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Cerium(IV)-mediated electrochemical oxidation process for destruction of organic pollutants in a batch and a continuous flow reactor

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Abstract−The mediated electrochemical oxidation (MEO) process with Ce(IV) and nitric acid as the oxidizing medium was employed for the destruction of various model organic pollutants in batch and continuous organic feeding modes. A near complete destruction was observed for all the model organic pollutants studied. The effects of organic concentration, temperature, concentration of Ce(IV), concentration of nitric acid and feeding time on the organic destruction efficiency were investigated. Under the experimental conditions of 80 °C and 0.95 M Ce(IV) in 3 M nitric acid, nearly 90% destruction was achieved based on CO_2 production and 95% based on TOC and COD nearly for all the organic compounds studied in batch organic addition. In the case of continuous organic addition with *in situ* electroregeneration of Ce(IV) by the electrochemical cell a good destruction efficiency was obtained. For long term organic feeding (120 min) the destruction efficiency was found to be 85% based on CO_2 evolution and 98-99% based on TOC and COD analyses. A model was proposed for calculating the CO_2 formation constant during the continuous process of organic addition. The model predicted a steady state CO_2 evolution pattern for the destruction process during continuous organic feeding. The experimental results obtained confirmed the predicted trends for the destruction process. The changes in enthalpy, entropy, activation energy and free energy for EDTA degradation were found to be 26.7 kJ/mol, −230 J/(mol·K), 29.7 kJ/mol, and 118 kJ/mol respectively.

Key words: Mediated Electrochemical Oxidation, Electrochemical Cell, Cerium(IV), Organic Destruction

INTRODUCTION

The mediated electrochemical oxidation (MEO) process was originally developed for the dissolution of radioactive materials such as plutonium oxide in nuclear waste processing units [1,2]. But later this process turned out to be an excellent treatment method for the destruction of organic pollutants and waste streams including POP's and dioxins [3-6]. The United Nations Environmental Programme (UNEP) [7] identifies this process as one of the most promising future technologies. Steele [8] reviewed the early developments of this process and explained the role of Ag(II) as the mediator ion and Nelson [5] reviewed the commercially developed installation for organic destruction with Ce(IV) as a mediator ion in nitric acid. The main advantages of the MEO process are the optimum working conditions of ambient temperature (less than 100 °C) and pressure; the products formed are only CO_2 and water; and the regeneration and reuse of the oxidant within the system thus minimizing the production of secondary wastes [9].

In the MEO process an electrochemically oxidized metal ion (in an acidic medium) is used as an oxidant [8,10,11]. This mediator ion in acidic medium completely destroys virtually any organic material that comes in contact with it in a totally enclosed chamber without any harmful emissions. During organic destruction metal ions are reduced to their original state and again reoxidized *in situ* by the electrochemical cell, thus forming a closed loop. The net result is the utilization of electrical energy for the destruction of organics. The organic compounds are completely oxidized to CO_2 and water and usually little CO are also formed [12]. The inorganic atoms present in the wastes are converted to the corresponding oxides.

The core component of the MEO system is an electrochemical cell. The construction and working of laboratory scale electrochemical cells for metal ion oxidation with various electrode materials and cell configurations have been reported for cerium [13,14]. Although several metal ions are available for use in the MEO process, cerium is preferred because of good oxidizing behavior (E^o=1.62 V vs NHE) [15] and less water oxidation. Nitric acid is chosen as the electrolyte medium since it has low viscosity, good solubility towards the cerium salts and also a good oxidizing agent by itself towards organics [16].

Since the main objective of the MEO process in the environmental research is to convert organic compounds into carbon dioxide and water, the efficiency of the process can be estimated based on CO_2 production. Many researchers have reported the measurement of CO_2 in MEO processes [3,9,12,17-22]. In the literature on MEO processes reported so far, only the final destruction efficiencies of the organics are given and the available data are too abstract [4,15,17]. There seems to be no report available on the actual destruction efficiencies of organic compounds with time in the case of continuous organic feeding. Although concentrated chemicals and slurries were the targets of destruction in the MEO processes in the present investigation, only aqueous solutions were used [5]. Since the intention was to obtain CO_2 pattern with respect to time and to compare it with the stoichiometric value, solutions of organics with known concentration were employed in this study. We have previously reported the Ce(III) oxidation kinetics in nitric acid medium using electrochemical cell and the destruction of phenol in a batch reactor without simultaneous regeneration of Ce(IV) [14].

