

Cobalt(III)-mediated oxidative destruction of phenol using divided electrochemical cell

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Abstract—Mediated electrochemical oxidation is one of the suitable processes for the destruction of hazardous organic compounds and the dissolution of nuclear wastes at ambient temperature and pressure. The electrochemical oxidation of Co(II) was carried out in an undivided and divided electrochemical cell. The formation of Co(III) was studied in an divided electrochemical cell by varying conditions such as temperature and concentration of nitric acid in a batch type electrochemical reactor in recirculation mode. It was found that the formation of Co(III) increased with increasing nitric acid concentration and decreased with increasing temperatures. The produced Co(III) oxidant was then used for the destruction of phenol. It was noted that phenol could be mineralized to CO₂ and water by Co(III) in nitric acid under different nitric acid concentrations and temperatures. The evolved CO₂ was continuously measured and used for the calculation of destruction efficiency. The destruction was increased with increasing nitric acid concentration as well as the temperature. The maximum efficiency was observed to be 78% based on CO₂ evolution for 5,000 ppm phenol solution at 60 °C in a continuous feed mode. The destruction efficiency was increased 28% by addition of silver at 25 °C.

Key words: Mediated Electrochemical Oxidation, Cobalt(II), Destruction Efficiency, Phenol, Organic Destruction, Carbon Dioxide

INTRODUCTION

The mediated electrochemical oxidation (MEO) process oxidizes the organic components of waste to carbon dioxide and water while operating at near ambient pressure and temperature in aqueous systems [1-4]. The MEO process is one of the latest advanced technologies for the complete mineralization of organic pollutants. This process has been identified by the United Nations Environmental Programme as one of the most promising future technologies for use in the developing nations [5]. Steel et al. [6] have reported that the MEO might provide a new alternative way for the safe disposal of chemical wastes, where the mediator metal ion in acid medium that is regenerated electrochemically is used as an oxidant for the destruction of organics in a closed cycle. The mediator ion, typically a transition metal in its highest valency state, is generated at the anode of an electrochemical cell and dispersed throughout the anolyte solution. After the oxidation of organics, the reduced mediator ion is reoxidized at the anode in the electrochemical cell and thus cycled infinitely.

The MEO process has been investigated and reported by many researchers with various mediator metal ions both in laboratory and also in pilot scale systems [1,7-16]. Farmer et al. [1] reported that the oxidation of ethylene glycol and benzene with silver as the mediator ion using rotating cylindrical gold electrode and also the destruction of chlorinated organics in the presence of cobalt mediator using rotating cylindrical platinum electrode [11]. Chung and Park described the destruction of aniline by cerium and cobalt using RuO₂ coated titanium electrode [17]. Nelson [2] discussed about the applications of the commercially developed equipment for organic destruction with cerium mediator in nitric acid. Galla et al. [18] investigated the

destruction of pesticides using silver mediator in nitric acid medium. Zhang and Park studied the oxidation of cellulose and its model compounds using Mn(II) as a mediator [19]. It was concluded from the above references that the MEO process could be employed for both concentrated organic wastes and aqueous wastes. Although various metal ions are employed as the mediator, cobalt is found to be good based on the following aspects. It does not form precipitate unlike silver which forms precipitate salt by anions liberated during the destruction of halogenated organics. The leakage of Co quantities through the electrode separator is less compared to the silver [11]. The more frequently used Ce(IV)/Ce(III) redox couple in MEO system has less oxidizing strength compared with cobalt in the nitric acid medium. The electro-oxidation of cobalt in nitric acid medium has been patented [20-22], but the electrochemical oxidation and destruction data have not been properly reported.

The objectives of the present study are (i) to compare the performance of the undivided and divided electrochemical cell for the oxidation of cobalt in the nitric acid medium at constant current, (ii) to form Co(III) in a batch type divided electrochemical reactor with recirculation mode by varying operating parameters such as temperature and nitric acid under the constant concentration of cobalt and current mode, (iii) to investigate the effect of cobalt oxidation by adding silver into the anolyte solution, and (iv) to study the destruction of phenol in the continuous feeding mode under the optimum Co(III) production condition.

