

Electro-oxidation Kinetics of Cerium(III) in Nitric Acid Using Divided Electrochemical Cell for Application in the Mediated Electrochemical Oxidation of Phenol

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The electrochemical oxidation of cerium(III) was carried out using divided and undivided electrochemical cells in nitric acid medium. It was found that divided cell with Nafion 324 as the separator gave good conversion yield with high current efficiency compared to the undivided cell. The efficiency of the divided electrochemical cell was further optimized in terms of cell voltage, temperature, flow rate of solution recirculation, concentrations of Ce(III) and nitric acid. The better conditions for 1 M Ce(III) in 3 M nitric acid were found to be 2.5 V, 363 K and 100 mL/min recirculation flow rate based on the current efficiency under the experimental conditions investigated. The Ce(IV) oxidant produced was used as a mediator for the mineralization of phenol. The mineralization efficiency of the cerium mediated electrochemical oxidation was found rapid and higher compared to the direct electrochemical oxidation based on CO₂ evolution under the same conditions.

Key Words : Direct electrochemical oxidation. Mediated electrochemical oxidation. Cerium. Nitric acid. Phenol

Introduction

The electrochemical destruction of organic wastes could be carried out either by direct electrochemical oxidation (DEO) or by mediated electrochemical oxidation (MEO). MEO process is one of the latest and advanced technologies for the complete mineralization of organic pollutants. In this process a mediator metal ion in acid medium is used as an oxidant for the destruction of organics which is regenerated electrochemically in a closed cycle. DEO processes have been carried out for a variety of organic compounds.¹ In these processes the organic compounds are oxidized to CO₂ and H₂O at the anode surface. The most common side reaction is the anodic oxidation of water to give oxygen and it is often impossible to suppress this side reaction completely and as the consequence the obtained current yields are low.²⁻⁵ Other disadvantages of the DEO processes are the reduced mass transfer of the organics from the bulk solution to the anode surface due to the low miscibility of most of the organics with water and the poisoning of the electrode surface^{6,7} and hence the reduced electrode activity. Where as considerable better yields are achieved with MEO processes in the above aspects. In the MEO process the organic is mineralized in the bulk solution by a mediator metal ion in the higher oxidation state. After the oxidation of organics, the reduced mediator ion is reoxidized *in situ* by the electrochemical cell and thus cycled infinitely. The MEO process was investigated and reported by many researchers with various mediator metal ions both in laboratory and in pilot scale systems as follows. Farmer *et al.*⁸ have reported the oxidation of ethylene glycol and benzene with silver as a mediator ion using rotating cylindrical gold electrode and destruction of chlorinated organics in presence of cobalt mediator using rotating cylindrical platinum electrode.⁹ Lehmani *et al.*¹⁰ studied the oxidation kinetics of organic

compounds by potentiometric method. Nelson *et al.*¹¹ have reported the first commercial scale cerium mediated destruction of organic hazardous wastes containing 50% water by CerOx system 4. Galla *et al.*¹² investigated the destruction of pesticides using silver mediator in nitric acid medium. Varela *et al.*¹³ have described the cerium mediated electrochemical oxidation for organic waste destruction in the pilot plant with a 40 kW electrochemical cell unit containing platinum coated titanium electrodes. They have stated that, the 40 kW plant produced about 320 mole of Ce(IV) oxidant per hour which is capable of destroying 1.2 kg of chlorobenzene per hour or 0.8 kg of benzene per hour. Turner¹⁴ has documented the silver MEO process in the pilot scale plant and stated that to maximize the process efficiency the concentration of total organic carbon in the feed is normally kept in the range 1-5 g/lit. Armenta *et al.*¹⁵ studied the oxidation of benzoic acid using electro-generated Ce(IV) in sulfuric acid solution using cyclic voltammetry. Steele¹⁶ reviewed the early stages of the silver MEO process. Nelson reviewed¹⁷ the cerium MEO process and explained their larger sized installation which treated successfully the aqueous chemical wastes containing 15-20% organic compounds. It was concluded from the above references that MEO process can be employed for both concentrated organic wastes and aqueous wastes. Although, various metal ions were employed as the mediator, cerium was found to be good based on the following aspects. It does not form precipitate with chloro-organic compounds like silver, the rate of water oxidation is negligible in the case of cerium whereas silver and cobalt oxidize water with high rate.¹⁸ Ce(IV)/Ce(III) redox couple has good oxidizing strength due to high redox potential ($E^{\circ} = 1.62$ V in nitric acid)¹⁷ and can be recovered and reused without much loss.¹³

Therefore studies on the electrochemical oxidation of cerium became an important topic of several researchers.