The objectives of the present investigation were (i) to study the

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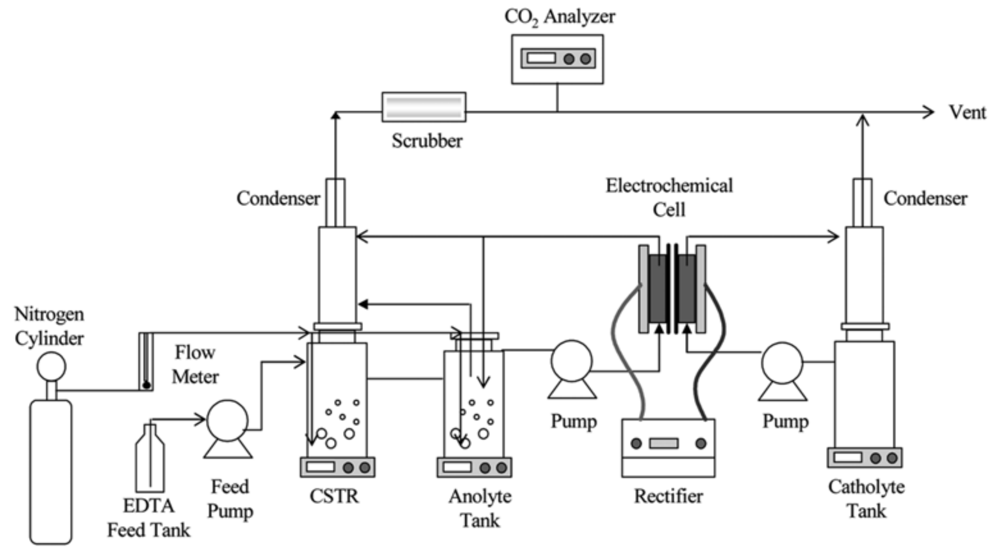

Fig. 1. Schematic diagram of MEO process setup.

destruction of various model organic pollutants such as EDTA, phenol and aniline in batch organic addition mode and to find the effect of various system parameters on the destruction efficiency; (ii) to find the destruction efficiencies of EDTA, phenol, benzoquinone, hydroquinone, catechol, maleic acid and oxalic acid during the continuous organic addition mode with *in situ* Ce(IV) regeneration at various initial Ce(IV) concentrations, and temperatures, (iii) to propose a mathematical model for the calculation of rate constant for the organic destruction in continuous organic addition mode and to calculate the thermodynamic parameters, and (iv) to observe the performance of the electrochemical cell for Ce(IV) regeneration under constant current mode during the organic destruction.

THEORY

The MEO process involves the following reactions:

(i) The electrochemical generation of Ce(IV) oxidant at anode:

$$2[Ce(NO_3)_6]^{3-} \rightarrow 2[Ce(NO_3)_6]^{2-} + 2H^+ + 2e^-$$

(ii) The cathode reaction is the reduction of nitric acid to nitrous acid:

$$2H^+ + 2e^- + HNO_3 \rightarrow H_2O + HNO_2$$

(iii) The destruction of organic compounds (e.g. for phenol) by the produced Ce(IV) oxidant:

$$28[Ce(NO_3)_6]^{2-} + C_6H_5OH + 11H_2O \rightarrow 28[Ce(NO_3)_6]^{3-} + 6CO_2 + 28H^+$$

Overall, there is no consumption of either cerium or nitric acid in the net reaction. The protons are formed in the anolyte but are consumed in the catholyte. So for organic destruction the only consumables are electric power and the oxygen or air used for nitric acid regeneration in the catholyte.

EXPERIMENTAL

1. Experimental Set Up

The overall schematic diagram of the continuous MEO process is shown in Fig. 1. The system consisted of an anolyte tank, a catholyte tank and a reactor, each with a capacity of 1.5 L coupled to an electrochemical cell. The electrolyte used as the anolyte was 1 M Ce(III) nitrate in 3 M nitric acid and as the catholyte 4 M nitric acid. The catholyte vessel was provided with a gas scrubber to convert the nitrous oxide vapors into nitric acid. The anolyte and catholyte solutions were circulated through the cell by using magnet pumps. The dimensions and characteristics of the electrochemical cell are previously reported [14,23]. The cell was operated under a constant current of 10 A throughout all the experiments.

2. Organic Destruction

The organic destruction experiments were carried out in a continuous stirred tank reactor (CSTR), which was attached with the electrochemical cell through the anolyte tank. The reactor and anolyte tanks were filled with 2.5 L of 1 M Ce(III) in 3 M nitric acid solution and Ce(III) was oxidized to Ce(IV) before starting the organic addition. The organic solution was continuously fed at a fixed rate (3 ml/min) and for a fixed duration (30 min) to the CSTR by means of a peristaltic pump. The flow rate of the oxidant solution and organic feed was fixed in such a way that the majority of organic destruction occurred in the CSTR and the exposure of the cell components to the organic was minimized. Also, the rate of organic addition was matched to the rate of Ce(IV) regeneration. A packed bed column which was placed above the CSTR with a down flow of Ce(IV) solution ensured the effective destruction of any gaseous organic components present in the off gas. The dilution of oxidant solution by the added organic was balanced by capturing the water vapor from the anolyte tank. Since the concentration of nitric acid is well below its azeotropic point, the vapor condensed was found to be rich in water with very little acid. This acid loss was compensated manually only for 120 min. EDTA feeding experiment. The reaction was carried out under specific temperatures by using a thermostatic control.

