

Technical Note

# Mineralization of phenol by Ce(IV)-mediated electrochemical oxidation in methanesulphonic acid medium: A preliminary study

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## Abstract

The mediated electrochemical oxidation (MEO) process using cerium(IV) in methanesulphonic acid (MSA) as the oxidizing medium was employed for the mineralization of phenol in batch and continuous feeding modes. Although nitric acid was an extensively studied electrolyte for organic mineralization reactions in MEO processes it does possess the problem of  $\text{NO}_x$  gas production during the reduction of nitric acid in the cathode compartment of the electrochemical cell. This problem could be circumvented by proper choice of the electrolyte medium such as MSA. The mediator cerium in MSA solution was first oxidized to higher oxidation state using an electrochemical cell. The produced Ce(IV) oxidant was then used for the destruction of phenol. It was found that phenol could be mineralized to  $\text{CO}_2$  by Ce(IV) in MSA. The evolved  $\text{CO}_2$  was continuously measured and used for the calculation of destruction efficiency. The destruction efficiency was observed to be 85% based on  $\text{CO}_2$  evolution for 1000 ppm phenol solution at 80 °C in continuous feed mode. © 2007 Elsevier Ltd. All rights reserved.

**Keywords:** Mediated electrochemical oxidation; Cerium(IV); Methanesulphonic acid; Phenol mineralization;  $\text{CO}_2$

## 1. 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 (Ryan et al., 1992). 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 (Bringmann et al., 1998; Nelson et al., 2000). 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 (GEF, 2004). Steele (1990) reviewed the early developments of the Ag(II)-MEO process in nitric acid and Nelson (2002) reviewed the applications of the commercially developed installation for organic destruc-

tion with cerium mediator in nitric acid. The main advantages of the MEO process are the optimum working conditions of ambient temperature (<100 °C) and atmospheric pressure, the products formed are only  $\text{CO}_2$  and water and an easy electrochemical regeneration and reuse of the oxidant minimizing the production of secondary wastes (Balazs et al., 1997).

In the MEO process an electrochemically generated metal ion is used as an oxidant (Steele, 1990). This mediator ion in acidic medium destructs virtually any organic material into  $\text{CO}_2$  and water, in a totally enclosed chamber without any harmful emissions like PCDDs/PCDFs. Usually, transition and inner transition metal ions such as silver, cobalt, manganese, and cerium are used as mediator ions owing to their high redox potentials. During the organic destruction metal ion oxidant is reduced and again reoxidized *in situ* by the electrochemical cell thus forming a closed loop. The metal ions act as electron carriers and therefore the net result is the utilization of electrical energy for the destruction of organics. The superiority of the MEO

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process compared to the conventional direct electrochemical oxidation lies in the fact that the organic compounds are completely oxidized to CO<sub>2</sub> in a shorter duration of time (Galla et al., 2000). The inorganic hetero atoms present in the wastes are converted to their corresponding oxides.

The core component of the MEO system is an electrochemical cell. The electrochemical cells for metal ion oxidation with various electrode materials and cell configurations have been reported for different metal ions (Raju and Ahmed Basha, 2005; Wei et al., 2005; Matheswaran et al., 2007). Although several metal ions are available for use in MEO system cerium is preferred in our studies due to the following reasons: cerium has good oxidizing behavior due to its high redox potential ( $E^0 = 1.61$  V in MSA) (Lozar and Savall, 1995), water oxidation by formed Ce(IV) is less which is an unwanted side reaction (Nelson, 2002), cerium does not form precipitate with chlorine like silver and it can be recovered and reused without much loss.