Although cerium oxidation was investigated as early as 1986 by Bludska and Vondrak¹⁹ it has got much attention in the recent past due to its wide spectrum of application. It has been shown that Ce(III) can be electro oxidized using gold, glassy carbon,^{20,21} PbO₂,^{22,23} SnO₂²⁴ electrodes. Klekens *et al.*²⁵ have reported that the reduction of Ce(IV) was independent of the electrode materials. But for oxidizing Ce(III) various electrode materials had different effects in different electrolyte media. Spotnitz *et al.*²⁶ have reported the electrochemical generation of cerium in methanesulphonic acid and used the same for naphthalene oxidation to 1,4-naphthoquinone. Been and Oloman²⁷ studied the electrode kinetics for cerium oxidation in sulfuric acid medium. Devadoss *et al.*²⁸ compared the voltammetric behaviour of cobalt and manganese with cerium in methanesulphonic acid medium. Raju and Basha²⁹ compared the cerium oxidation efficiencies of undivided, divided and commercial electrochemical cells in methanesulphonic acid medium using DSA electrodes. Wei *et al.*³⁰ and Sedneva *et al.*³¹ have reported the voltammetric studies of cerium oxidation in nitric acid medium in a three electrode system.

Although the electro-oxidation of cerium in nitric acid medium is well reported in literature using voltammetric techniques, it was felt that the oxidation studies using divided electrochemical cell would reveal the dependence of various parameters on the real conversion rates and throw some light on Ce(IV) oxidant production at high concentrations *ca.* 0.7-0.9 M, for applying the same to destroy organic pollutants. The previous studies in our laboratory revealed that a high concentration of Ce(IV) is required to be maintained to obtain a good mineralization efficiency during the organic destruction and also to inhibit electrode passivation due to the organic contamination.^{7,32-38}

The objectives of the present investigation were to study the kinetics of oxidation of Ce(III) in nitric acid using a laboratory scale divided electrochemical cell containing IrO₂/Ti DSA anode and Ti cathode, to find the optimum conditions under which a maximum conversion could be obtained and to compare the mineralization efficiencies of cerium mediated and direct electrochemical oxidation of phenol as the model organic pollutant.

Experimental Section

The electro-oxidation of cerium was carried out in two different types of assemblies namely undivided and divided cells. In case of undivided cells cerium oxidation was carried out at 313 K in batch mode using IrO₂/Ti DSA (Dimensionally Stable Anode) anode and Ti cathode each with geometrical surface area of 4 cm² (effective surface area: 2.6 cm²) and an inter-electrode gap of 1 cm. In the case of divided cell the anode and cathode, of similar type and area used in the undivided cell, were kept separated by a Nafion[®] 324 proton exchange membrane. The anode and cathode compartments of the cell were coupled to anolyte and catholyte vessels respectively and the solutions were circulated through anodic and cathodic compartments repeatedly at a

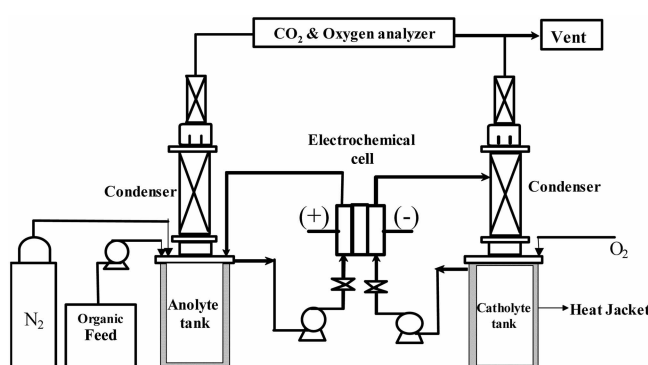


Figure 1. Schematic of the MEO experimental set up.

