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Destruction of organic pollutants by cerium(IV) MEO process: A study on the influence of process conditions for EDTA mineralization

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Abstract

The mediated electrochemical oxidation (MEO) process with cerium(IV) and nitric acid as the oxidizing medium was employed for the destruction of various model organic pollutants in continuous organic feeding mode. A near complete destruction was observed for all the organics studied. The effects of various experimental conditions were evaluated with respect to EDTA mineralization. The key parameters varied in the process were concentration of EDTA (67–268 mM), temperature (70, 80 and 95 °C), concentrations of Ce(IV) (0.7, 0.8 and 0.95 M), nitric acid (2, 3 and 4 M) and duration of organic addition (30 and 120 min). 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 analyses for all the organic compounds studied. The *in situ* regeneration of mediator ion by the electrochemical cell was found to be good during the organic destruction within the range of experimental conditions studied. In the case of long term organic feeding (120 min) the destruction was calculated after the CO_2 evolution attained the steady state and under this condition the destruction efficiency was found to be 85% based on CO_2 evolution.

Keywords: Mediated electrochemical oxidation; Electrochemical cell; Cerium; Organic destruction; EDTA mineralization

1. Introduction

The development of mediated electrochemical oxidation (MEO) process dates back to late 1980s when the process originally intended 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 persistent organic pollutants (POP's) [3,4]. This process is identified as one of the most promising future technologies by the United Nations Environmental Program (UNEP) [5]. Steele [6] reviewed the early developments of this process with respect to silver mediator and Nelson [7] reviewed the applications of the commercially developed installation for organic destruction with cerium mediator in nitric acid. 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_2 and water; and regeneration and reuse of the oxidant, minimizing the production of secondary wastes [8].

In the MEO process, an electrochemically generated metal ion is used as an oxidant [9]. This mediator ion in acidic medium destructs virtually any organic material comes in contact with it completely, in a totally enclosed chamber without any harmful emissions. 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 organic destruction metal ions are reduced to their original state and again reoxidized 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 [10]. The inorganic atoms present in the wastes are converted to corresponding oxides.

The core component of the MEO system is an electrochemical cell. The electrochemical cells for metal ion oxidation with

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various electrode materials and cell configurations have been reported for different metal ions [11,12]. Although several metal ions are available for use in MEO system cerium is preferred in our studies due to the following reasons: it possesses good oxidizing behavior due to its high redox potential ($E^\circ = 1.62$ V) [7]; the rate of water oxidation is less which is an unwanted reaction and reduces the activity of mediator ion; it does not form precipitate with chlorine containing compounds; it can be recovered and reused without much loss.

The selection of an acid is very important and plays a key role as the coulombic efficiency of the electrochemical cell depends on the viscosity of the acid employed and hence its mass transfer coefficient. Also, the solubilizing capacity of the acid towards the metal salt is an important consideration. Sulphuric acid possesses low solubility [13], and moreover, can be used only for partial oxidation of organics. Perchloric acid is explosive in nature. Hydrochloric acid cannot be used because of instability of chloride ion. Therefore, in this study nitric acid is employed which has low viscosity, good solubility towards cerium salts and also it is a good oxidizing agent by itself towards organics [14].

The MEO process finds application in synthetic organic chemistry as well as in environmental pollution abatement. The main objective in environmental research is to convert organic compounds into carbon dioxide and water [15–21]. 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. Zoher Chiba [22] reported on the destruction of Trimsol, a cutting oil of mixed waste processing and cellulose by silver and cobalt mediated electrochemical oxidations using continuous CO_2 measurements. Balazs et al. [8] reported on the bench scale destruction of a number of organics by silver and cobalt MEO processes through continuous CO_2 monitoring. They stated that CO_2 produced was insufficient to account for complete destruction eventhough TOC showed absence of any organic in the anolyte. Galla et al. [10] evaluated the silver mediated destruction of pesticides on a lab scale as well as semi-technical pilot plant through online CO_2 measurements in the off gas and calculated the destruction efficiencies and coulombic efficiencies of the system. As understood from the literature on MEO processes, an organic is destructed to CO_2 not by simple one step conversion but a series of intermediates adopting many reaction pathways [23]. Although studies on intermediate analyses had been carried out to trace the actual rate of formation and decomposition of a particular species it was felt difficult to arrive at a solid conclusion about mechanistic reaction pathway of destruction. This kind of study on quantitative intermediate analysis with modeling was attempted by Farmer et al. [23] for the destruction of ethylene glycol and benzene by silver(II) in nitric acid. Therefore, it is evident from these literature reports that following the rate of destruction of an organic compound through concentration changes of the reactants or intermediates is tedious and cumbersome. But, the kinetics of the intended product, i.e. CO_2 could be followed by continuous measurement in the off gas stream and the quantum of CO_2 produced can be utilized for the calculation of destruction efficiency and columbic efficiency of the process.