3. Liquid Phase Analysis

The samples at different time intervals were taken and analyzed for total organic carbon content with a TOC analyzer (Shimadzu

TOC-5000A). The concentration of Ce(IV) ion in the solution during the organic destruction was also measured from the redox potential. From the stoichiometric amount of Ce(IV) consumed, the extent of organic destruction was calculated. COD_{Cr} was measured with a COD reactor and spectrometer by using HACH procedure.

4. Gas Phase Analysis

The concentration of carbon dioxide produced during the organic decomposition was measured continuously with a CO_2 analyzer (Environmental Instruments, Anagas CD 98). Carbon dioxide formed was purged by the carrier gas stream (nitrogen) and taken to the analyzer. 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.

RESULTS AND DISCUSSION

1. Destruction of Organics in Batch Process

The overall stoichiometric equations for the organic destruction by Ce(IV) oxidant for various organics are given in Table 1. The batch process was carried out with phenol and aniline as the target organic pollutants, and in this case the previously prepared Ce(IV) in nitric acid (oxidant solution) was first heated to the reaction temperature and then mixed with a specific volume of concentrated organic solution which was added so as to get the desired concentrations of both Ce(IV) and organic. The destruction was monitored by measuring the CO_2 in the off gas stream and also by TOC or COD analyses of the liquid samples.

Table 1. The overall stoichiometric equations for Ce(IV) mediated destruction of various organics

Organic	Reactants			Products		
	Organic	Ce(IV)	H_2O	CO_2	Ce(III)	H^+
Phenol	C_6H_6O	28	11	6	28	28
Benzoquinone	$C_6H_4O_2$	24	10	6	24	24
Hydroquinone	$C_6H_6O_2$	26	10	6	26	26
Catechol	$C_6H_6O_2$	26	10	6	26	26
Maleic acid	$C_4H_4O_4$	12	4	4	12	12
EDTA	$C_{10}H_{14}O_8N_2Na_2$	40	12	10	40	38

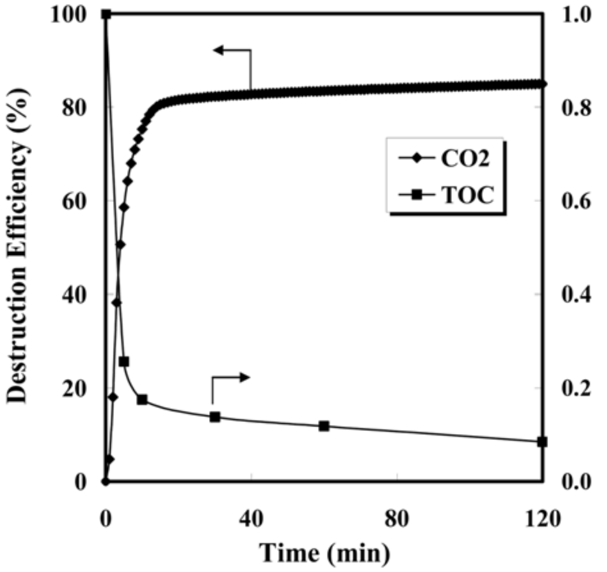

Fig. 2. Destruction efficiency from CO_2 and C/Co from TOC results vs. time for the destruction of phenol in the batch MEO process (Experimental conditions: [Phenol]: 250 ppm; [Ce(IV)]: 0.95 M; [HNO_3]: 3 M; Temp.: 80 °C).

1-1. Effect of Organic Concentration

In Fig. 2 the variation of destruction efficiencies based on CO_2 and TOC for phenol (250 ppm) at 80 °C obtained with 0.95 M Ce(IV)

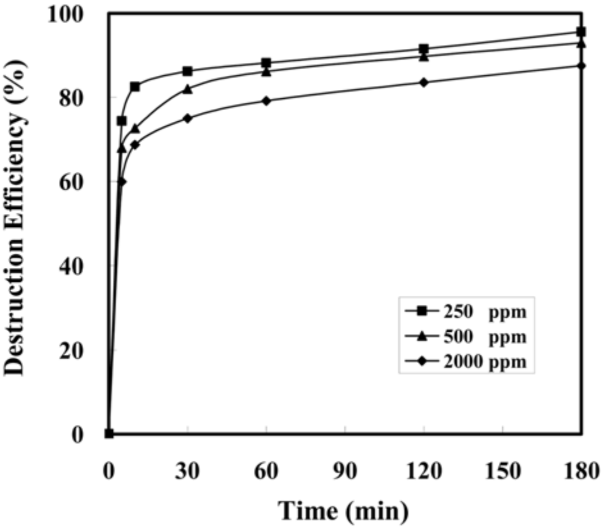

Fig. 3. Destruction efficiencies from TOC results for different initial concentrations of phenol in the batch MEO process (Experimental conditions: [Ce(IV)]: 0.95 M; [HNO_3]: 3 M; Temp.: 80 °C).

