

## **Destruction of phenol by mediated electrochemical oxidation using combined cerium – silver redox couple in nitric acid medium**

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### **Introduction**

Mediated Electrochemical Oxidation (MEO) process was primarily developed to dissolve the organic contaminated radioactive materials such as plutonium oxide in nuclear waste processing units. But, later this process turned out to be an excellent treatment method for the destruction of organic pollutants and waste streams including persistent organic pollutants [1]. 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 [2]. The main advantages of the MEO process are the optimum working conditions of ambient temperature (less than 100°C) and atmospheric pressure, the products formed are only CO<sub>2</sub> and water and an easy electrochemical regeneration and reuse of the oxidant minimizing the production of secondary wastes.

Both the direct electrochemical and the MEO processes for organic pollutant destruction suffer from the disadvantage of higher energy requirements. It has been reported that silver acts as a catalyst for the oxidation of glycine by Ce(IV) oxidant. The results of the above reports indicate that the rate of organic oxidation by Ce(IV) is enhanced in the presence of metal ion catalysts. It was also shown by Comninellis and Plattner [3] that the addition of small quantities of silver has increased the current efficiency of cobaltous and manganous sulfate electrochemical oxidation in concentrated sulfuric acid medium. Eysseric et al. [4] have reported that the cerium(III) conversion rate was increased in the presence of silver catalyst and proposed a model for calculating the cerium mass transfer coefficient using the mass transfer coefficient for silver electrochemical oxidation. Therefore it was thought that to increase the current efficiency of the metal ion oxidation by electrochemical means, the addition of small quantities of a suitable co-metal ion with higher redox potential is one of the possible ways.

The objectives of the present investigation were (i) to study the electro-oxidation kinetics of Ce(III) in nitric acid in the presence of varying quantities of silver(I); (ii) to find out the destruction efficiencies of phenol by the electrochemically oxidized cerium and silver mixed metal mediator oxidants during the continuous organic addition mode with *in situ* regeneration of the mediators under various experimental conditions such as silver(I) concentration, total Ce(III) concentration, temperature and phenol feed concentration and (iii) to compare the organic destruction efficiencies by silver catalyzed and non-catalyzed Ce(IV) oxidant.

## **Experimental**

### *Materials*

Cerium(III) nitrate hexahydrate (99%) from Sigma-Aldrich, silver(I) nitrate (99.8%) from Junsei Chemical Co. Ltd. Japan, phenol (99%) and nitric acid (60%) from Sam Chun Chemicals, Korea were used as received.

### *Methods*

The electro-oxidation of cerium was carried out in a divided electrochemical cell fabricated using IrO<sub>2</sub>/Ti DSA anode and Ti cathode each with geometrical surface area of 4 cm<sup>2</sup> (effective surface area: 2.6cm<sup>2</sup>). The electrodes were kept separated Nafion<sup>®</sup> 324. The anode and cathode compartments of the cell were coupled to the anolyte and catholyte vessels respectively and the electrolyte solutions were circulated through the anodic and cathodic compartments. The anolyte vessel was charged with 50 ml of 1 M Ce(III) nitrate in 3 M nitric acid (with or without silver nitrate catalyst) and catholyte vessel with 4 M nitric acid solutions. All the experiments were carried out under a constant current of 1 A. The temperature of the solutions was maintained using a thermostatic control. During the experiment, Ce(III) was oxidized to Ce(IV) and nitric acid was reduced to nitrous acid respectively as the result of anodic and cathodic electron transfer reactions. During the electrolysis samples were collected at different time intervals and Ce(IV) concentration was estimated by potentiometric titration with standard ferrous sulfate solution. From the concentration of Ce(IV) the current efficiency was calculated.