In the literature on MEO process reported so far, only the final destruction efficiencies of the organics were given and the available data were too abstract [7,10,23]. There seems to be no report available on the actual destruction efficiencies of organic compounds with time in case of continuous organic feeding. In this laboratory, we have developed a bench scale MEO system for organic destruction and the results obtained are presented in this paper. Although concentrated chemicals and slurries were the targets of mineralization in MEO process, in the present investigation only aqueous solutions were used. Since the intention was to obtain CO_2 pattern with respect to time and to compare it with theoretical value, solutions of organics with known concentration were employed in this study. In our previous report, we have documented the destruction of phenol by MEO process in a batch reactor with one time organic addition without simultaneous regeneration of Ce(IV) [24].

The objectives of the present investigation were (i) to study the destruction of various model organic pollutants such as EDTA, phenol, benzoquinone, hydroquinone, catechol, maleic acid and oxalic acid during 30 min continuous organic addition mode; (ii) to find out the destruction efficiency for EDTA under various process conditions such as concentration of EDTA, concentrations of cerium(IV) and nitric acid, temperature, and feeding time and (iii) to observe the performance of the electrochemical cell for Ce(IV) regeneration under constant current mode during the organic destruction.

2. Experimental

2.1. Materials

Cerium(III) nitrate hexahydrate (Terio Corporation, China), phenol, ethylenediaminetetraacetic acid disodium salt dihydrate (Daejung chemicals and metals Co. Ltd., Korea), Benzoquinone (Acros Organics, Belgium), hydroquinone (Yakuri, Japan), catechol, maleic acid, oxalic acid (Junsei Chemical Co. Ltd., Japan), and nitric acid (60%) (Sam Chun Chemicals, Korea) were used as received.

2.2. Methods

2.2.1. Cerium(IV) production

The overall schematic diagram of the continuous MEO process is shown in Fig. 1. The system consisted of an anolyte, a catholyte and a reactor, each with a capacity of 1.5 L coupled to an electrochemical cell. The electrolyte used in the anolyte was 1 M Ce(III) nitrate and 3 M nitric acid and in the catholyte 4 M nitric acid was taken. 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 using ceramic pumps.

The dimensions of the electrochemical cell are given in Table 1 [25]. The cell consisted of an anode and cathode separated by a Nafion® 324 membrane. The anode and cathode were respectively made of IrO_2/Ti and Ti mesh type DSA electrodes. The role of the Nafion membrane in MEO process is well documented elsewhere [26]. A fluoropolymer sheet (viton) was used