The acid electrolyte used extensively in most of the reported MEO processes is nitric acid. Although nitric acid is found to be the good choice in terms of solubilizing capacity, oxidizing capability etc., it does possess the problem of NO<sub>x</sub> gas formation at the cathode compartment due to the reduction of nitric acid and also lower boiling point of nitric acid results in the loss of acidity and hike the pH of the solution during long term operations (Balaji et al., 2007b). To circumvent these problems methanesulphonic acid (MSA) is chosen in this study which has, high boiling point (167 °C) compared to nitric acid (120 °C for 68% HNO<sub>3</sub>). MSA has been used by some researchers as the electrolyte medium in the mediated electrochemical synthesis of various organic intermediates (Spotnitz et al., 1990; Cho and Romero, 1998). The use of MSA produces hydrogen in the cathode compartment which can be recovered and utilized in fuel cells thus a part of the energy spent in the MEO process can be recovered back (Spotnitz et al., 1990; Farmer et al., 1996). The solubilizing capacity of an acid towards the metal salt (mediator) is another important consideration in the MEO processes and it has been observed that in the electrochemical oxidation a higher concentration of the metal ion yields a higher coulombic efficiency (Raju and Ahmed Basha, 2005). Sulfuric acid has higher boiling point than nitric acid but has low solubilizing capacity for cerium (Paulenova et al., 2002). Therefore, in this study MSA is employed as an electrolyte medium for Ce(IV)-MEO of phenol.

The Ce(IV)-MEO process finds application in both synthetic organic chemistry and the environmental pollution abatement. The main objective in environmental research is to convert the organic compounds into carbon dioxide and water and the efficiency of the organic destruction process can be estimated based on the CO<sub>2</sub> evolved. Therefore, in the MEO processes the kinetics of the intended product i.e., CO<sub>2</sub> is followed by continuous measurement in the off gas stream and the quantum of CO<sub>2</sub> evolved could be

utilized for the calculation of destruction efficiency of the MEO process.

Although concentrated chemicals and slurries were the targets of mineralization in the MEO processes, the present investigation uses only aqueous solutions since the intention was to obtain the CO<sub>2</sub> evolution pattern with respect to time during the organic oxidation and to compare it with the theoretical value for complete destruction. Therefore only the aqueous phenol solutions of known concentration were employed in this study. In our previous report the destruction of phenol by Ce(IV)-MEO process in nitric acid medium with batch mode organic addition without *in situ* regeneration of Ce(IV) was documented (Balaji et al., 2007a, 2007c; Kokovkin et al., 2007; Lee et al., 2007). There seems to be no report available for the destruction studies of phenol using Ce(IV)-MEO in MSA medium.

The objectives of the present investigation were (i) to obtain the oxidation kinetics of Ce(III) in MSA medium under the constant current electrolysis, (ii) to investigate the mineralization of phenol with *in situ* regeneration of Ce(IV) oxidant in batch and continuous organic addition modes, under various conditions of temperature, feed concentration of phenol, and anolyte MSA concentration and (iii) to compare the destruction efficiencies between MSA and nitric acid for phenol destruction in continuous addition mode.

## 2. MEO reaction chemistry

In the MEO processes the metal ion oxidant is produced in the electrochemical cell and used for the organic destruction. The cell reaction for metal ion oxidation is reported elsewhere (Nelson, 2002). The destruction of organics by the produced metal ion oxidant takes place through a number of intermediates and the reaction mechanism is somewhat complex. As per the reported literature on MEO for the organic destruction reactions, free radicals such as •OH, •HO<sub>2</sub>, etc., are produced by the interaction between the oxidized metal ion and water also called water oxidation reaction (Steele, 1990; Farmer et al., 1992). Another possible source of free radicals is from the direct electrolysis of acids in the cell. These secondary oxidation species together with the metal oxidant mineralize the organic compounds to CO<sub>2</sub> and water (Bremer and Carson, 2002). The redox potential of silver and cobalt are high therefore the oxidized form of the metal is highly unstable even at room temperature and hence undergoes self reduction by oxidizing water molecules (Po et al., 1968; Bringmann et al., 1995). In the case of cerium the water oxidation by the produced Ce(IV) is very minimum (Varela et al., 2001) yet water oxidation may proceed directly at the anode surface to some extent and produce the radical species which aid the organic mineralization reactions. A separate study on free radicals and intermediates in the MEO process may unveil the actual chemistry.

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