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Mediated electrochemical oxidation process: Electro-oxidation of cerium(III) to cerium(IV) in nitric acid medium and a study on phenol degradation by cerium(IV) oxidant

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Abstract

Cerium(III) in nitric acid medium was oxidized electrochemically using a flow type electrochemical cell fabricated in our laboratory. The variation of applied cell current, temperature and the concentration of the electrolyte were studied to determine the oxidation efficiency of Ce(III) in the electrochemical cell. The conversion yield of cerium(IV) in nitric acid was 97% in a short duration of 90 min. A bench scale degradation of phenol has been carried out by mediated electrochemical oxidation process using this oxidised Ce(IV) species. The influence of the concentration of phenol, temperature, amount of cerium, and the concentration of the electrolyte were studied on phenol destruction in a batch type reactor. It was found that nearly 70% of phenol was found to be destructed within 10 min. A good degradation yield was obtained above 70 °C. The effects of concentrations of cerium and nitric acid on phenol degradation were found to be moderate within the range investigated. The course of the reaction was followed by TOC analysis, estimating the CO_2 evolved, and also measuring the potential of the Ce(IV)/Ce(III) redox couple.

Keywords: Mediated electrochemical oxidation (MEO); Cerium(III) oxidation; Cerium(IV) mediator; Phenol; Nitric acid; CO_2; TOC; Redox potential

1. Introduction

Mediated electrochemical oxidation (MEO) is an emerging and one of the most promising technologies for the destruction of organics as it is capable of completely mineralizing the organics into carbondioxide and water, without emission of any toxic materials like dioxins [1–8]. MEO process offer several advantages: first, the oxidation reaction takes place at ambient temperatures and pressures; second, the products of destruction are contained in the reaction vessel itself with the exception of gases; third production of secondary waste is minimized and this avoids additional treatment methods.

In MEO process a metal ion in acid medium is oxidized from its lower oxidation state to higher oxidation state and this oxidized species destructs the organic compounds into carbondioxide and water and get reduced. Therefore, the metal ion is not consumed in the reaction and acts as a mediator. The mediator ion used is usually a transition metal with high redox potential like silver, cerium and cobalt. These mediators in acid medium act as a powerful oxidants and destruct the organic compounds. Cerium possesses good oxidizing behaviour due to its high redox potential ($E^0 = 1.62$ V) [9] and does not form any insoluble precipitate with chlorine containing compounds as in the case of silver MEO system [10]. Cerium can be recovered and reused without much loss and therefore it is preferred to other metal ions such as silver, cobalt, etc., and hence used in our study. Electrochemical oxidation was employed by a few researchers for the oxidation of Ce(III) in nitric acid in the low concentration ranges (0.02 M) [11,12]. But there is lack of information in the literature on the production of Ce(IV) in high concentration region, which is essential for the mineralization of organic pollutants.

MEO process and the associated electrochemical cells, like CerOx-T cell [13], ElectroCell, ICI cell, etc., find commercial applications for organic waste destruction and metal ion oxidation, respectively, and the technical details of the processes have been patented [14,15]. A few research groups around the world are developing MEO process, with different metal ions, towards the commercial scale [16]. Chiba [17] studied the MEO process taking 0.5 M Ag(II) as mediator in sulphuric acid medium

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for the destruction of a number of organic compounds. Bringmann et al. [18] reported their work on Ag(II)-MEO system for the destruction of hydrocarbons and pesticides in sulphuric acid medium. Nelson [19] reported mineralization results on organic compounds and a wide variety of pesticides by Ce(IV)-MEO process in nitric acid. The earlier reported works dealing with MEO process provided the data of final destruction efficiencies without showing any trend of destruction with respect to time and also the effects of influencing parameters were not shown and discussed. However, there has been no report in the literature for the production of Ce(IV) using bench scale electrochemical cell. Also, no preliminary data was available for organic destruction efficiency of the MEO process with respect to time based on TOC and CO_2 results. This prompted us to investigate the Ce(IV) production in a bench scale system and the actual course of organic destruction with time for fundamental understanding of the MEO process.