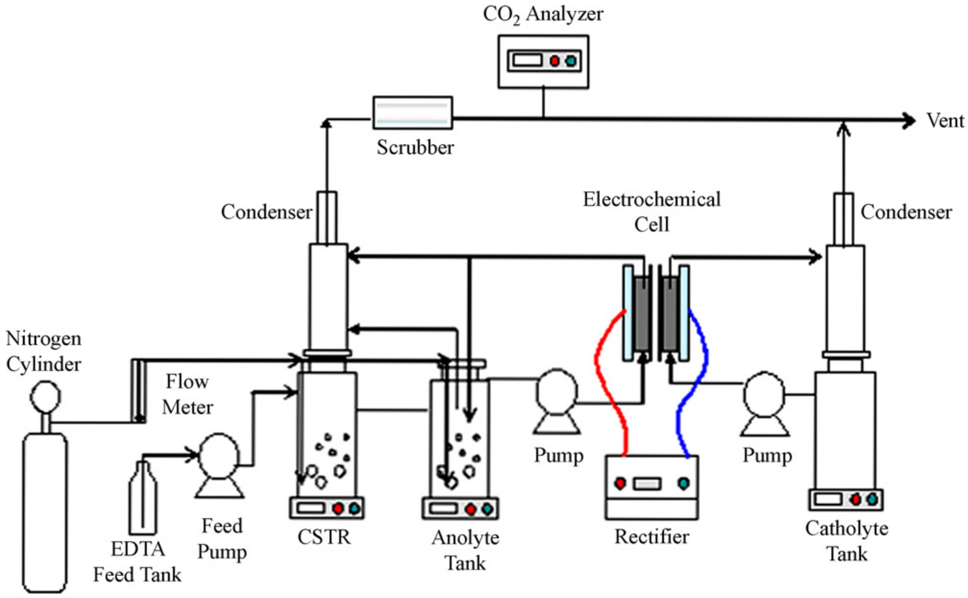

Fig. 1. The schematic diagram of MEO process.

as the separator between the electrodes. The electrochemical cell was operated under a constant current of 10 A, throughout all the experiments.

The concentration of Ce(IV) solution was checked online by measuring the redox potential using an Orion pH/ISE meter (Model no. 720 A, Orion Co. Ltd., USA) with Pt–Ag/AgCl combined electrode [13]. From the measured redox potential, concentration was calculated using a calibration graph. The Ce(IV) concentration was also cross checked at random by potentiometric titration with standard ferrous sulfate [12].

2.2.2. 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 cerium(III) and 3 M nitric acid solution and Ce(III) was oxidized to Ce(IV) before starting organic addition for destruction reaction. 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 dilution of oxidant solution by the added organic was reduced by capturing the water vapor from anolyte tank. Since the concentration of nitric acid is well below its azeotropic point the vapor condensed was richer 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 using a thermostatic control. The concentration of carbon dioxide produced during the organic destruction was measured continuously using a CO_2 analyzer (Environmental Instruments, Anagas CD 98). Carbon dioxide formed was purged by the carrier gas stream (nitrogen with flow rate ~2.0 L/min) and taken to the analyzer. The concentration of CO_2 evolved in terms of ppm was continuously recorded and then converted into volume and was used to calculate the destruction efficiency in terms of CO_2 production. The CO_2 measurements were carried out at room temperature and all gas volume calculations were done at 25 °C. At the end of each experiment the liquid samples were taken and analyzed for total organic carbon content by a TOC analyzer (Shimadzu, TOC-5000A) containing high sensitivity TC catalyst. The percentage of destruction was calculated based on the initial and final TOC values of the organic compounds. The destruction efficiencies were calculated as follows:

$$\text{Destruction efficiency (\% of CO}_2) = \left(\frac{\text{Expt. volume}}{\text{Theo. volume}}\right) \times 100$$

$$\text{Destruction efficiency (\% TOC)} = \left(\frac{\text{Initial TOC}-\text{Final TOC}}{\text{Initial TOC}}\right) \times 100$$

Table 1
Dimensions and characteristics of the electrochemical cell

Parameter	Dimensions and characteristics
Anode area	140 cm^2 (IrO_2/Ti, mesh type)
Cathode area	140 cm^2 (Ti, mesh type)
Anode to membrane gap	2 mm
Volume (each compartment)	70 cm^3
Membrane	Nafion® 324

2.2.3. Ce(IV) regeneration

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 the actually spent, was calculated during each destruction reaction.

Table 2
The mineralization of various organics by cerium(IV) mediated oxidation process at 80 °C ([Ce(IV)] = 0.95 M; $[HNO_3]$ = 3 M; feed rate = 3 mL/min)

Organic compound	Feed concentration		D.E. based on CO_2 (%)	D.E. based on TOC (%)
	(ppm)	(mM)		
Phenol	10,000	106	89.9	99.2
Benzoquinone	2,500	23	90.6	95.0
Hydroquinone	10,000	91	93.3	99.0
Catechol	10,000	91	91.4	99.4
Maleic acid	10,000	86	99.2	99.0
Oxalic acid	10,000	111	88.5	99.5
EDTA	25,000	67	89.8	98.8