EXPERIMENTAL

Fig. 1 shows a schematic diagram of the mediated electrochemical oxidation process. 50 ml solution of 0.5 M Co(II) in nitric acid and nitric acid solution were taken in the anolyte and catholyte reservoirs, respectively. The electrolyte solution was continuously circulated through the anolyte and catholyte compartments of the reac-

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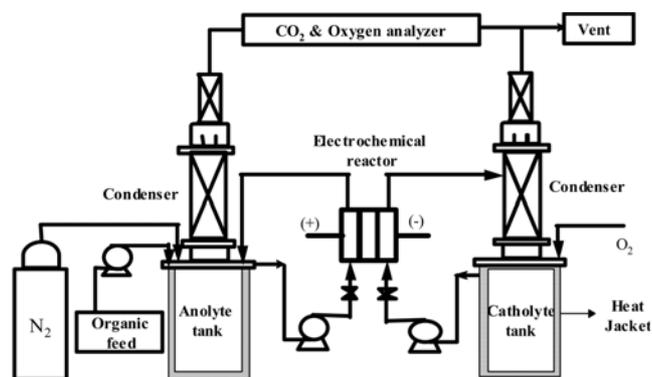
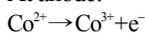


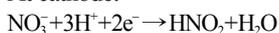
Fig. 1. Schematic diagram of MEO system.

tor at a constant flow rate. In both the anolyte and catholyte reservoirs, the temperature was maintained constant throughout the reaction with thermostatted mantles. The flow type electrochemical reactor consists of two compartments separated by a Nafion® 324 membrane. The membrane is capable of allowing protons from anodic to cathodic compartment to maintain the current flow. IrO₂ coated titanium and titanium mesh type electrodes with an area of 4 cm² (2 cm×2 cm×0.5 cm) were used as anode and cathode, respectively. A constant current 0.5 A was applied between the electrodes during the oxidation reaction. During the oxidation, cell voltage was noted and varied from 2.54 to 2.85 V. In the case of undivided electrochemical cell, without membrane the electrodes were kept apart at 4 cm distance. The anolyte solution only circulated at a constant flow rate (*q*) of 100 ml/min. During the oxidation experiment, Co(II) was oxidized to Co(III) at the anode and nitric acid was reduced into nitrous acid at the cathode. In the catholyte reservoir, NO produced during the reduction of nitric acid was reoxidized into NO₂ with continuous passage of atmospheric oxygen and NO₂ was then dissolved in water to get back nitric acid. The anodic and cathodic reactions can be represented as follows [20]:

At anode:

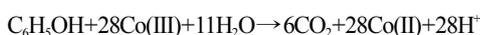


At cathode:



During the electrochemical oxidation, the concentration of Co(III) in solution was determined efficiently by using the method previously reported. The procedure involved in the quantitative oxidation of Ce(III) to Ce(IV) by Co(III) followed by the potentiometric titration of the Ce(IV) concentration at a fixed nitric acid concentration.

After the suitable and optimum operating condition for cobalt oxidation was found, the phenol was destroyed in continuous feeding mode. In the case of continuous organic feeding, phenol was added into the anolyte after the concentration of Co(III) attained steady state. The phenol solution (5,000 ppm) was constantly fed at the rate of 0.05 ml/min up to 60 min by using a syringe pump. The phenol was oxidized into carbon dioxide and water along with the mediator ion reduction.



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

Destruction Efficiency (% of CO₂)

$$= (\text{Expt. Volume} / \text{Theo. Volume}) \times 100$$

RESULTS AND DISCUSSION

1. Electrochemical Oxidation of Co(II) to Co(III)

1-1. Comparison of Electrochemical Cell

The formation of Co(III) was studied in an undivided and a divided electrochemical cell at a fixed temperature, concentration of Co(II) and nitric acid. Fig. 2 shows the concentration of Co(III) with respect to reaction time in different electrochemical cells. The concentration of Co(III) was observed 0.06 M and 0.082 M in 2 hr by undivided and divided electrochemical cells, respectively, for the initial conditions such as 0.5 M of Co(II) in 3 M nitric acid and current 0.5 A at time 2 hr. That the rate of formation of Co(III) was lower in the undivided electrochemical cell may be due to the Co(III) and nitric acid reduction of in the cathode. In the divided electrochemical cell, the cathode and anode were separated by membrane and hence the metal ion movement was prevented. The percentage conversion of Co(III) and current efficiency achieved in the undivided and divided cells are 12%, 10% and 18%, 15% respectively. The further oxidation and destruction experiments were carried out by using the divided electrochemical cell.