Phenol is one of the most common pollutants found in the effluents of many industries such as pharmaceuticals, dyes, synthetic chemical plants, petroleum refineries, pesticides and herbicides, and treated by several technologies [20–25] and was chosen as the target organic species in the present study. The goals of the present work were: (i) to investigate Ce(III) electro-oxidation in presence of nitric acid medium using an electrochemical cell, and to find the influence of applied cell current, temperature, and concentration of nitric acid over Ce(IV) yield and (ii) to evaluate the systematic degradation of the target organic pollutant, phenol, by the produced Ce(IV) mediator ion, in a batch reactor. The effects of operating parameters, such as concentration of phenol, temperature, concentrations of cerium and nitric acid on the destruction process were studied.

2. Experimental

2.1. Materials

Ammonium cerium nitrate was obtained from Aldrich, cerium(III) nitrate hexahydrate was procured from TERIO Corporation, China, phenol and nitric acid (60%) were obtained from Sam Chun Chemicals, Korea. All chemicals were used as received.

2.2. Methods

2.2.1. Cerium(IV) production

The overall schematic diagram of the MEO system is shown in Fig. 1.

The system essentially consists of an anolyte and a catholyte each with a capacity of 1.5 L, attached with an electrochemical cell (Table 1). The electrolyte used in the anolyte was Ce(III) nitrate in nitric acid, and in the catholyte nitric acid was taken. The catholyte vessel was provided with a gas scrubber to convert the nitrous oxide vapours into nitric acid. The anolyte and catholyte solutions were circulated through the cell using ceramic pumps.

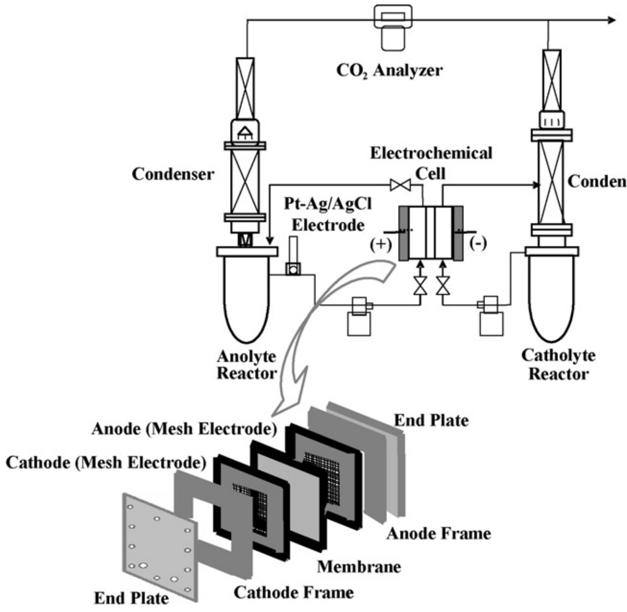

Fig. 1. Schematic diagram of the MEO process.

The electrochemical cell fabricated in our laboratory [26], with the dimensions as given in Table 1, was employed for the oxidation of Ce(III). The cell consists of an anode and a cathode separated by Nafion 324 membrane. Titanium coated with IrO_2 mesh type DSA electrode was used as anode and cathode was titanium mesh electrode. A fluoropolymer sheet (viton) was used as the separator between the electrodes. The power supply was provided to the cell by means of a constant dc voltage.

During the oxidation, concentration of Ce(IV) solution was checked by measuring the redox potential using Orion pH/ISE meter with Pt–Ag/AgCl combined electrode (model no. 720A, Orion Co. Ltd., USA) and using a calibration plot for cerium redox couple, shown in Fig. 2. In addition to the evaluation on the oxidation of Ce(III), studies on the performance of the cell were also examined. The effects of applied current, temperature of the solution, and the concentration of the nitric acid, on Ce(III) oxidation were studied. The optimization parameters for the cell were coulombic efficiency (CE), which is the percentage of the total current used for oxidation, and energy consumption (EC).