particular flow rate using peristaltic pumps till the conversion reach a steady state. The membrane used was of low resistivity and able to pass a current density of approximately 5 kA/m².¹⁴ Figure 1 shows the schematic diagram of mediated electrochemical oxidation system. The anolyte vessel was charged with 50 mL of Ce(III) nitrate in nitric acid and catholyte vessel with nitric acid solutions. All the experiments were carried out under a constant voltage mode. 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 reactions. The NO_x gases evolved from nitrous acid was re-oxidized with continuous passage of atmospheric oxygen to NO₂, which then solubilizes in water to form nitric acid. The samples were collected at different time intervals and Ce(IV) concentration was checked by potentiometric titration with standard ferrous sulfate solution. From the concentration of Ce(IV) the current efficiency, and the apparent mass transfer coefficient (k_m) were calculated as per the reported methods.²⁶ It is to be noted here that the calculation of k_m from the conversion data as reported by Spotnitz *et al.*²⁶ is commonly employed in real applications.

Under the optimum conditions of the cell for Ce(III) oxidation, phenol mineralization was carried out in continuous addition mode at 353 K. The phenol solution (0.1 M, *ca.* 7.6 g/L of total organic carbon) was constantly fed at the rate of 0.05 mL/min into the anolyte reservoir up to 30 min. Phenol was oxidized to carbon dioxide and water, while Ce(IV) was reduced to Ce(III). The reduced Ce(III) was continuously regenerated *in situ* by the electrochemical cell. The CO₂ formed as the result of complete organic mineralization was brought out by passing a carrier gas (nitrogen; 500 mL/min) and measured. The mineralization efficiency of the process was calculated from the accumulated CO₂ volume. The concentrations of CO₂ and oxygen evolved were continuously measured using an infra red CO₂ analyzer (Anagas CD 98, Environmental Instruments).

Results and Discussion

Oxidation of Cerium(III) Nitrate. Preliminary experiments were conducted to check the efficiency of undivided

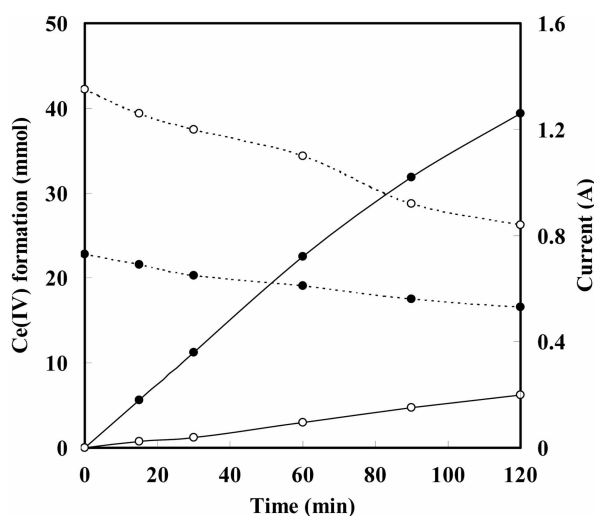


Figure 2. Comparison of Ce(IV) formation rates (—) and current change (---) between undivided (○) and divided (●) electrochemical cells (Conditions: $[Ce(III)]_{initial}$: 1 M; $[HNO_3]$: 3 M; Temp: 313 K; Cell voltage: 2.5 V; Recirculation flow rate: 100 mL/min).

and divided electrochemical cells for Ce(III) oxidation. A comparison between them in terms of Ce(IV) formation and current change at 313 K is shown in Figure 2. From the figure it can be seen that the efficiency of the divided electrochemical cell is nearly 4 times than that of undivided cell due to the membrane separator which inhibits the metal ion reduction at the cathode. Therefore Ce(IV) production was carried out in divided electrochemical cell and various parameters were investigated to find the optimum conditions. Figure 3 shows the current voltage curves of 3 M nitric acid without and with 1 M cerium using DSA electrodes in the divided electrochemical cell. As can be seen in the figure, a limiting current plateau was observed and the oxidation of Ce(III) takes place at voltages above 1.6 V and a diffusion pseudo-plateau is observed around 2.75 V.