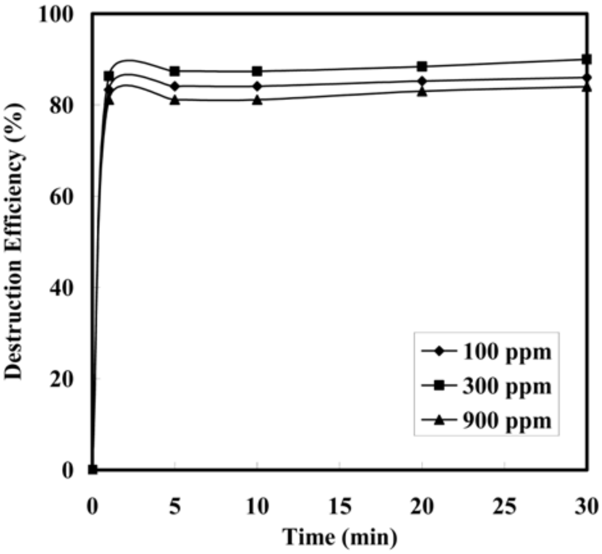

Fig. 4. Destruction efficiencies from COD results for different initial concentrations of aniline in the batch MEO process (Experimental conditions: [Ce(IV)]: 0.95 M; [HNO_3]: 3 M; Temp.: 80 °C).

3 M nitric acid is shown. In Figs. 3 and 4 the destruction efficiencies at various initial concentrations of phenol and aniline at 80 °C are shown. It was observed that the degradation of phenol takes place quickly during the initial stages but a near complete destruction was achieved after 3 h. The higher initial concentration of phenol was found to undergo relatively lesser destruction, whereas at the lower initial concentrations a near complete destruction was achieved. It can also be observed from the CO_2 and TOC results that a maximum destruction occurs within 10 min nearly in all cases. A close proximity between these two analyses clearly shows that the MEO process is more efficient for a wide range of organic concentrations. Although the amount of CO_2 formed was not sufficient to account for complete destruction, the TOC analyses showed no remaining organic in the liquid phase. A similar observation was noted by Balazs et al. [9] during the destruction of a range of organic materials by Ag(II)-MEO process and explained that this difference might arise due to the volatilization of organics before complete destruction.

1-2. Effect of Temperature

The effect of temperature on the destruction efficiencies at a fixed initial phenol concentration of 500 ppm was investigated. At 50 °C, a dark brown material was found floating on the solution surface, which might have resulted due to the incomplete destruction. A similar case was observed by Chiba et al. [17] during the destruction of trimsol oil by MEO process using silver mediator ion at room temperature. At the higher temperatures of 70-90 °C the destruction efficiency was found to be 90-95%. This is about 12-17% higher compared to 50 °C. It was observed that above 70 °C the added phenol completely disappeared within a short period of less than 10 min and no black colored waxy foam was observed on the surface.

1-3. Effect of Initial Cerium(IV) Concentration

The effect of initial Ce(IV) concentration on aniline (300 ppm) degradation was studied to unveil the effect of oxidant concentration on the organic destruction. It was seen that the enhancement in the destruction efficiency was nearly 20% between 0.5 M and 0.95 M Ce(IV) concentrations. The redox potentials measured during the reaction clearly showed a rapid 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 beginning stage of the reaction itself.

1-4. Effect of Nitric Acid Concentration in the Anolyte

A small variance in the destruction efficiency of ca. 3-5% was observed within the range of 2-3.5 M nitric acid concentration. Since Ce(IV) concentration was high it strongly oxidized any organic molecule by its highly favored electron releasing tendency. Therefore, this observed increase in the oxidizing ability of the medium might be due to the combined effect of both Ce(IV) and nitric acid and might not be solely expected from increase in nitric acid concentration.

Table 2. Destruction of various organics by continuous MEO process at 80 °C ([Ce(IV)]: 0.95 M; [HNO_3]: 3 M; Temp.: 80 °C; Feed rate: 3 ml/min)

Organic compound	[Organic] (ppm)	D.E. based on CO_2 (%)	D.E. based on TOC (%)
Phenol	10,000	89.9	99.2
Benzoquinone	2,500	90.6	95.0
Hydroquinone	10,000	93.3	99.0
Catechol	10,000	91.4	99.4
Maleic acid	10,000	99.2	99.0
Oxalic acid	10,000	88.5	99.5
EDTA	25,000	89.8	98.8

2. Continuous Process of Organic Destruction

The destruction experiments in continuous process mode were performed with several organics like EDTA, phenol, benzoquinone, hydroquinone, catechol, maleic acid and oxalic acid at a fixed mediator concentration of 0.95 M Ce(IV) at 80 °C. The feed concentrations, destruction efficiency values based on CO_2 and TOC are given in Table 2. The evolution patterns of CO_2 and CO versus time