Under the optimum conditions of the cell for Ce(III) oxidation, phenol mineralization was carried out in continuous addition mode. The phenol solution of known concentration was constantly fed at the rate of 0.05 ml min<sup>-1</sup> into the anolyte reservoir up to 60 min. Phenol was oxidized into CO<sub>2</sub> and water, while Ce(IV) was reduced to Ce(III). The reduced Ce(III) was continuously regenerated *in situ* by the electrochemical cell. The CO<sub>2</sub> formed was brought out by passing a carrier gas (nitrogen; 500 ml min<sup>-1</sup>) and the concentration was measured using an infra red CO<sub>2</sub> analyzer (Anagas CD 98, Environmental Instruments). The mineralization efficiency of the process was calculated as the ration between the accumulated CO<sub>2</sub> volume and the theoretical volume assuming 100% mineralization.

## **Results and Discussion**

### *Cerium(III) oxidation in presence of Silver*

In the present investigation the purpose of using the silver ion as the catalyst has dual purpose. The first one is to increase the coulombic efficiency for Ce(III) electro-oxidation and the other one is to decrease the temperature for organic destruction. Therefore all our experiments were carried out at 40°C. Therefore the oxidation of electrolyte solution containing 1 M Ce(III) nitrate in 3 M nitric acid with varying amounts of silver was carried out at 40°C at 1 A applied cell current. The Percentage conversion of Ce(III) as a function of time at different concentration of silver catalyst is given in Fig. 1.

It is seen from the figure that at the end of 90 min the formation of Ce(IV) was found to be 56% in the case of uncatalyzed cerium oxidation. The use of silver catalyst has significantly increased the formation yield of Ce(IV). The increment in the Ce(IV) formation yields was found to be 15%, 19% and 23% respectively for 0.025, 0.05 and 0.1 M initial Ag(I) concentrations. The use of silver catalyst has increased the yield for Ce(III) oxidation even at 40°C, which is otherwise could be reached only at higher temperatures i.e. 80-90°C. Based on the high coulombic efficiency obtained 0.1 M of Ag(I) concentration was chosen as the optimum catalyst concentration for further studies.

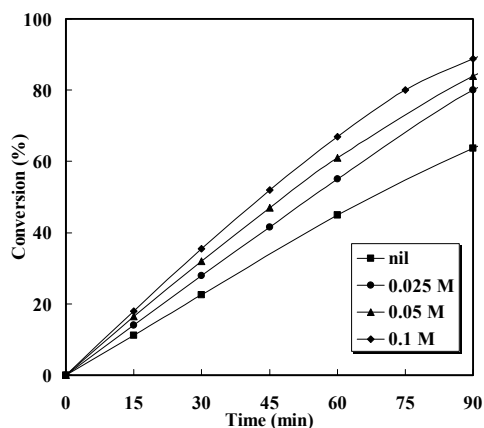


Fig. 1. Percentage of Cerium(III) conversion as a function of time for different concentration of silver.

( $C_{\text{Ce(III)}}$ : 1 M,  $C_{\text{HNO}_3}$ : 3 M, Current : 1 A and T: 40°C)

#### *Ce(IV) mediated oxidation of phenol in presence of silver catalyst*

To find the optimum total cerium concentration for maximum mineralization, experiments were conducted at varying initial Ce(III) concentrations. The destruction efficiencies with time for different initial concentrations of Ce(III) with 0.1 M Ag(I) at 40°C is shown in Fig. 2(a). It was observed that the maximum destruction efficiency was seen in the case of 1 M total Ce(III) than at lower concentrations. The increased Ce(IV) oxidant concentration along with silver destroys the organics effectively than at lower initial Ce(III) concentrations. This means that the current utilization is more effective for the organic destruction reaction if the total cerium concentration is high enough. It can be observed that the destruction efficiency of phenol was significantly increased when catalyzed by Ag(I) compared to the silver ion uncatalyzed Ce(IV) mediated oxidation of phenol and the increase in the destruction efficiency was found to be ca. 30% with 0.1 M silver under the same experimental conditions. The effect of feed concentration of phenol on the mineralization efficiency was studied at different phenol concentrations with the electrolyte composition of 1 M Ce(III), 0.1 M Ag(I). The plots of real time concentrations are depicted in Fig. 2(b) for silver catalyzed Ce(IV) mediated oxidations. It can be seen that even at the reaction temperature of 40°C, the mineralization efficiencies for 1000, 2500 and 5000 ppm of phenol were found to be quite high ca. 79-82%, whereas for 10000 ppm phenol the destruction efficiency was only 63%. But for 10000 ppm phenol concentration the increase in destruction efficiency is the highest compared to the non-catalyzed oxidation.