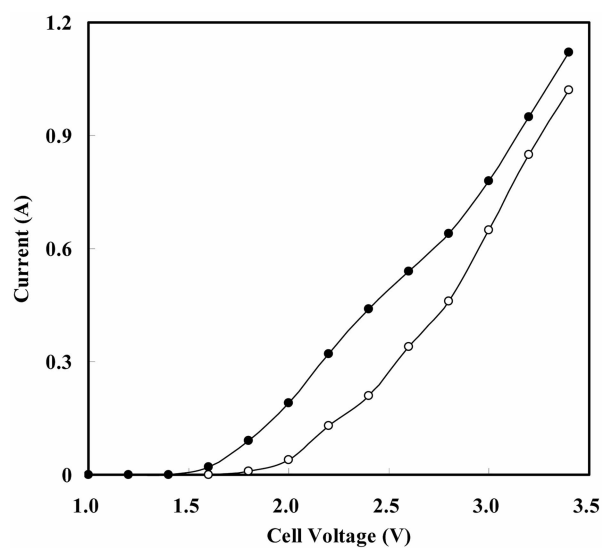


Figure 3. Current-voltage curves obtained with DSA electrodes in 3 M nitric acid: (○) without cerium and (●) with 1 M cerium(III) at 353 K.

Therefore the voltage window of 1.5-3.5 V was taken for Ce(III) oxidation. This current-voltage curve is analogous to the one reported by Spotnitz *et al.*²⁶ for cerium in methane-sulphonic acid system with platinum wire electrode. The current-voltage curves obtained either with cell voltages or potentials are found similar in their behaviour while the former method is more suitable to know the behavior of larger sized electrochemical cells and to avoid the complications associated with the incorporation of Luggin capillary in the reactor. Also placement of the Luggin probe may even alter the hydrodynamics in the electrolyte channel.

Effect of Applied Cell Voltage. The effect of applied cell voltage on Ce(III) oxidation was studied in the range 1.5-3.5 V under the fixed initial concentration of 1 M Ce(III), 3 M nitric acid, at 100 mL/min recirculation flow rate at 353 K. The variation in the Ce(IV) production yields during the electrochemical oxidation at different applied voltages is shown in Figure 4. It can be seen from the figure that the oxidation rate increased linearly and then slowed down. This inflexion point was observed at nearly 80% conversion in the case of higher applied voltages and around 50% in the case of lower applied voltages. It can be explained that once the equilibrium is attained between Ce(III) and Ce(IV), the conversion slowed down and depending on the voltage applied the shifting of equilibrium to the right side take place. For practical purposes the current efficiency is an important design factor than conversion. The current efficiency for Ce(IV) formation was found higher at the optimum applied voltage of 2.5 V compared to the other voltages as shown in Table 1. It is known that the redox couple of Ce^{4+}/Ce^{3+} in nitric acid medium is far above the over potential for oxygen evolution.³⁹ Therefore the oxygen evolution is going hand in hand with cerium oxidation under the experimental cell voltage range of 1.5-3.5 V. At the cell voltage of 2.5 V, the maximum oxidation rate was found for cerium and above and below this value oxygen evolution

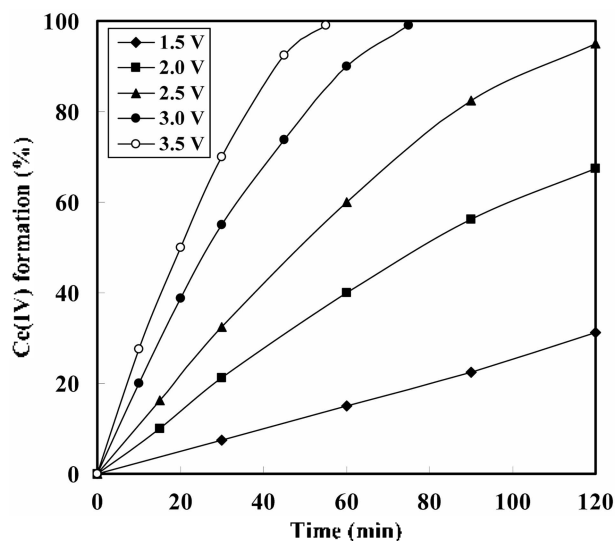


Figure 4. Percentage of Ce(IV) formation at various applied cell voltages (Conditions: $[Ce(III)]_{initial}$: 1 M; $[HNO_3]$: 3 M; Temp: 353 K; Recirculation flow rate: 100 mL/min).