2.2.2. Organic destruction

Phenol destruction studies were carried out in a batch type reactor, which was separated from the electrochemical cell. The

Table 1
Dimensions and characteristics of the electrochemical cell

Parameters	Dimensions and characteristics
Anode area	140 cm^2 (DSA mesh type, IrO_2 on Ti)
Cathode area	140 cm^2 (mesh type, Ti)
Anode to membrane gap	0.2 cm
Length parallel to the electrolyte flow	9.7 cm
Length perpendicular to the electrolyte flow	14.5 cm
Volume	70 cm^3
Internal diameter of the ports	0.8 cm
Membrane	Nafion 324

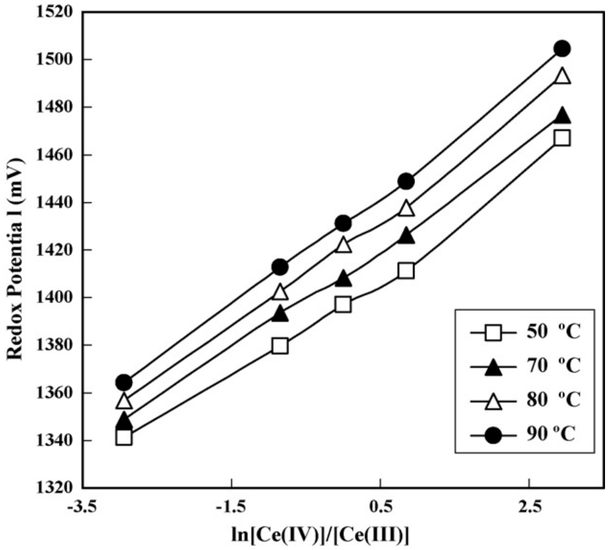

Fig. 2. Calibration plots of Ce(IV)/Ce(III) redox couple for various compositions at different temperatures ([Ce(III)] + [Ce(IV)] = 1.0 M in 3.0 M HNO_3).

reactor was filled with Ce(IV) in nitric acid solution prepared by the oxidation of the corresponding Ce(III) solution. The top of the reactor contained four inlets each one for nitrogen purge, temperature sensor, sampling port and condenser. The organic feed solution was prepared by weighing specific quantities of phenol and dissolving in known volumes of high purity reverse osmosis water. The reaction was carried out under specific temperatures using a thermostatic control. The organic feed solution and the MEO solution were mixed continuously by a magnetic stirrer.

2.2.3. Liquid phase analysis

The samples at different time intervals were taken and analysed for total organic carbon content using TOC analyzer (Shimadzu TOC-5000A) containing high sensitivity TC catalyst. The percentage of destruction was calculated based on the initial and final TOC values. The concentration of Ce(IV) ion in the solution during organic destruction was measured from the redox potential. From the stoichiometric amount of Ce(IV) consumed, extent of organic destruction was calculated:

$$28\text{Ce(IV)} + C_6H_5OH + 11H_2O \rightarrow 28\text{Ce(III)} + 6CO_2 + 28H^+$$

2.2.4. Measurement of carbon dioxide

The concentration of carbon dioxide produced during the organic decomposition was measured continuously using a CO_2 analyser (Environmental Instruments, Anagas CD 98). Carbon dioxide formed was purged by the carrier gas stream (nitrogen) and taken to the analyser. The flow rate of the carrier gas was kept constant (2.0 L/m) throughout the experiment. The concentration of CO_2 evolved in terms of ppm was continuously recorded and the values were then converted into volume and used to calculate the destruction efficiency in terms of CO_2 produced.

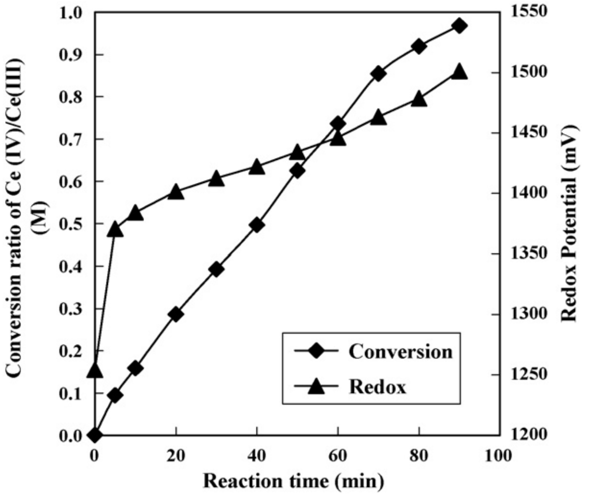

Fig. 3. Plots of conversion ratio of Ce(IV)/Ce(III) and redox potential vs. reaction time at 80 °C with 10 A cell current ($[\text{Ce(III)}]_{\text{initial}}$ = 1.0 M in 3.0 M HNO_3).