1-2. Effect of Nitric Acid

The effect of nitric acid on the electrochemical oxidation of Co(II) was studied in the range of 3-8 M at a fixed Co(II) concentration

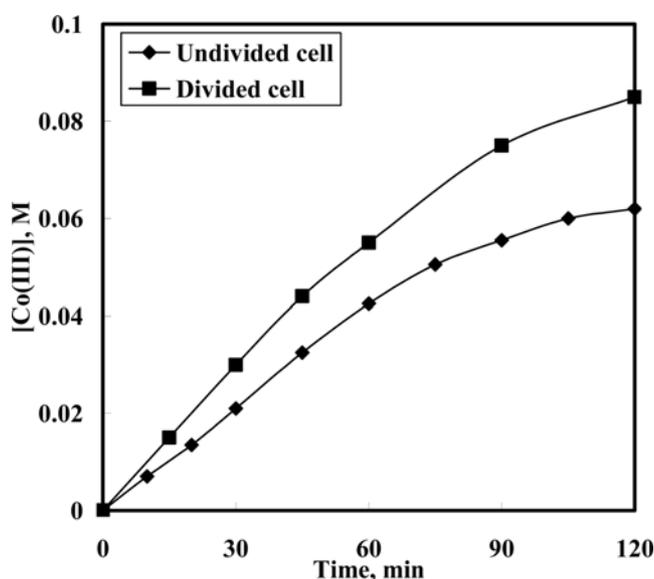


Fig. 2. Comparison of undivided and divided electrochemical cell on the formation of Co(III) ([Co(NO₃)₂]: 0.1 M; T: 25 °C; Applied current: 0.5 A; *q*: 100 ml/min).

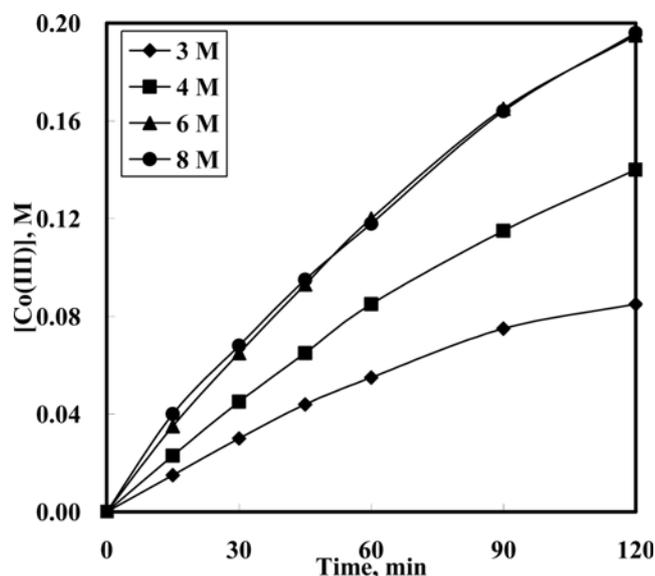


Fig. 3. Effect of different nitric acid concentrations on the formation of Co(III) ($[\text{Co}(\text{NO}_3)_2]$: 0.1 M; T: 25 °C; Applied current: 0.5 A; q: 100 ml/min).

and temperature. Fig. 3 shows the concentration of Co(III) production with respect to reaction time at different nitric acid concentrations. From the figure, it can be observed that the formation of Co(III) increases with increasing nitric acid concentration. The rate of oxidation increased with increasing nitric acid concentration of up to 6 M and no change in the oxidation rate was observed for the further increment in the concentration. The current efficiency was increased from 15 to 33% due to increasing of nitric acid concentration. A conversion of 38% Co(III) was obtained for 0.5 M of Co(II) in 6 M nitric acid at 2 hr.