3. Results and discussion

3.1. Destruction of various organics

The destruction experiments were performed for EDTA, phenol, benzoquinone, hydroquinone, catechol, maleic acid and oxalic acid with 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 difference in destruction efficiency values observed between CO_2 and TOC estimations. This could be explained as due to the removal of volatile organic carbon at the experimental temperature investigated. Balazs et al. have observed the same trend in the destruction efficiency values between CO_2 and TOC measurements [8]. The evolution pattern for CO_2 and CO versus time for phenol destruction is shown in Fig. 2. It was observed from CO_2 evolution patterns of various organics that though the feeding was stopped at 30th min the evolution continued up to several hours. The maximum CO_2 evolution ceased at around 60 min in all cases and then a small quantity of CO_2 was evolved up to 240 min to reach a negligible minimum value. This kind of behavior was also observed during the destruction of phenol in batch MEO process [24]. In the batch process when the organic was introduced into the system the evolution of CO_2 started immediately and reached a maximum within a few minutes and then decreased to a low level and lasted for several hours to reach negligible levels. The same trend was observed during liquid phase TOC analyses. From the destruction reaction of several organics in batch and in continuous feeding processes it was observed that nearly 70% of the destruction took place within several minutes and the remaining 30% took several hours. Galla et al. have reported the same trend in CO_2 evolution pattern for the destruction of pesticides in batch and continuous feeding MEO processes [10]. 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 duration CO_2 was measured up to 240 min to calculate the destruction efficiency. Almost 95% destruction was achieved for all the organics in terms of TOC values. The difference between CO_2 and TOC analyses were observed and reported by Balazs et al. [8]. The difference in two analyses methods may also partially be due to the partial oxidation of organics in to CO, which was observed for all organic compounds investigated and the content of CO was decreased as the temperature of the system increased. The CO accounted for 1–3% in all cases. Despite the differences between the two analyses methods a reasonable agreement in destruction efficiency values were seen.

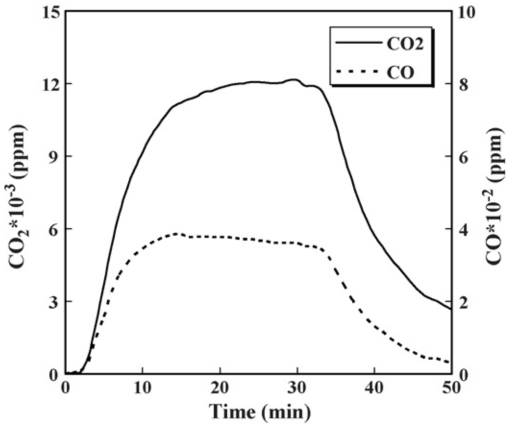

Fig. 2. The real time evolutions of CO_2 and CO obtained during the destruction of phenol by MEO process at 80 °C ([Ce(IV)] = 0.95 M; $[HNO_3]$ = 3 M; [phenol] = 106 mM; feed rate = 3 mL/min; duration of feeding = 30 min).

3.2. Destruction of EDTA

The overall reaction between EDTA and Ce(IV) can be represented as follows (40 electron process).

$$C_{10}H_{14}O_8N_2Na_2 + 40Ce(IV) + 10H_2O \rightarrow 10CO_2 + 40Ce(III) + 38H^+ + N_2 + 2Na^+ \quad (1)$$

The effects of various operating parameters such as the organic feed concentration, the concentrations of nitric acid and cerium(IV), the temperature and the feeding time were evaluated with respect to EDTA destruction.

3.2.1. Effect of EDTA feed concentration

In Fig. 3, the variation of destruction efficiencies with respect to time for 67, 134 and 268 mM EDTA are given. The CO_2 evolution started after 2–3 min of feeding and increased during the feeding duration of 30 min. After EDTA addition was stopped the CO_2 evolution did not decrease immediately but approximately after 3–5 min. Since the destruction efficiency is being calculated based on CO_2 production it was necessary to capture all CO_2 evolved. So, in all cases CO_2 was measured up to 240 min to ensure complete organic destruction. Also it was observed from Fig. 3 that at the end of 30 min