Table 1. Summary of conversion and current efficiency for the oxidation of 1 M Ce(III) in 3 M nitric acid at 353 K at various cell voltages (Electrolyte recirculation flow rate: 100 mL/min)

Voltage (V)	Ce(IV) Formation (%)	C.E. (%)	Ce(IV) Formation (%)	C.E. (%)
1.5	40	61	60	59
2.0	40	85	80	70
2.5	40	89	80	82
3.0	40	78	80	68
3.5	40	74	80	65

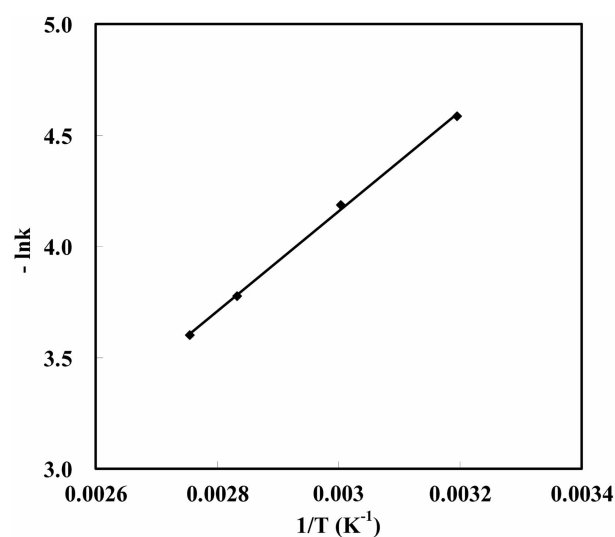
Table 2. Mass transfer coefficients for the oxidation of 1 M Ce(III) in 3 M nitric acid at 353 K at various flow rates under the cell voltage of 2.5 V

Solution Recirculation Flow rate (mL/min)	k_m (cm ² /s)
25	0.0111
50	0.0160
100	0.0201

was thought to be predominant. The lower current efficiency at lower cell voltages may be due to the lowered fraction of current spent for cerium oxidation over the oxygen evolution reaction where as at the higher cell voltages the evolution of oxygen obviously is the reason for lower current efficiency.

Effect of Electrolyte Recirculation Flow Rate. The effect of electrolyte circulation flow rates was studied in the range of 25-100 mL/min for 1 M Ce(III) (50 mmol), 3 M nitric acid, at 353 K under the constant cell voltage of 2.5 V. It was observed that the conversion rate enhanced with increase in the flow rate of the solution recirculation. At the end of 2 hour electrolysis the Ce(IV) conversion was found to be 42 mmol and 48 mmol respectively for 25 and 50 mL/min flow rates whereas for 100 mL/min flow rate 48 mmol was obtained in 90 min. The mass transfer coefficients calculated for various flow rates is shown in Table 2. The apparent mass transfer coefficient calculated using conversion data is comparable to the literature values reported by Wei *et al.*, (0.004-0.026 cm² s⁻¹) for Ce(III) oxidation in nitric acid medium based on cyclic voltammetry results.³⁰ Sedneva has reported that the rate of Ce(III) oxidation in nitric acid solution in an undivided electrolyzer, increased with the stirring rate signifying the role of mass transfer on cerium oxidation.³¹ The current efficiency was also increased from 81% to 89% with increase in the recirculation flow rate from 25 to 100 mL/min indicating that the electrochemical oxidation is a mass transfer controlled reaction under the experimental conditions investigated.