3. Results and discussion

3.1. Oxidation of cerium(III) in nitric acid medium

Fig. 3 shows the Ce(IV) yield and the change in redox potential against reaction time at 10 A. It was found that at about 90 min nearly 0.97 M Ce(IV) was obtained. Fig. 4 shows the conversion ratio of Ce(IV) to Ce(III) with reaction time at various cell currents. Fig. 5 shows the CE and EC plotted against applied cell current. It was observed that at 10 A, CE was high with low EC, compared to other two values. The experiments were conducted at this 10 A current and at various temperatures and the CE and EC values were plotted against temperature in Fig. 6. It was observed that at 80 °C, CE was high while maintaining low EC. From these results, it was concluded that 10 A and 80 °C were observed to be the favourable conditions for

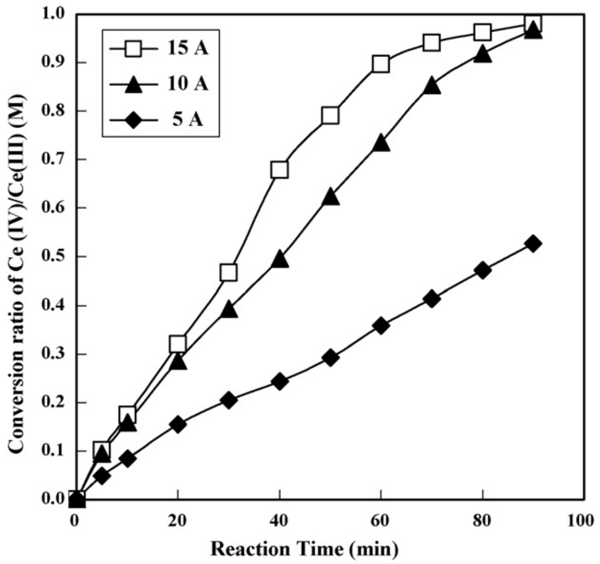

Fig. 4. Variation of conversion ratio of Ce(IV)/Ce(III) with time at different applied cell currents at 80 °C ($[\text{Ce(III)}]_{\text{initial}}$ = 1.0 M in 3.0 M HNO_3).

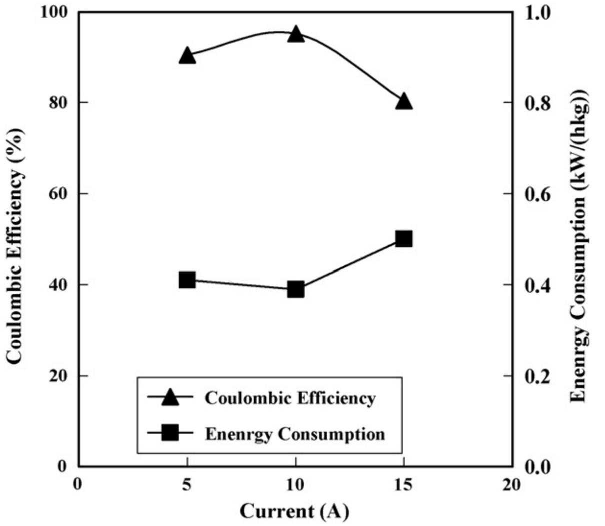

Fig. 5. Dependencies of coulombic efficiency and energy consumption on the applied cell current at 80 °C ($[Ce(III)]_{initial} = 1.0$ M in 3.0 M HNO_3).

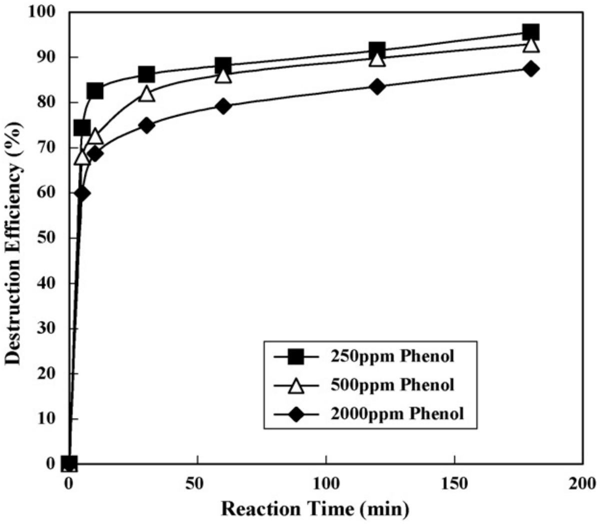

Fig. 7. Variation of destruction efficiencies vs. reaction time for different initial concentrations of phenol at 80 °C ($[Ce(IV)]_{initial} = 0.95$ M in 3.0 M HNO_3 and $[Ce(III) + Ce(IV)] = 1.0$ M).

