

Ag(I)/Ag(II) 산화-환원계를 이용한 전기매개 산화 공정에서 페놀 분해

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Destruction of Phenol by Mediated Electrochemical Oxidation Process using Ag(I)/Ag(II) Redox System

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Introduction

The Mediated Electrochemical Oxidation (MEO) process has been identified as one of the most promising future technologies for the destruction of organic waste materials by the United Nations Environmental Programme[1]. In this process the hazardous or mixed organic waste streams can be destructed at ambient temperatures and atmospheric pressure. In the MEO process the mediator oxidant is continuously regenerated by an electrochemical cell to minimize the production of secondary wastes[2-4]. Steel et al[5] 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 Ag(II)/Ag(I), Ce(IV)/Ce(III), Mn(III)/Mn(II) and Co(III)/Co(II). Among them Ag(II)/Ag(I) redox pair is the most powerful oxidizing agent in acid media owing to its high redox potential ($E^0 = 1.98 \text{ V}$). 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 present study was to investigate the systematic destruction of phenol as the target organic pollutant by Ag(II)/Ag(I) redox MEO process. Since the intention was to obtain CO_2 pattern with respect to time during the phenol oxidation and to compare it with the theoretical value for its complete destruction. The objective of this study is to investigate the mineralization of phenol with *in situ* regeneration of Ag(II) oxidant in batch mode, under various conditions of temperature, feed concentration of phenol and anolyte nitric acid concentration.

Experimental

Silver nitrate (99.8%) and phenol (99%) from Junsei Chemical Co. Ltd. and nitric acid (60%) from Sam Chun Chemicals were used as-received. 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 900 ml solution of Ag(I) in nitric acid and only sulphuric 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 current 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) was checked by titration with ammonium iron(II) sulfate hexahydrate (Samchun Pure Chemical Co. Ltd. Korea).

Phenol destruction was carried out in simultaneous addition of organic and mediator ion in batch mode in the anolyte. The reduced Ag(I) was continuously regenerated *in situ* by the electrochemical cell. The concentration of CO₂ evolved during the phenol decomposition was measured continuously using a CO₂ analyzer (Anagas CD 98, Environmental Instruments). CO₂ formed was purged by the carrier gas stream (N₂) and taken to the analyzer. The flow rate of the carrier gas was kept constant (1 l/min) throughout the experiment. The concentration of CO₂ evolved in terms of ppm was continuously recorded and converted into volume and used to calculate the destruction efficiency in terms of CO₂. The overall reaction for phenol oxidation can be expressed as follows. It should be pointed out here that the mole ratio between Ag(II) and phenol is 28:1 irrespective of the electrolyte medium.

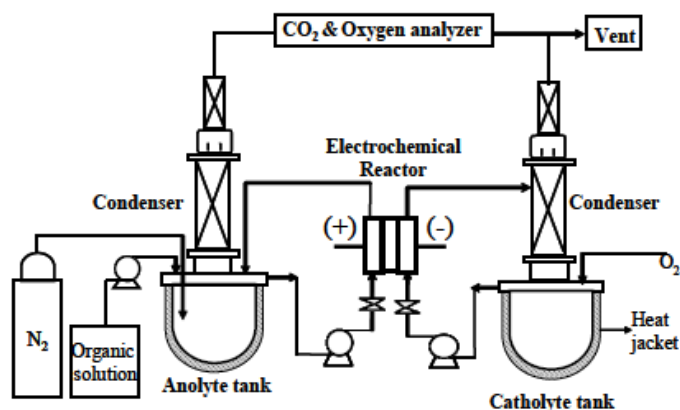
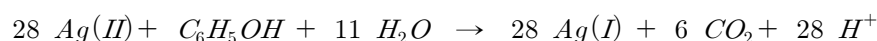


Figure 1. Schematic diagram of destruction of phenol in MEO process.

Results and Discussion

Figure 2 and 3 show the concentration of Ag(II) and destruction efficiencies against reaction time at various nitric acid concentration in anolyte based on CO₂ measurements, respectively, at a 200 ppm initial phenol concentration. In Figure 2, the area under the curve should be proportional to the total volume of CO₂ formed and also the degree of mineralization. The pattern of the curve shows concentration of CO₂ goes through maximum within 5–10 min of reaction time and then decreases to zero and also the destruction was found to be nitric acid concentration dependent. The concentration of Ag(II) in anolyte measured during the reaction showed a fast depletion of Ag(II) concentration at the start of the reaction. After maximum destruction, concentration of Ag(II) was recovered at initial Ag(II) concentration with regeneration in electrochemical cell. From Figure 2 it was seen that the effect of nitric acid concentration is much pronounced in the MEO process and the volume of CO₂ produced varies with concentration of nitric acid. Figure 3 shows the destruction at higher nitric acid

concentration of 10–13 M was higher compared to reaction at 6 M. Increasing the nitric acid concentration, the Ag(II) concentration was high, it strongly oxidizes any organic molecule by its highly favoured electron releasing tendency. The organic oxidizing ability of the medium would likely be the combined effect of both Ag(II) and nitric acid and might not be solely from nitric acid, at least within the range studied.