Effect of Temperature. The effect of temperature on the electrochemical oxidation of 1 M Ce(III) in 3 M nitric acid was studied in the range 313-363 K at 2.5 V and 100 mL/min recirculation flow rate. The Ce(IV) formation yields and current efficiencies at different temperatures are shown in Table 3. It can be seen that the rate of Ce(III) conversion increased with the increase in solution temperature. When

**Figure 5.** Plot of $-\ln k$ versus $1/T$ for the oxidation of Ce(III) in nitric acid (Conditions: $[Ce(III)]_{initial}$: 1 M; $[HNO_3]$: 3 M; Recirculation flow rate: 100 mL/min; Cell voltage: 2.5 V).

the logarithm of rate of oxidation was plotted against the reciprocal of the absolute temperature (Figure 5), a straight line was obtained and the activation energy calculated from the slope of this line was found to be 18.7 ± 2.0 kJ/mol. Horbez *et al.*¹⁰ have reported that for Ce(III) oxidation in sulfuric acid medium using platinum coated titanium electrode, if the operating cell voltages is above 1.1 V vs SCE then the evolution of oxygen is inevitable and occurs parallel to the cerium oxidation. Considering the above fact the activation energy reported in this work may taken to be representing the combined process of Ce(III) oxidation and oxygen evolution under the applied cell voltage of 2.5 V. The calculated activation energy is in agreement with the one reported by Wei *et al.*³⁰ (16.3 kJ/mol) for Ce(III) oxidation in nitric acid using cyclic voltammetric data. Also the current efficiencies were found increased with increase in the temperature.

Effect of Nitric Acid Concentration in the Anolyte. The effect of nitric acid concentration on Ce(III) oxidation was studied for 1 M Ce(III), under fixed conditions of 2.5 V and 100 mL/min recirculation flow rate at 353 K. Table 3 shows the formation yields of Ce(IV) and current efficiencies at different nitric acid concentrations (1-5 M). By increasing the concentration of nitric acid from 1 M to 5 M, the yield of Ce(IV) was increased significantly. Wei *et al.*³⁰ and Pleecher *et al.*³⁹ have reported that the formal potential of Ce^{3+}/Ce^{4+} redox couple is independent of both proton and nitrate concentrations while the standard rate constant increases with added proton but is independent of nitrate concentration. A similar trend was observed in our laboratory during the oxidation of Ce(III) by ozone in which Ce(IV) formation increased with nitric acid concentration.⁴¹ The absolute viscosity of 1 M Ce(III) in 3 M nitric acid was measured to be 0.79 cP at 25 °C and 0.66 cP at 80 °C. Although the absolute viscosity increased slightly as the concentration of nitric acid was increased from 1 to 5 M, the

Table 3. The conversion and current efficiency values obtained for the oxidation of 1 M Ce(III) at various temperatures and nitric acid concentrations under the applied cell voltage of 2.5 V and 100 mL/min recirculation flow rate

Parameter	Ce(IV) Formation (%)	C. E. (%)
Temp. (K)	313	77
	333	81
	353	88
	363	93
HNO ₃ (M)	1	70
	2	76
	3	88
	4	88
	5	91

effect of small increase in the viscosity on the diffusion coefficient and hence the mass transfer may become negligible at 353 K. Therefore the increase in the conversion may be considered to arise from the sole contribution of increase in the nitric acid concentration. Also, it can be seen from Table 3 that the current efficiency increases with increasing nitric acid concentration. The highest current efficiency of 90% was obtained for the concentration 5 M nitric acid.

Effect of Initial Cerium(III) Concentration. The effect of initial Ce(III) concentration was studied in the range 0.25–1.25 M (12.5–62.5 mmol initial Ce(III)) in 3 M nitric acid, with 100 mL/min recirculation flow rate at 353 K under the cell voltage of 2.5 V. It was observed that the formation of Ce(IV) increased from 12 mmol to 38 mmol when the concentration was increased from 0.25 to 1 M, at the end of 60 min. However at the highest studied concentration of 1.25 M Ce(III), the oxidation rate was slow as compared to 1 M. The current efficiency increased steadily and significantly from 37% to 88% when the concentration of Ce(III) was increased from 0.25 M to 1 M. Been and Oloman²⁷ have already reported that the limiting current density was increased with initial Ce(III) concentration. Therefore the lower current efficiency at lower Ce(III) concentrations may be due to the reduced limiting current under the same experimental conditions.