1-3. Effect of Temperature

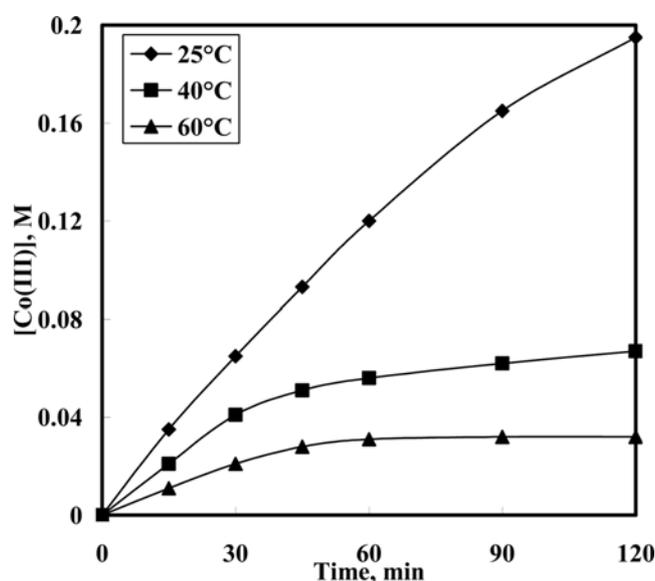


Fig. 4. Effect of different temperatures on the formation of Co(III) ($[\text{Co}(\text{NO}_3)_2]$: 0.5 M; $[\text{HNO}_3]$: 6 M; Applied current: 0.5 A; q: 100 ml/min).

The electrochemical oxidation of Co(II) was studied at different temperatures in the range of 25–60 °C at a fixed 0.5 M Co(II) and 6 M nitric acid concentrations. The concentration of Co(III) formation with respect to the reaction time at different temperatures is shown in Fig. 4. It is clear the concentration of Co(III) decreases with increasing the temperature. This is probably because during the anodic oxidation of Co(II), cobalt nitrate complex was not present [11]. So the Co(III) formation was simultaneously accompanied by HNO_3 oxidation. By increasing the temperature, nitrous acid production increased in the anolyte and, as a result of this, nitric acid concentration decreased in the anolyte. This reduced nitric acid concentration lowered the stability of Co(III) concentration and hence Co(III) concentration also decreased. A similar trend result was also observed by Sequeira et al. [23].

1-4. Effect of Silver Addition

The effect of silver addition into the electrolyte on the electrochemical oxidation of Co(II) was studied at constant Co(II) and nitric acid concentrations as well as temperature. Fig. 5 shows that the concentration of Co(III) production with respect to reaction time. From the figure, the increasing rate of oxidation of Co(II) is detected by addition of silver at initial stage of reaction (>30 min). The silver catalyst significantly increases the formation of Co(III). In the past, many researchers used silver as a catalyst for the electrochemical oxidation of Ce, Mn and Co [22–25]. Comminellis and Plattner [24, 25] showed that the addition of small quantities of silver increased the current efficiency of cobaltous and manganous sulfate electrochemical oxidation in concentrated sulfuric acid medium. The researchers [26,27] reported that the cerium(III) conversion rate was increased in the presence of silver catalyst.

2. Destruction of Phenol during Continuous Organic Feeding

2-1. Effect of Nitric Acid

The destruction of phenol was carried out at different nitric acid concentrations with a fixed concentration of 0.5 M Co(II) and 25 °C temperature. The Co(II) was oxidized into Co(III) until a steady