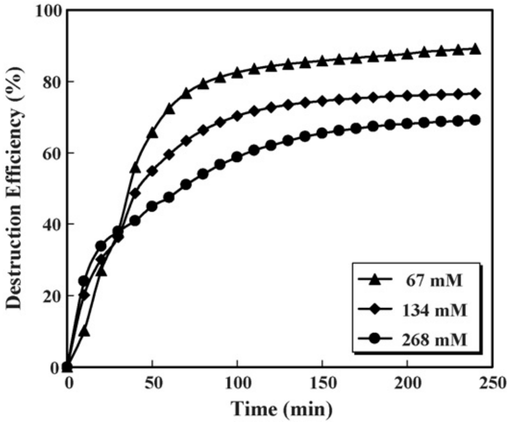

Fig. 3. The destruction efficiencies for various feed concentrations of EDTA vs. time by MEO process at 80 °C ([Ce(IV)] = 0.95 M; [HNO_3] = 3 M; feed rate = 3 mL/min; duration of feeding = 30 min).

nearly 40% destruction efficiency was obtained and the maximum destruction efficiency was obtained nearly after 60 min. It can be seen that though the initial destruction efficiencies are high for higher EDTA concentrations as the time increased the maximum destruction occurred for 67 mM compared to the other two higher concentrations. It is to be mentioned here that 268 mM concentration corresponds to the maximum solubility of EDTA in water (at room temperature) and this highest concentration could be destructed nearly 70% by continuous MEO process. The reason for lowering of destruction efficiency for 268 mM may be due to the reduced Ce(IV) level under the fixed applied cell current of 10 A. Based on the consumption of Ce(IV) by the EDTA and its regeneration by the cell under the applied cell current of 10 A, the concentration of EDTA was fixed at 67 mM for all the remaining experiments to study the influence of variables such as temperature, concentrations of nitric acid and Ce(IV).

3.2.2. *Effect of nitric acid concentration in the anolyte*

The effects of various nitric acid concentrations in the anolyte with 0.95 M Ce(IV) on EDTA destruction are depicted in Fig. 4.

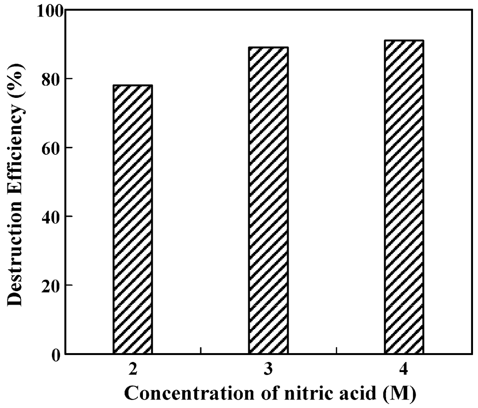

Fig. 4. The final destruction efficiencies (based on CO_2) obtained for EDTA at different nitric acid concentrations in the anolyte by MEO process at 80 °C ([Ce(IV)] = 0.95 M; [EDTA] = 67 mM; feed rate = 3 mL/min; duration of feeding = 30 min).

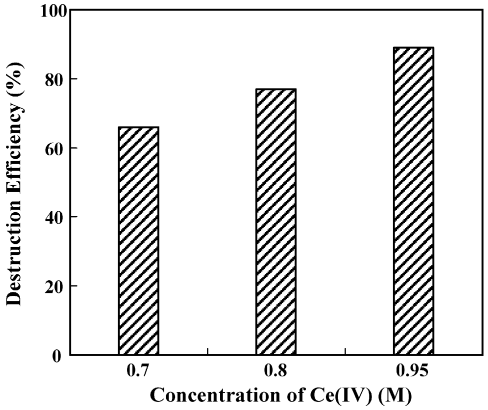

Fig. 5. The final destruction efficiencies (based on CO_2) obtained for EDTA at different cerium(IV) concentrations by MEO process at 80 °C ([HNO_3] = 3 M; [EDTA] = 67 mM; feed rate = 3 mL/min; duration of feeding = 30 min).

In all cases the catholyte nitric acid concentration was 4 M except for 4 M anolyte concentration of nitric acid, whereas, 5 M nitric acid was taken in the catholyte. It was observed that the destruction increased as the concentration of nitric acid was increased in the anolyte. This may be due to two reasons: first, nitric acid itself is a strong oxidizing agent; second, the increased potential of Ce(IV) at higher nitric acid concentrations. Chiba [15] observed during the mineralization of Trimsol oil by silver-MEO process that the destruction increased dramatically as the concentration of nitric acid was increased. In the case of silver-MEO process a high concentration of nitric acid (8–12 M) is usually employed compared to the cerium-MEO process (3–4 M) [9]. This is to maintain the stability of silver(II) ion [27]. But, in the case of cerium-MEO process there was no dramatic increase for the increase in nitric acid concentration and moderate nitric acid concentration of 3–3.5 M was usually found sufficient for effective mineralization [28].