Mineralization of Phenol by Cerium Mediated and Direct Electrochemical Oxidation. As the main application of the mediated electrochemical oxidation process is in the environmental organic pollution removal, the following experiments were designed to check the efficiency of the cerium mediated and direct electrochemical mineralization of phenol taken as the model organic pollutant. In our earlier reported work on phenol mineralization by Ce(IV) oxidant in batch mode, carried out without *insitu* Ce(IV) regeneration, it was observed that a high concentration of Ce(IV) oxidant is required to be maintained to have a good mineralization efficiency. Therefore in order to maintain the same level of high concentration of Ce(IV) the addition of phenol was carried out in continuous feeding mode with *insitu* Ce(IV) regeneration. Both the mediated and direct

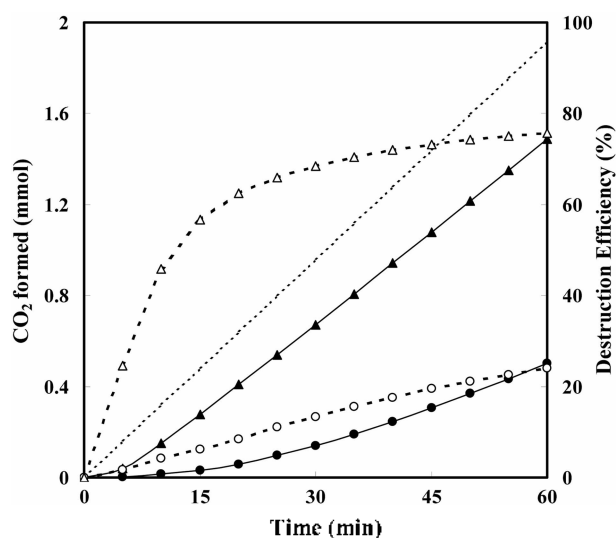


Figure 6. Comparison between the theoretical (---) and experimental CO₂ evolution patterns (●, ▲) and the destruction efficiency (○, △) with time for phenol mineralization by DEO (circle) and MEO (triangle) processes.

electrochemical oxidation of phenol (0.1 M) was carried out under the same experimental conditions. In the case of cerium mediated oxidation 1 M Ce(III) in 3 M nitric acid solution was initially electrolyzed under the constant cell voltage of 2.5 V till 0.9 M Ce(IV) concentration was reached and then the phenol solution was added with the flow rate of 0.5 mL/min using a syringe pump. The direct electrochemical oxidation of phenol was carried out under the identical conditions without cerium. Figure 6 depicts the destruction efficiencies and cumulative volumes of CO₂ evolved in mmol during the mediated and direct electrochemical mineralization of phenol with respect to reaction time together with the theoretical CO₂ amount for 100% mineralization. The destruction efficiency calculated based on CO₂ evolved in the case of direct electrochemical oxidation was found to be only 23% which is much less compared to the cerium mediated electrochemical oxidation process (75%). It should be noted here that the destruction efficiency of cerium mediated oxidation calculated from the quantity of CO₂ evolved start increasing initially and nearly after 40 min reaching a steady state value of 75%. The destruction efficiency could be improved by optimizing the process parameters in the case of continuous organic feeding. This demonstrates clearly the efficiency of the MEO process for organic mineralization compared to the DEO processes without mediator oxidant.

Conclusions

The electrochemical oxidation of Ce(III) in nitric acid medium was investigated with a divided electrochemical cell in batch type recirculation mode. The rate of cerium(IV) formation was found to strongly depend on applied cell voltage, nitric acid concentration, temperature, initial concentration of Ce(III) and flow rate of solution recirculation.

The coulombic efficiency of the process increased with increasing applied voltage initially and then decreased with an optimum value of 2.5 V. The oxidation rate was found to be mass transfer controlled under the experimental conditions of flow rates studied. The above investigation lead to the optimum conditions of 1 M Ce(III), 5 M nitric acid, 2.5 V, 90 °C and a recirculation solution flow rate of 100 mL/min based on current efficiency.

Phenol mineralization experiments were carried out under the optimum cell conditions for Ce(IV) production. The destruction efficiency of 75% based on CO₂ production was achieved during continuous organic feeding with *in situ* Ce(IV) regeneration. The destruction efficiency of the direct electrochemical oxidation of phenol was nearly 3 times less than MEO. It was also observed that Ce(IV) could be easily regenerated during the organic addition implying that the DSA electrodes can be used in the cell construction for MEO applications.

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