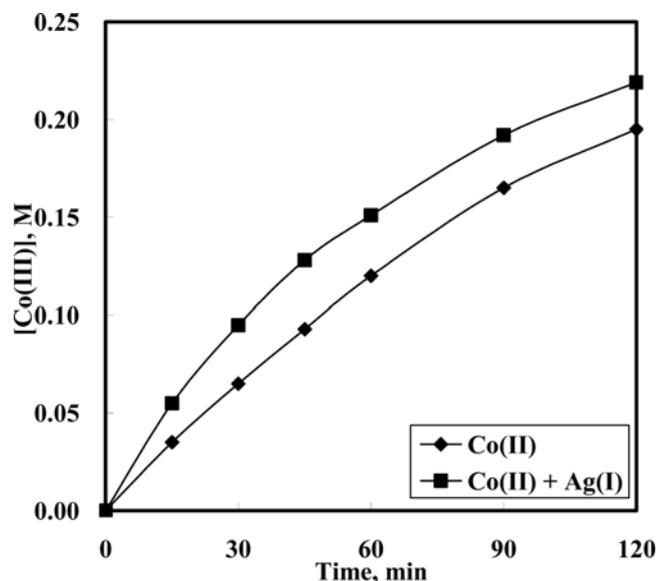


Fig. 5. Effect of silver addition on the formation of Co(III) ($[\text{Co}(\text{NO}_3)_2]$: 0.5 M; $[\text{AgNO}_3]$: 0.025 M; $[\text{HNO}_3]$: 8 M; T: 25 °C; Applied current: 0.5 A; q: 100 ml/min).

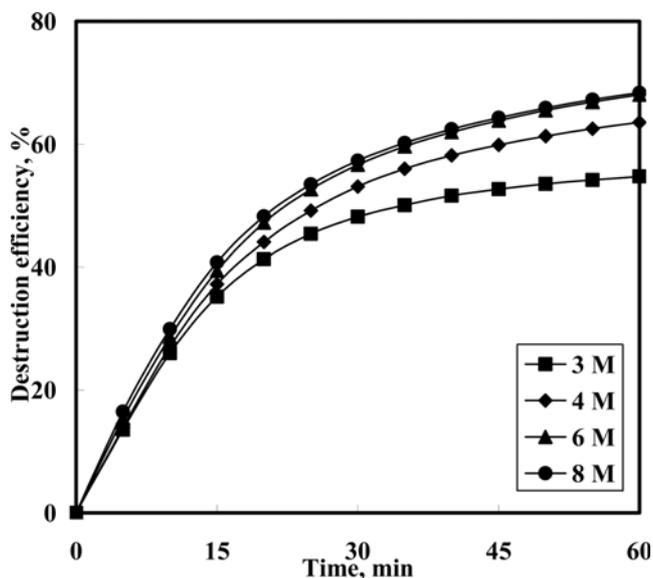


Fig. 6. Effect of different nitric acid concentration on the destruction efficiency of phenol ($[\text{Co}(\text{NO}_3)_2]$: 0.5 M; Applied current: 0.5 A; T: 25 °C; q: 100 ml/min).

state in Co(III) concentration was established, when the rates of electrochemical generation of Co(III) and its loss by reduction of water were equivalent. After reaching this steady state the organic solution was continuously fed into the anolyte for 60 min. The organic fed to the anolyte was oxidized into carbon dioxide and water. Fig. 6 shows the destruction efficiency for various nitric acids at fixed concentration of 0.5 M Co(II) and temperature 25 °C in the continuous feeding mode. The destruction efficiency increases with increasing nitric acid concentration up to 6 M, and further increase in acid concentration to 8 M did not enhance the destruction efficiency.

2-2. Effect of Temperature

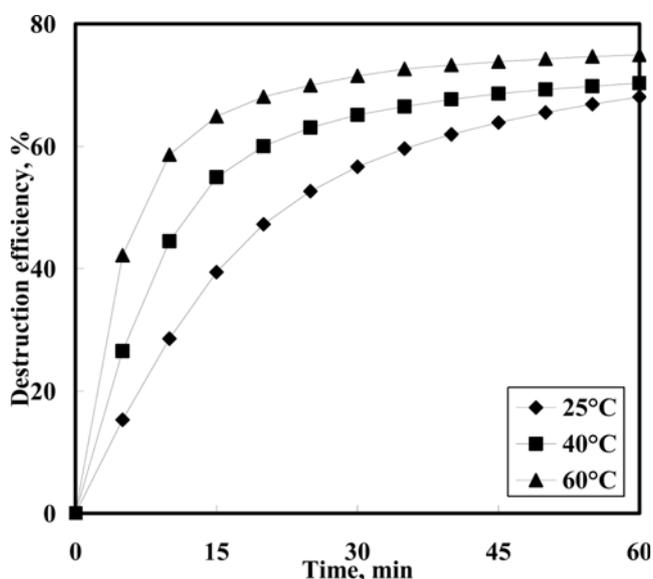


Fig. 7. Effect of different temperatures on the destruction efficiency of phenol ($[\text{Co}(\text{NO}_3)_2]$: 0.5 M; $[\text{HNO}_3]$: 6 M; Applied current: 0.5 A; q: 100 ml/min).