3.2.3. *Effect of cerium(IV) concentration*

The destruction efficiencies of 67 mM EDTA by 0.7, 0.8 and 0.95 M Ce(IV) in 3 M nitric acid at 80 °C are shown in Fig. 5. It can be observed that for 0.7 and 0.8 M Ce(IV) the destruction efficiencies are lower than 0.95 M. Since a high Ce(IV) concentration gave maximum destruction it was maintained for all the experiments to have good destruction yields. A similar trend was observed in the case of batch reaction with phenol as the target organic [24]. But it is to be mentioned here that at 0.7 and 0.8 M, Ce(IV) has got good regeneration ability at the applied cell current of 10 A compared to 0.95 M. This means that increase in Ce(IV) concentration per unit time is less compared to either 0.8 or 0.7 M. In case of 0.95 M, the maximum CO_2 evolution was attained in 100 min compared to 0.8 (160 min) and 0.7 M (180 min).

3.2.4. *Effect of temperature*

The effects of various reaction temperatures on the destruction of 67 mM EDTA at 70, 80 and 95 °C are shown in Fig. 6. It is evident that the maximum destruction was found at 95 °C than at 80 and 70 °C. At the highest studied temperature of 95 °C destruction proceeds more rapidly as observed from CO_2

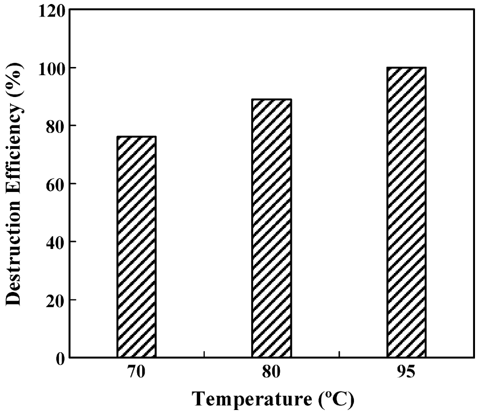

Fig. 6. The final destruction efficiencies (based on CO_2) obtained for EDTA at different temperatures by MEO process ([Ce(IV)] = 0.95 M; [HNO_3] = 3 M; [EDTA] = 67 mM; feed rate = 3 mL/min; duration of feeding = 30 min).

evolution and maximum destruction efficiency was observed in just 70 min compared to the other two temperatures. Although the maximum destruction was obtained at 95 °C, all destruction experiments were carried out at 80 °C to minimize the solution evaporation rate. Also at the higher temperatures the regeneration rate of Ce(IV) in the electrochemical cell was found good. As a result the coulombic efficiency of the destruction process increased at higher temperatures. At 70 °C, the coulombic efficiency for 95% destruction was found to be only 45%, whereas, at 95 °C, it increased to ca. 62%. From the literature on the MEO processes, it was found that as the temperature increased the coulombic efficiency of the system also found increased [22].

3.2.5. *Effect of feeding time*

The effect of feeding time was tested for EDTA destruction for the duration of 30 and 120 min under the conditions of 67 mM EDTA feed, 0.95 M Ce(IV) in 3 M nitric acid at 80 °C. The CO_2 produced with respect to time is presented in Fig. 7 for 120 min feeding. It was observed from the previous experiments that during 30 min EDTA feeding the CO_2 evolution increased linearly during feeding. But, in the case of 120 min feeding CO_2 evolution increased initially and then attained a steady state. The destruction efficiency in this case was calculated from the period of steady state attainment in terms of CO_2 production till the end of feeding. The destruction efficiency from 46 to 120 min was found to be 85% based on CO_2 production. This indicates that good destruction efficiency can be obtained for long time feeding under the experimental conditions studied.

3.3. *Ce(IV) regeneration during EDTA destruction*

The regeneration of Ce(IV) during organic destruction in all cases was carried out by continuous cell operation under a constant current of 10 A. Although Ce(IV) regeneration depends on the cell current, it was found to depend on the concentration of organic feed, the temperature, the initial Ce(IV) concentration, etc. The influences of these parameters on the extent of Ce(IV) regeneration are discussed briefly below.