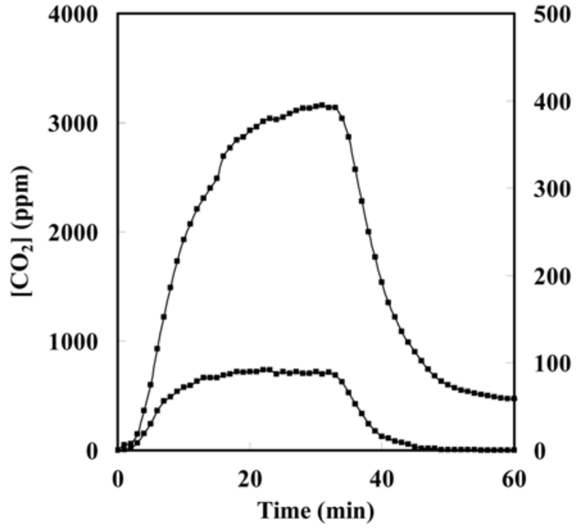

Fig. 5. Real time evolution of CO_2 and CO during the destruction of benzoquinone in the continuous MEO process (Experimental conditions: [BQ]: 2,500 ppm; [Ce(IV)]: 0.95 M; [HNO_3]: 3 M; Temp.: 80 °C; Feed duration: 30 min; Feed flow rate: 3 ml/min).

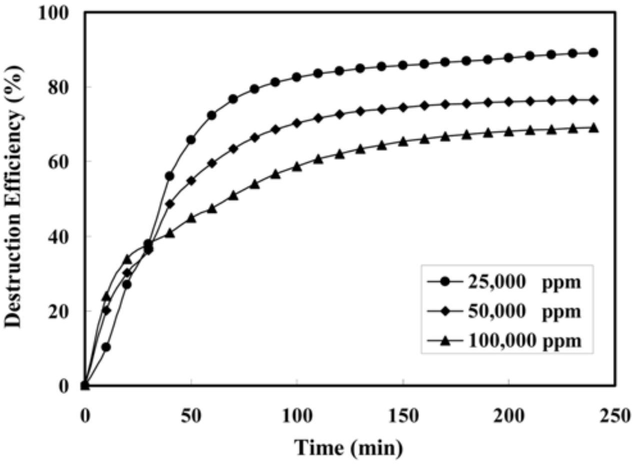

Fig. 6. Destruction efficiency of EDTA from CO_2 data at different feed concentrations during the continuous MEO process (Experimental conditions: [Ce(IV)]: 0.95 M; [HNO_3]: 3 M; Temp.: 80 °C; Feed duration: 30 min; Feed flow rate: 3 ml/min).

for the destruction of benzoquinone are shown in Fig. 5. In Fig. 6, the destruction efficiencies for different initial concentrations of EDTA with time are shown. It was observed from the CO_2 evolution patterns of various organics that even after the organic feeding was stopped the CO_2 evolution continued up to several hours. The maximum CO_2 evolution ceased at around 60 min in almost all cases with 30 min feed duration and then a small quantity of CO_2 evolution was continued up to 240 min to reach a negligible minimum value. This kind of behavior was also observed previously during the destruction of phenol by batch MEO process [14]. From the destruction reaction of several organics in batch and in continuous processes, it was observed that a major portion of the reaction, i.e., 70-80% of the destruction takes place within several minutes and the remaining 30-20% after several hours. This trend in CO_2 evolution pattern was also reported by Galla et al. [12]. for the destruction of commercial grade pesticides in batch and continuous feeding processes In the batch process they have measured CO_2 till 180 or 300 min to get a near zero value. Therefore, in all experiments of 30 min feeding, the CO_2 was measured up to 240 min in order to calculate the destruction efficiency of the process. In all cases almost 95% destruction was achieved for all the organics in terms of TOC values. This difference between CO_2 and TOC analyses was observed and reported by Balazs et al. [9]. This difference in the two analytical methods may partially be due to the partial oxidation of organics in to CO, which was observed for all organic compounds investigated. Also, it was observed in all cases that the content of CO was decreased as the temperature of the system increased. The CO accounted for 1-3% nearly in all cases. Despite the differences between the two methods a reasonable agreement in the destruction efficiencies was seen.

2-1. Effect of Initial Ce(IV) Concentration in the Continuous Process

Since a high Ce(IV) concentration gave maximum destruction in batch reaction for all experiments in continuous organic addition mode, a high oxidant concentration was maintained. A similar trend was observed as in the case of batch reaction with phenol as the target organic [14]. But an important thing to be noted here is that in the continuous process the Ce(IV) regeneration is carried out *in situ* by the electrochemical cell, and at 0.7 or 0.8 M Ce(IV) concentration the regeneration was found to be good at the applied cell current of 10 A compared to 0.95 M Ce(IV). But in the case of 0.95 M the maximum CO_2 evolution was attained within 100 min compared to 0.8 M (160 min) and 0.7 M (180 min).

