in the solution. This was due to the increased reactivity of Ag(II) with water and corresponding decrease in the stability of Ag(II). By increasing the temperature, nitrous acid production was increased in the anolyte.

The oxidation of silver was studied under different initial concentrations of Ag(I) at a fixed concentration of nitric acid of 8M at 25°C. Figure 3 shows the increase in Ag(II) concentration with

time at different initial concentrations of Ag(I). It can be seen that the percentage conversion of Ag(II) formation was decreased with increase in the concentration of Ag(I). At 0.1M of Ag(I), 45% of Ag(II) at steady state was reached. In this case the steady state concentration of Ag(II) was attained around 30 min for all except at 1M Ag(I).

The destruction of phenol was carried out at different temperatures under a constant concentration of 0.1 M Ag(I) and 8 M nitric acid. The Ag(I) was oxidized into Ag(II). Initially Ag(II) concentration was increasing with time and reached the steady state after 30 min. The steady state Ag(II) concentration was established when the rates of Ag(II) generation and loss were equivalent. At this point, the only loss of Ag(II) was due to the reduction by water. The organic fed to the anolyte was oxidized into carbon dioxide and water. Also a minor quantity of carbon monoxide was detected during the destruction reaction. Figure 4 shows the destruction efficiency for various temperatures in the continuous mode. The destruction efficiency was calculated based on the volume of CO₂ produced up to the end point of organic feeding (30 min).

Figure 5 shows compare the destruction efficiency of phenol by Ag and Ce in the nitric acid medium at 80°C. The destruction efficiency of phenol was 78% by Ag(II) higher than Ce(IV) with 52%. It was due to higher oxidation potential of Ag than of Ce in the nitric acid.

Conclusions

The electrochemical oxidation of Ag(I) was studied with various parameters such as temperature, concentration of nitric acid and mediator in an electrochemical cell. The concentration of Ag(II) was increased with increase in the concentration of nitric acid and decreased with increase in temperature. The conversion ratio was decreased with increase in the initial concentration of Ag(I). The destruction of phenol was carried out at different temperature in continuous process modes under the optimum oxidations for Ag(II) production of the cell. The destruction efficiency in the continuous mode was around 78% based on the CO₂ evolution. Continuous organic feeding experiments showed the efficiency of the process towards large amount of organic destruction and consistent Ag(II) production by the cell.

The destruction efficiency of phenol was 78% by Ag(II) higher than Ce(IV) with 52%. It was due to higher oxidation-reduction potential of Ag than of Ce.

Acknowledgement

This work was supported by the Ministry of Commerce, Industry and Energy (MOCIE) through the project of Regional Innovation Center (RIC).

References

1. C. A. C. Sequeira, D. M. F. Santos and P. S. D. Brito, *Applied Surface Science*, 252, 6093(2006).
2. D. F. Steele, D. Richardson, J. D. Campbell, D. R. Craig, and J. D. Quinn, *Trans, ChemE*, 68, 115

(1990).

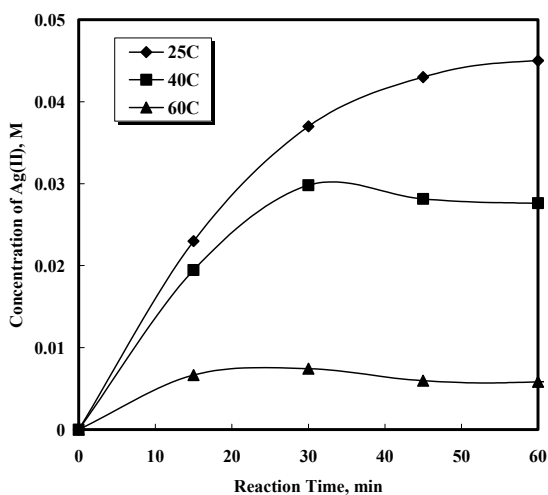
3. A. A. Noyes, D. De Vault, C. D. Coryell and T. J. Deahl, *J. Am. Chem. Soc.*, 59, 1326 (1937).

Figure 2. Effect of Temperature on the formation of Ag(II). (Experimental conditions: $[AgNO_3] : 0.1M$, $[HNO_3] : 8M$, $T : 25^\circ C$, $V : 2.5V$.)

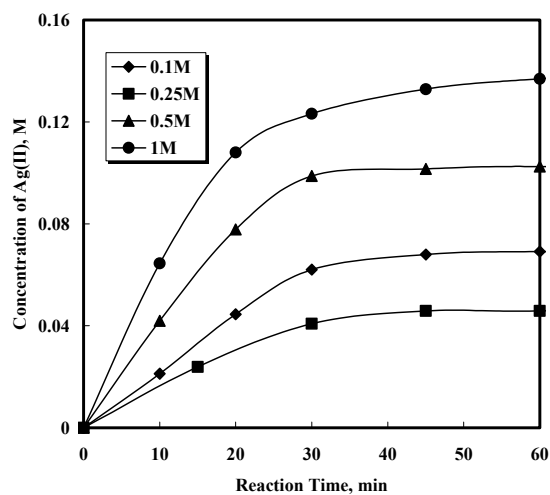


Figure 3. Effect of initial Ag(I) concentration on the formation of Ag(II). (Experimental conditions: $[HNO_3] : 8M$, $T : 25^\circ C$, $V : 2.5V$.)

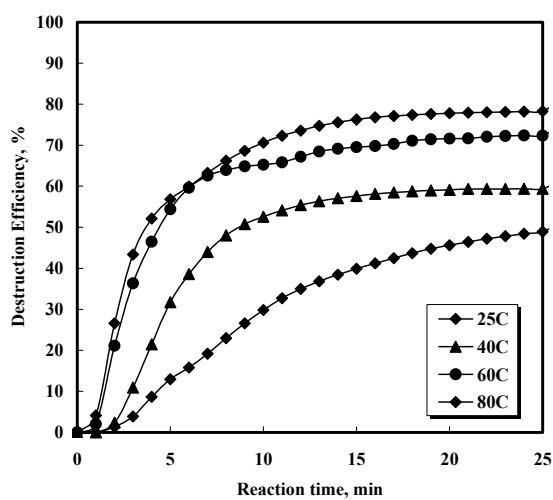
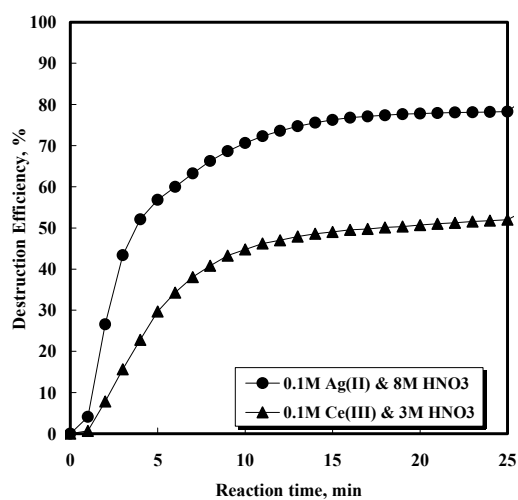


Figure 4. Effect of temperature on the destruction efficiency of phenol in the continuous mode (Experimental conditions: $[AgNO_3] : 0.1 M$,



$[HNO_3] : 8M$, $V : 2.5V$, feed time : 30 min)
Figure 5. The comparison of Ag and Ce for the destruction of phenol at $80^\circ C$