the production of Ce(IV) with better current efficiency. At these conditions of 10 A and 80 °C concentrations of nitric acid were varied from 2 to 3.5 M, and it was observed that the yield of Ce(IV) increased with the increase in nitric acid concentration. The similar pattern of Ce(IV) yield was obtained for the low concentration region of Ce(III) oxidation using GC electrode by Wei et al. and this was attributed to the high proton concentration which is electrochemically favourable for electron transfer of the redox couple [12].

3.2. *Organic destruction by MEO process*

3.2.1. *Effect of phenol concentration*

Fig. 7 shows the variation of destruction efficiency based on TOC for various phenol concentrations at 80 °C at a fixed Ce(IV) and nitric acid concentration. It was observed that the degradation of phenol takes place quickly during the initial stages and almost complete mineralization was achieved after 3 h. The higher initial concentration of phenol was found to undergo relatively lesser mineralization, whereas at the lower initial concentrations a near complete destruction with very little residual carbon was achieved. It was also observed from TOC data that maximum amount of phenol was destructed within 10 min in all cases. A close proximity between these curves clearly shows the destruction efficiency of MEO process in the wide range of high organic concentrations studied. The amount of CO_2 formed was not sufficient to account for complete destruction even though TOC analysis indicated almost complete destruction of organics in the solutions. Similar observation was noted by Balazs et al. [10] during the destruction of a range of organic materials by Ag(II)-MEO process and was explained that this difference would arise due to the volatilization of organics before complete destruction.

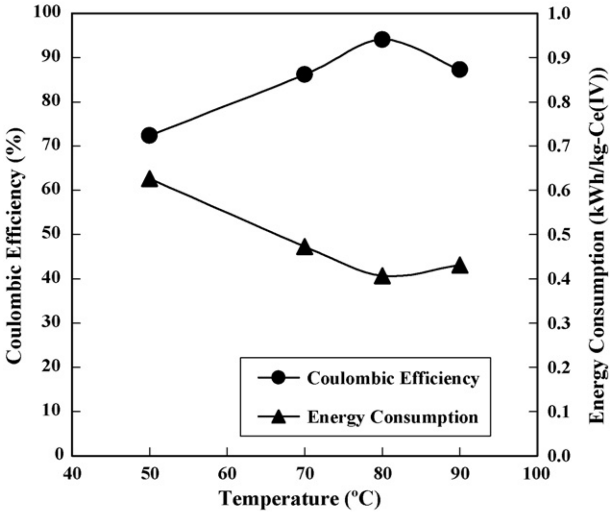

Fig. 6. Effect of temperature on the coulombic efficiency and energy consumption with 10 A cell current ($[Ce(III)]_{initial} = 1.0$ M in 3.0 M HNO_3).

3.2.2. *Effect of temperature on phenol destruction*

Figs. 8 and 9 show the destruction efficiencies against reaction time at various temperatures based on CO_2 and TOC measurements, respectively, at a fixed initial phenol concentration. In Fig. 8, the area under the curve should be proportional to the total volume of CO_2 formed and also the degree of mineralization [10,27]. The pattern of the curve shows concentration of CO_2 goes through maximum within 5–10 min of reaction time and then decreases to zero and also the destruction was found to be temperature dependent. At 50 °C, dark brown floating materials were observed on the solution surface resulting in incomplete mineralization. A similar case was observed by Chiba [17] during the destruction of trimsol oil by MEO process using silver mediator ion at room temperature. From Fig. 8 it was seen that the effect of temperature is much pronounced in the MEO process and the volume of CO_2 produced varies with temperature.

At higher temperatures of 70–90 °C the destruction was higher compared to reaction at 50 °C, as seen in Fig. 9.