The changes in Ce(IV) level during the destruction of various concentrations of EDTA are shown in Fig. 8. After stopping organic addition Ce(IV) concentration was found increasing as expected. It can be observed that the decrease in Ce(IV) concentration was high for 268 mM and minimum for 67 mM of EDTA. This clearly showed that the regeneration capacity of the cell, at the applied current of 10 A, is optimum only for 67 mM EDTA and reduced as the organic loading was increased. Therefore, 67 mM was fixed as the optimum initial feed concentration for all the other experiments. The level of Ce(IV) regeneration was not much influenced by temperature changes under the experimental conditions studied. The effect of initial concentration of the mediator ion on Ce(IV) regeneration was found to be good for 0.7 and 0.8 M and in these two cases the initial concentration was maintained nearly the same during organic addition, whereas, for 0.95 M the concentration steadily decreased during organic addition and finally reached to 0.91 M at the 30 min and then after stopping organic feed increased slowly. Therefore, under the given conditions of cell current at 80 °C, the regeneration of Ce(IV) was observed to be almost equal to its consumption only at 0.7 M initial Ce(IV) concentration. This is an important factor for long time organic feeding where the level of Ce(IV) should not be less than 0.7 M to have good mineralization.

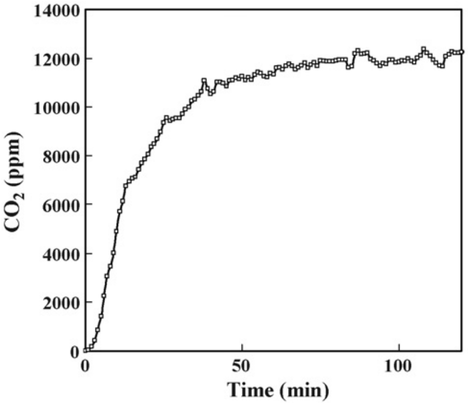

Fig. 7. The real time CO_2 evolution pattern obtained during the destruction of EDTA by MEO process at 80 °C ([Ce(IV)] = 0.95 M; [HNO_3] = 3 M; [EDTA] = 67 mM; feed rate = 3 mL/min; duration of feeding = 120 min).

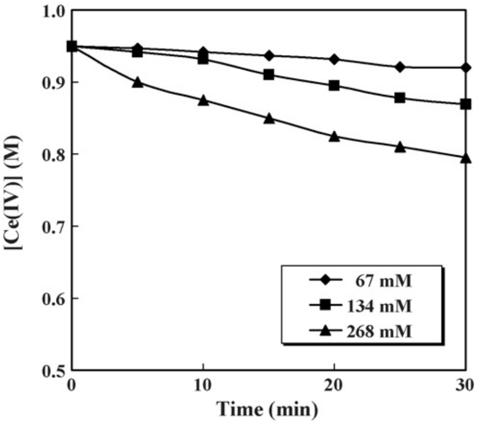

Fig. 8. The changes in Ce(IV) concentrations with time during the destruction of EDTA by MEO process at 80 °C ([Ce(IV)] = 0.95 M; [HNO_3] = 3 M; feed rate = 3 mL/min; duration of feeding = 30 min).

3.4. Reactivation of electrodes

The resistance of the DSA electrodes of the electrochemical cell was found increased during the continuous process of organic destruction due to the presence of small portion of remaining organics. At constant current mode 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 [29]. This contamination was minimized and electrodes were reactivated by circulating 5% nitric acid for 60 min. After the acid treatment the resistance of the cell found to be decreased and the *I–V* response of the electrodes regained. The maintenance of electrode activity is crucial in the continuous process of organic addition and further studies are being carried out to optimize the system for minimizing electrode contamination.