2-2. Effect of Temperature

The effect of temperature for the destruction of phenol is shown in Fig. 7. It is evident that the maximum destruction was found at 95 °C than at 70 and 80 °C. At the highest studied temperature of 95 °C the destruction took place more rapidly as observed from the CO_2 evolution, and maximum destruction efficiency was observed in 70 min compared to 70 or 80 °C. Although the maximum destruction was obtained at 95 °C, all destruction experiments were carried out at 80 °C to minimize the evaporation rate of water and to maintain the acidity of the oxidant solution throughout the reaction. Chiba et al. [17] have reported that as the temperature was increased the coulombic efficiency of the system for organic destruction was also found to increase.

3. Kinetics of Organic Destruction

The rate of forward reaction for organic destruction can be represented as follows:

$$\text{Rate} = -\frac{dC_{org}}{dt} = k_1[\text{organic}][\text{Ce(IV)}][H_2O] \quad (1)$$

When the concentration of Ce(IV) and water are in large excess, then the pseudo-first order kinetics can be applied to the above rate equation.

$$\text{Rate} = -\frac{dC_{org}}{dt} = k[\text{organic}] \quad (2)$$

Where, $k=k_1[\text{Ce(IV)}][H_2O]$=constant;

The rate of forward reaction can also be described through the

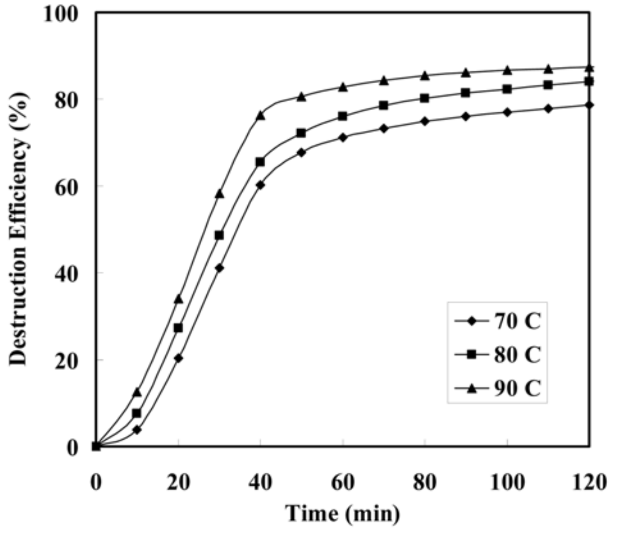

Fig. 7. Variation of temperature on the destruction efficiency of phenol in the continuous MEO process from CO_2 data (Experimental conditions: [Phenol]: 10,000 ppm; [Ce(IV)]: 0.95 M; [HNO_3]: 3 M; Feed duration: 30 min; Feed flow rate: 3 ml/min).

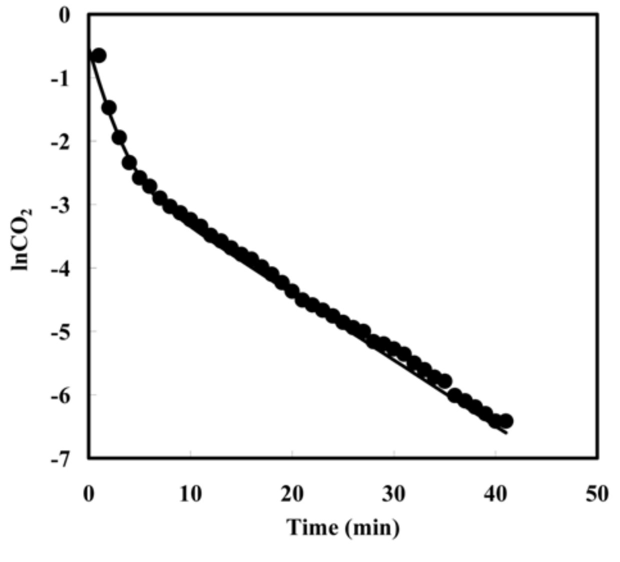

Fig. 8. Plot of $\ln CO_2$ vs time for the destruction of EDTA in batch MEO process (Experimental conditions: [EDTA]: 500 ppm; [Ce(IV)]: 0.90 M; [HNO_3]: 3 M; Temp.: 80 °C).

changes of concentration of products like CO_2:

$$\mathrm{Rate} = -\frac{dC_{org}}{dt} = \frac{1}{n}\frac{dX}{dt} = k\left(C_o - \frac{X}{n}\right) \tag{3}$$

The integral form of this equation can be written as follows:

$$X = X_o \cdot (1 - \exp^{(-k \cdot t)}) \tag{4}$$

The differential form of Eq. (4) for the product can be given as follows:

$$\frac{dX}{dt} = X_o k \exp^{(-kt)} \tag{5}$$

The above equations were used for the batch process of organic destruction and the plot of lnC vs time is shown in Fig. 8 for the destruction of EDTA in batch organic addition mode.