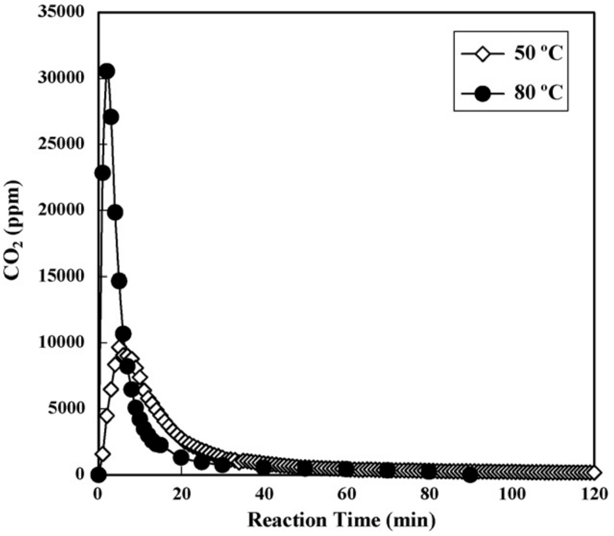

Fig. 8. Effect of temperature on CO_2 evolution for 500 ppm phenol ($[Ce(IV)]_{initial}$ = 0.95 M in 3.0 M HNO_3 and [Ce(III) + Ce(IV)] = 1.0 M).

Particularly above 70 °C the added phenol completely disappeared within a short period, and no floating material was observed on the surface.

3.2.3. *Effect of cerium(IV) concentration*

The effect of mediator ion concentration on phenol degradation is given in Fig. 10. It can be seen that there was not much enhancement in the destruction efficiency between 0.5 and 0.95 M Ce(IV) concentrations. The redox potential measured during the reaction showed a fast depletion of Ce(IV) concentration during the initial stages of reaction. This trend was found to corroborate the TOC and CO_2 results that maximum destruction takes place at the start of the reaction. The destruction efficiency calculated from the amount of Ce(IV) consumed for the oxidation was compared with the TOC and CO_2 data and tabulated in Table 2.

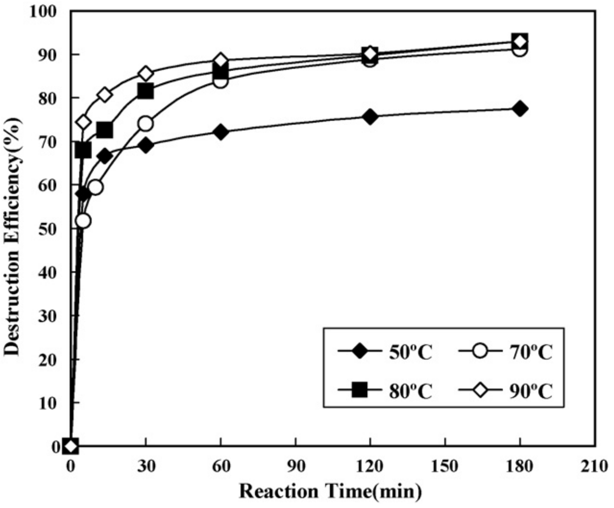

Fig. 9. Effect of temperature on the destruction efficiency for 500 ppm phenol ($[Ce(IV)]_{initial}$ = 0.95 M in 3.0 M HNO_3 and [Ce(III) + Ce(IV)] = 1.0 M).

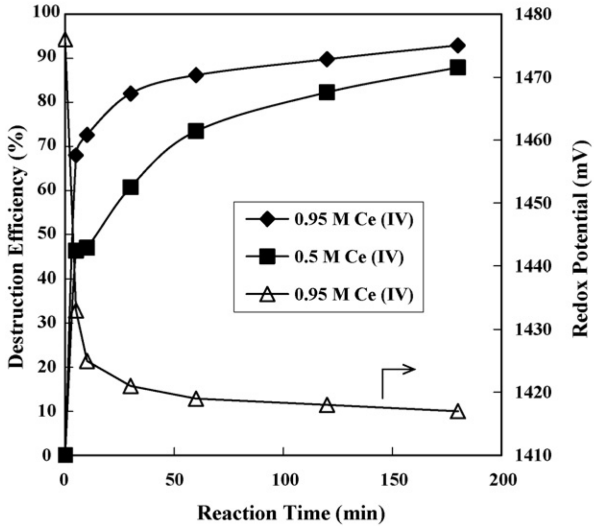

Fig. 10. Variation of destruction efficiencies and redox potential vs. reaction time for 0.5 and 0.95 M cerium(IV) in 3 M nitric acid at 80 °C ([Ce(III) + Ce(IV)] = 1.0 M and $[phenol]_{initial}$ = 500 ppm).