The destruction of phenol was carried out at different temperatures with a fixed concentration of 0.5 M Co(II), 6 M nitric acid, and 0.5 A current. After Co(III) concentration reached a steady state, the organic solution was continuously fed into the anolyte for 60 min. Fig. 7 shows the destruction efficiency with respect to the temperatures in the continuous feeding mode. It is clear that the destruction efficiency increases with the increasing temperature. It must be mentioned that Co(III) generation is shown as opposite trend in Fig. 4, i.e., Co(III) concentration is low at high temperature. Thus the higher destruction efficiency at high temperature in spite of lower of Co(III) concentration may rise as a result of Co(III) oxidizing water producing OH^\bullet radical, which can destroy phenol at the high temperature. Chung and Park [15] observed a similar trend of result for the destruction of aniline.

2-3. Effect of Silver Addition

The effect of silver addition on the destruction of phenol was studied at a fixed concentration of 0.5 M Co(II), 8 M nitric acid and temperature. The destruction efficiencies for 5,000 ppm feed concentration of phenol with 0.025 M Ag(I) concentrations at 25 °C as a function of time are shown in Fig. 8. The destruction efficiency of the phenol without addition of silver in the electrolyte is also plotted in Fig. 8 for a comparison. Fig. 8 clearly shows that the destruction efficiency increases around 28% with the addition of silver.

CONCLUSION

The electrochemical oxidation of Co(II) has been studied by varying parameters, such as temperature and concentration of nitric acid in the divided electrochemical cell. The concentration of Co(III) increased with increasing concentration of nitric acid and decreased with increasing temperature. The rate of oxidation and current efficiency of Co(II) electrochemical oxidation using a divided cell was increased by the addition of small quantities of silver which acts as a catalyst. The destruction of phenol was carried out in the continuous

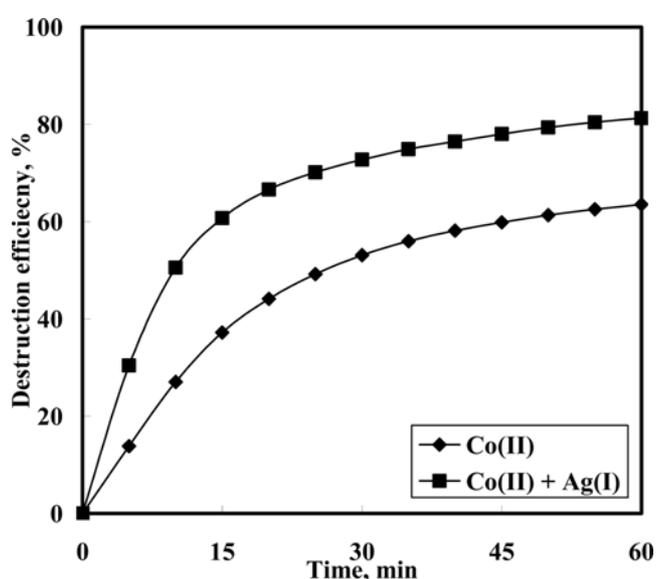


Fig. 8. Effect of silver addition on the destruction efficiency of phenol ($[\text{Co}(\text{NO}_3)_2]$: 0.5 M; $[\text{HNO}_3]$: 8 M; T: 25 °C; Applied current: 0.5 A; q: 100 ml/min).

feeding mode under the optimum oxidation conditions for Co(II) production. The destruction efficiency of the phenol increased with increasing temperature and concentration of nitric acid up to 6 M. By adding a small quantity of silver into the electrolyte, the destruction efficiency was increased by about 28%.

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