For continuous type organic addition the amount of organic added, reacted and products formed, and the remaining organic left behind in the solution must be calculated to predict the CO_2 evolution pattern and hence the pseudo first order CO_2 formation constant (k). The modeling approach for this type of calculation to find the actual concentration changes of reactants inside the system is described in brief. The experimental values of CO_2 analyzer in ppm are converted to volume in liters by taking into account the carrier gas flow rate at each interval of time. In Fig. 9, one of the experimental data for CO_2 formed is shown for 2.5% EDTA (flow rate 3 ml/min), at 80 °C with 0.95 M Ce(IV) in 3 M nitric acid. For the same concentration of organic and feed flow rate several modeling curves were obtained by using different arbitrarily chosen 'k' values. As can be seen in Fig. 9, a good enough agreement is seen between the experimental data and modeling, but during the organic addition the curve is more close to the modeling and after stopping organic some discrepancy is seen between the two; the experimental points change more sharply and the modeling curve is smoother.

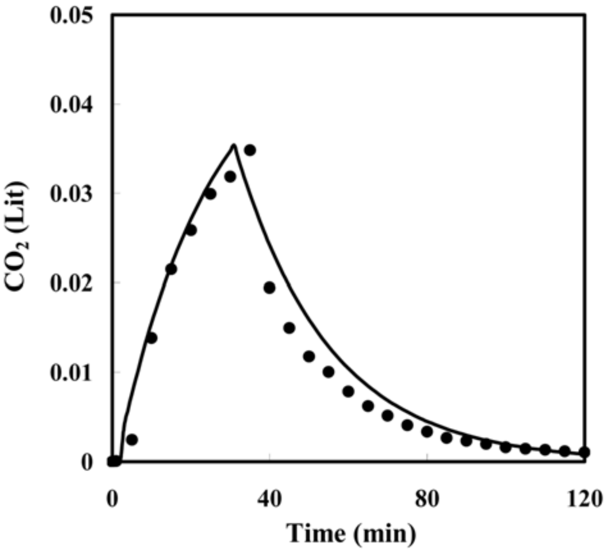

Fig. 9. Profiles of CO_2 evolution vs. time for the prediction based on the proposed procedure (solid line) and experimental values (points) (Experimental conditions: [EDTA]: 25,000 ppm; [Ce(IV)]: 0.95 M; [HNO_3]: 3 M; Feed duration: 30 min. Temp.: 80 °C; Feed flow rate: 3 ml/min).

Table 3. Pseudo first order rate constants for EDTA destruction obtained during the continuous organic feeding mode (Conditions: Feed time: 30 min.; Flow rate: 3 ml/min; [EDTA]: 2.5%)

No.	Anolyte Composition		Temp. (K)	k *10^4 (s^{-1})
	[HNO_3] (M)	[Ce(IV)] (M)*		
1	2.0	0.95	353	5.0
2	3.0	0.70	353	3.5
3	3.0	0.80	353	4.5
4	3.0	0.95	343	6.0
5	3.0	0.95	353	7.0
6	3.0	0.95	368	1.2

*Total concentration of Ce(III)+Ce(IV) is 1.0 M.

The 'k' value with minimum difference by LSM, which differs not more than 10% (relative), was chosen as the closest one with experiment. This procedure was used to obtain the CO_2 formation constants for all the experimental conditions of continuous organic feeding and presented in Table 3.

In Table 3, the various 'k' values obtained from the modeling fitting to the experimental data at different experimental conditions are presented. The concentration of Ce(IV) varied from 0.7-0.95 M with total cerium concentration of 1 M. The values of 'k' range from 3.5×10^{-4} to 1.2×10^{-3} for the overall process condition changes including the temperature dependence in the range 343-368 K. But between 0.7 and 0.8 M Ce(IV) concentration the reaction rate constant decreases nearly 2 times. The 'k' values for the temperature range 343-368 K were used to calculate the thermodynamic parameters at transition state according to Eyring's equation.

4. Evaluation of Thermodynamic Parameters for Organic Destruction

The graph of ln(k/T) vs (1/T) was plotted. From the slope, enthalpy change (26.7 kJ/mol), activation energy (29.7 kJ/mol) and from the intercept entropy change (−230 J/mol K) were calculated.