A brief study was carried out to check the degradation of phenol at low concentrations of Ce(IV) at 80 °C. In this study, for a fixed phenol concentration, various concentrations of Ce(IV) in the range 0.015–0.15 M were used as the oxidizing solution. It was observed that a good destruction in the liquid phase was achieved at the concentration of 0.15 M Ce(IV) and this corresponds to the Ce(IV) and organic ratio of 15:1 as against the theoretical ratio of 28:1. In our studies, a dark brown wax like material was found floating at the top of the reactor solution for low concentrations of Ce(IV). Therefore, it was concluded that though destruction was high in the solution this could not account for complete conversion to CO_2 because of the formation of some low-density organic compounds. This could justify our organic destruction studies with high initial concentration of Ce(IV). Therefore, a high concentration of oxidizing solution in the reactor could be employed for complete mineralization of fairly high concentration of organics.

3.2.4. *Effect of nitric acid concentration*

Fig. 11 shows the effect of nitric acid concentration on phenol degradation. The small variance in the destruction efficiency was observed within the range of nitric acid concentration studied.

Since Ce(IV) concentration was high and kept constant, it strongly oxidizes any organic molecule by its highly favoured electron releasing tendency. The organic oxidizing ability of the

Table 2
A comparison of phenol destruction efficiencies from TOC, CO_2 and redox measurements at different temperatures in the MEO process (phenol, 500 ppm; Ce(IV), 0.95 M; HNO_3, 3.0 M; [Ce(III) + Ce(IV)] = 1 M)

Temperature (°C)	Destruction efficiency (%)		
	TOC	CO_2	Redox
50	77.5	72.6	70.4
80	96.4	84.5	85.2
90	97.5	88.3	91.3

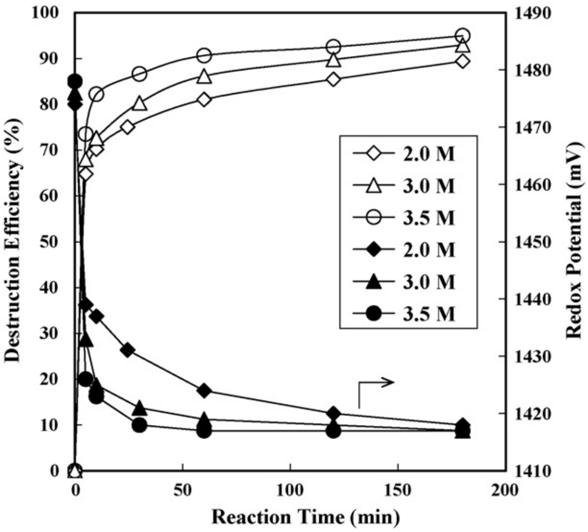

Fig. 11. Variation of destruction efficiencies and redox potentials vs. reaction time for different nitric acid concentrations at 80 °C ($[\mathrm{Ce(IV)}]_{\mathrm{initial}} = 0.95$ M, $[\mathrm{Ce(III)} + \mathrm{Ce(IV)}] = 1.0$ M and $[\mathrm{phenol}]_{\mathrm{initial}} = 500$ ppm).

medium would likely be the combined effect of both Ce(IV) and nitric acid and might not be solely from nitric acid, at least within the range studied.

4. Conclusions

Electro-oxidation of Ce(III) in nitric acid medium was carried out using the electrochemical cell developed in our laboratory. The oxidation was found to be influenced by the applied cell current, the temperature of the solution and the concentration of nitric acid. The current of 10 A and temperature of 80 °C were found to be favourable for better yields of Ce(IV). The increase in the concentration of nitric acid increased the production of Ce(IV). The MEO process was successfully tested for phenol destruction in a batch reactor by taking the produced Ce(IV) and nitric acid as the mediator solution. Almost complete destruction of high concentration of phenol was achieved with in the reaction time. The observed destruction trend in TOC was supported by CO_2 and redox measurements as well. The mineralization of phenol was found to be high at and above 70 °C. The increase in the concentration of Ce(IV) from 0.5 to 0.95 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 Ce(IV) and nitric acid, but not solely from nitric acid. This process is of great practical utility for a wide variety of organic compounds including POPs, and further experimental work is in progress for continuous organic destruction with simultaneous Ce(IV) regeneration.

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