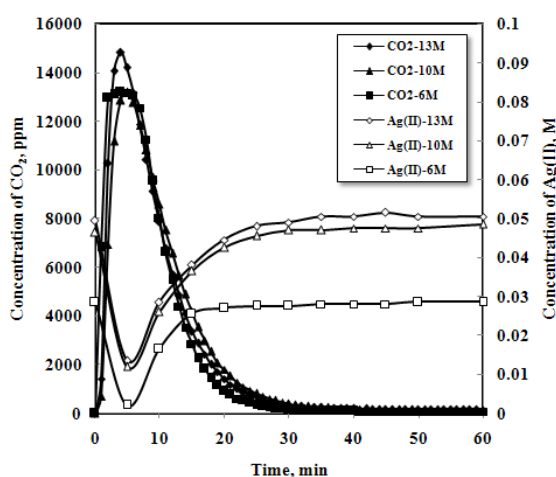


Figure 2. Effect of nitric acid concentration on CO_2 evolution and concentration of Ag(II) for 200 ppm phenol ($[\text{Ag(I)}]_{\text{initial}} = 0.1 \text{ M}$ at 25°C).

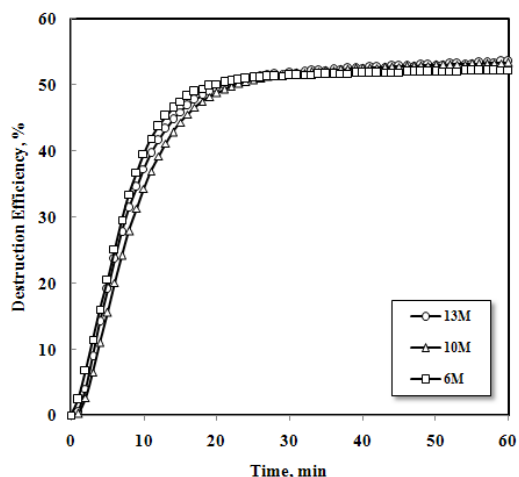


Figure 3. The destruction efficiencies of 200 ppm phenol at different nitric acid concentration ($[\text{Ag(I)}]_{\text{initial}} = 0.1 \text{ M}$ at 25°C).

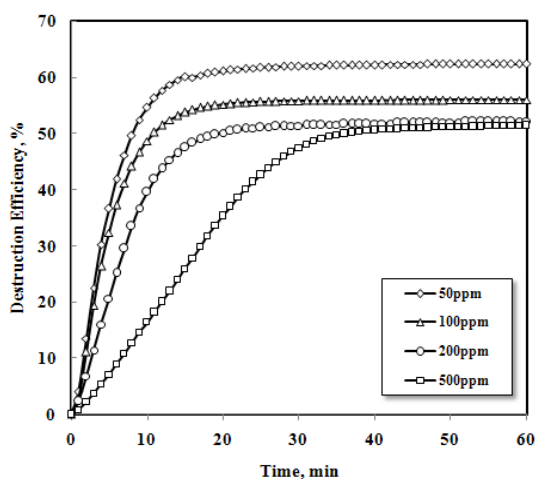


Figure 4. The destruction efficiencies of different initial concentration of phenol at 25°C ($[\text{Ag(I)}]_{\text{initial}} = 0.1 \text{ M}$ in 6 M HNO_3).

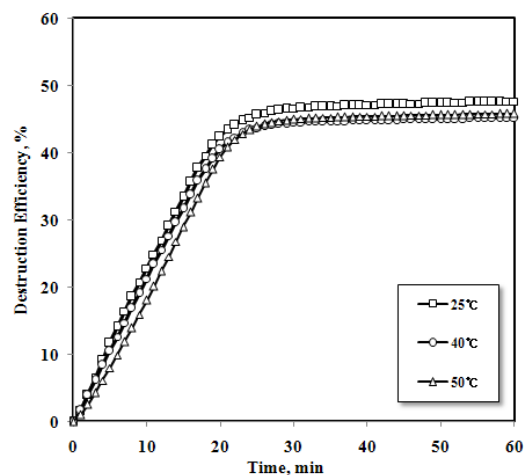


Figure 5. The destruction efficiencies of 500 ppm phenol at different temperature ($[\text{Ag(I)}]_{\text{initial}} = 0.1 \text{ M}$ in 6 M HNO_3).

Figure 4 shows the variation of destruction efficiency based on CO_2 measurements for various phenol concentrations at 25°C at a fixed Ag(II) and nitric acid concentration. It was

observed that the degradation of phenol takes place quickly during the initial stages. The higher initial concentration of phenol was found to undergo relatively lesser mineralization. The amount of CO₂ formed was not sufficient to account for complete destruction of phenol in the solutions. This low destruction efficiencies would arise due to the volatilization of organics before complete destruction.

Figure 5 shows the destruction efficiencies against reaction time at various temperatures based on CO₂ measurements at a fixed initial phenol concentration. The destruction was found to be lower dependence of temperature. In our studies, a dark brown material was found floating at the top of the reactor solution for all experimental conditions. This could not account for complete conversion to CO₂ because of the formation of some low-density organic compounds. A similar case was observed by Chiba [6] during the destruction of trimsol oil by MEO process using silver mediator ion at room temperature.

Conclusion

The MEO process was tested for phenol destruction in a batch reactor by taking the produced Ag(II) and nitric acid as the mediator solution. The increase in the concentration of nitric acid from 6 to 13 M increased the destruction efficiency, though less significantly. Within the nitric acid concentrations studied, it could be said that the oxidizing ability of the medium over the organics is the combined effect of both Ag(II) and nitric acid, but not solely from nitric acid. The increase in the temperature from 25 to 45 °C decreased the destruction efficiency due to the decreasing the oxidation efficiency of Ag(II).

Acknowledgment

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