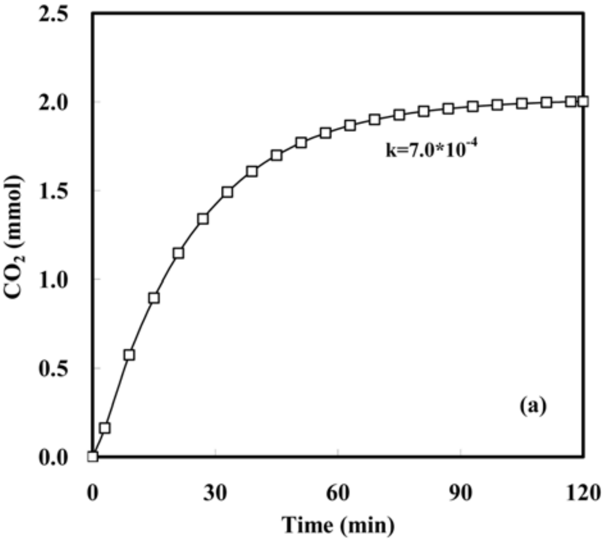

Fig. 10. Predicted curve for 2 hour organic feeding (based on the k value obtained for the conditions shown under Fig. 13).

These data were used to calculate the Gibbs free energy change (118 kJ/mol) of the destruction process at 353 K. The obtained values are comparable to the one reported by Lehmani et al. [24] for the oxidation of organics by Ag(II)-MEO process.

5. Long Term Organic Feeding

The model suggested before to obtain the rate constant was applied to the experimental conditions of 30 min feeding time. But in real applications long time feeding is needed (hours, days etc.), and during long term feeding the organic should not accumulate in the system and should be completely and constantly destroyed upon feeding. Therefore, in the destruction process some steady state regime should come into existence. So the model was tested for much longer time periods and the modeling curve is presented in Fig. 10 for 2 hr taking the k value 7.0×10^{-4} (the same experimental conditions as shown in Fig. 9). It can be seen that the model predicts a steady state CO_2 evolution pattern for continuous organic feeding. The subsequent experimental results obtained confirmed the model predictions.

6. Electrochemical Cell Efficiency during the Organic Destruction

The performance of the electrochemical cell for mediator regeneration was observed during the organic destruction experiments. The coulombic efficiency, which refers to the theoretical amount of electric charge needed to destroy the organics versus actually spent, was calculated during each destruction reaction. The efficiency of the cell for regenerating Ce(IV) is usually affected by the concentration of organics and initial Ce(IV) taken, and temperature. Among them the effect of Ce(IV) concentration on coulombic efficiency is an important consideration.

The effect of mediator concentration on coulombic efficiency was studied for three initial Ce(IV) concentrations, namely 0.7, 0.8 and 0.95 M. It was observed that the maximum coulombic efficiency was obtained for 0.7 M, compared to 0.8 M and for 0.95 M the minimum coulombic efficiency was obtained. Although a good destruction efficiency was obtained with 0.95 M Ce(IV) considering the coulombic efficiency, 0.7 M Ce(IV) was found to be the optimum oxidant concentration for continuous operation.

7. Reactivation of Electrodes

The resistance of the electrodes of the electrochemical cell was found to be increased during the continuous process of organic destruction due to the presence of small portion of remaining organics. At constant current mode, an increase in the voltage of the cell implies that the resistance of the electrode increases due to adsorption of the organic material on the electrode surface [25,26]. This contamination was minimized and electrodes were reactivated by circulating 2% nitric acid for 60 min. After the acid treatment the resistance of the cell was found to be decreasing and the I-V response of the electrodes regained. The maintenance of the electrode activity is crucial in the continuous process of organic addition and further studies are being carried out to optimize the system for minimizing the electrode contamination.

CONCLUSIONS

The mediated electrochemical oxidation process was successfully developed with Ce(IV) as the mediator ion in nitric acid medium and applied for the destruction of various organic compounds in batch and continuous organic feeding modes. Organics such as phenol, benzoquinone, hydroquinone, catechol, maleic acid, oxalic acid and EDTA were destroyed almost completely based on CO_2 and TOC analyses. The effects of various parameters such as the concentration of organics, temperature, concentrations of Ce(IV) and nitric acid and feeding time were studied. It was found that nearly 95% destruction took place within 10 min in the case of batch organic feeding mode. In the case of a continuous process the optimum conditions for maximum destruction of the organic compound were observed to be the following: 0.7 M Ce(IV), 3 M nitric acid, and 95 °C. The performance of the electrochemical cell was observed based on the rate of Ce(IV) regeneration and coulombic efficiency under a constant cell current of 10 A. A coulombic efficiency of 80-92% was obtained during the organic destruction in all cases. The high coulombic efficiency showed that an electrochemical cell with IrO_2/Ti DSA electrodes is ideally suitable for the MEO system. Further experiments are being carried out to check the destruction efficiency of various concentrated organics. The pseudo first order rate constants were evaluated by using a simple model proposed for the continuous organic feeding process based on CO_2 evolution and were used to calculate the thermodynamic parameters.

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NOMENCLATURE

C_{org} : concentration of the organic [M]
t : time [sec]
X : concentration of the product [M]
k : pseudo-first order rate constant [s^{-1}]
n : stoichiometric coefficient
E : activation energy [kJ mol^{-1}]

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