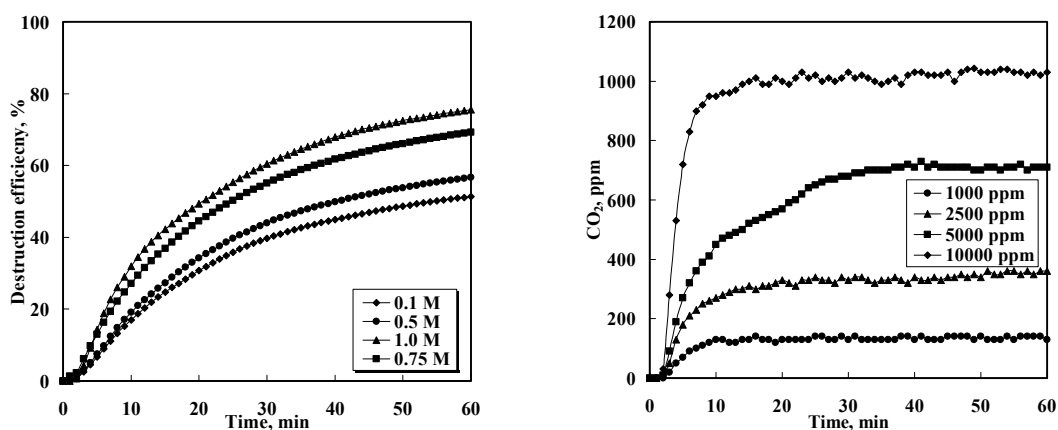


Fig 2. The destruction efficiency of phenol using cerium catalyst by silver (a) different concentration of cerium, (b) different of concentration phenol( $C_{\text{HNO}_3}$ : 3 M, Current : 1 A and T: 40°C)

### Conclusions

The current efficiency of Ce(IV) electrochemical oxidation using a divided electrochemical cell was found increased by the addition of small quantities of silver which acts as a catalyst. The silver concentration of 0.1 M was found to yield high current efficiency for 1 M total cerium concentration in 3 M nitric acid medium under the experimental conditions employed. The increase in the current efficiency was found to be 23% for 0.1 M silver in 1 M Ce(III) and 3 M nitric acid. The efficiency of the mixed mediator system i.e. Ce(IV) with silver catalyst in nitric acid was tested for phenol mineralization. It was found that phenol was mineralized well at the lower temperature of 40°C when catalyzed by silver.

### Acknowledgement

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### References

- [1] J. L. Ryan, A. L. Bray, E. J. Wheelwright, G. H. Bryan, Catalyzed electrolytic plutonium oxide dissolution in trans-uranium elements: A half century. L.R. Morss and J. Fuger Eds., American Chemical Society, Washington, D.C., (1992) P. 288.
- [2] GEF, On review of emerging innovative technologies for the destruction and decontamination of POPs and the identification of promising technologies for use in developing countries. Report of United Nations Environmental Programme for 2004, January 15 (2004).
- [3] Ch. Comninellis, E. Plattner, Electrochemical production of ceric sulphate in concentrated H<sub>2</sub>SO<sub>4</sub>, J. Appl. Electrochem, 13 (1983) 117.
- [4] C. Eysseric, H. Chifflet, S. Picart, J.M. Adnet, ATALANTE International Conference, France, Oct 24 – 26, 2000.