4. Conclusions

In this study, the efficiency of the MEO process for various model organic pollutants in continuous feeding mode was investigated. The organics such as phenol, benzoquinone, hydroquinone, catechol, maleic acid, oxalic acid and EDTA were destructed almost completely with good destruction efficiency based on CO_2 and TOC analyses. The effects of various parameters were evaluated for EDTA destruction such as the concentration of EDTA, temperature, concentrations of Ce(IV) and nitric acid and organic feeding time. Under the experimental conditions investigated the optimum destruction efficiency was achieved for the following conditions; EDTA concentration: 67 mM; temperature: 95 °C; Ce(IV) concentration: 0.95 M and nitric acid concentration: 3 M. The electrochemical cell performance was observed based on the rate of Ce(IV) regeneration and coulombic efficiency under a constant cell current of 10 A. The coulombic efficiency of 88–92% was obtained during the organic destruction in all cases. The high coulombic efficiency showed that the electrochemical cell with IrO_2/Ti DSA electrodes is ideally suitable for MEO system. Further experiments are being carried out to check the destruction efficiency of metal-EDTA complexes and Ce(IV) regeneration capacity with multi-stacking electrode pack for long term feeding of more concentrated organic pollutants.

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References

[1] Y. Zundelevich, The mediated electrochemical dissolution of plutonium oxide: kinetics and mechanism, J. Alloys Compd. 182 (1992) 115–130.

[2] J.L. Ryan, A.L. Bray, E.J. Wheelwright, G.H. Bryan, in: L.R. Morss, J. Fuger (Eds.), Catalyzed Electrolytic Plutonium Oxide Dissolution in Transuranium Elements: A Half Century, American Chemical Society, Washington, DC, 1992, pp. 288–304.

[3] N. Nelson, T. Neustedter, S. Oberg, J. Varela, The cerox process: new technology for organic hazardous waste destruction, Symposium on Emerging Technologies: Waste Management in the 21st Century, American Chemical Society Meeting, San Francisco, May, 2000.

[4] J. Bringmann, U. Galla, H. Schmieder, Mediated electrochemical oxidation for total degradation of HCH and other pesticides, 5th International HCH and Pesticides Forum, Leioa, Basque country, Spain, June 25–27, 1998.

[5] GEF, Report of United Nations Environmental Programme for 2004. On review of emerging innovative technologies for the destruction and decontamination of POPs and the identification of promising technologies for use in developing countries. January 15, 2004.

[6] D.F. Steele, Electrochemical destruction of toxic organic industrial waste, Plat. Met. Rev. 34 (1) (1990) 10–14.

[7] N. Nelson, Electrochemical destruction of organic hazardous wastes, Plat. Met. Rev. 46 (1) (2002) 18–23.

[8] B. Balazs, Z. Chiba, P. Hsu, P. Lewis, L. Murguia, M. Adamson, Destruction of hazardous and mixed wastes using mediated electrochemical oxidation in a silver(II) nitric acid bench scale system, Proceedings of the 6th International Conference on Radioactive Waste Management and Environmental Remediation, ICEM 97, Am. Soc. Mech. Eng. New York, USA, 1997, 541–545.

[9] D.F. Steele, D. Richardson, J.D. Campbell, D.R. Craig, J.D. Quinn, The low temperature destruction of organic waste by electrochemical oxidation, Trans. IChemE. 68 (B) (1990) 115–121.

[10] U. Galla, P. Kritzer, J. Bringmann, H. Schmieder, Process for total degradation of organic wastes by mediated electrooxidation, Chem. Eng. Technol. 23 (2000) 230–233.

[11] T. Raju, C. Ahmed Basha, Electrochemical cell design and development for mediated electrochemical oxidation—Ce(III)/Ce(IV) system, Chem. Eng. J. 114 (2005) 55–65.

[12] Y. Wei, B. Fang, T. Arai, M. Kumagai, Electrolytic oxidation of Ce(III) in nitric acid and sulphuric acid media using a flow type cell, J. Appl. Electrochem. 35 (2005) 561–566.

[13] A. Paulenova, S.E. Creager, J.D. Navratil, Y. Wei, Redox potentials and kinetics of the Ce(III)/Ce(IV) redox reaction and solubility of cerium sulfates in sulfuric acid solutions, J. Power Sources 109 (2002) 431–438.

[14] S.R. Joshi, K.L. Kataria, S.B. Sawant, J.B. Joshi, Kinetics of oxidation of benzyl alcohol with dilute nitric acid, Ind. Eng. Chem. Res. 44 (2005) 325–333.

[15] S. Balaji, V.V. Kokovkin, S.J. Chung, I.S. Moon, Destruction of EDTA by mediated electrochemical oxidation process: monitoring by continuous CO_2 measurements, Water Res. 41 (2007) 1423–1432.

[16] J.-W. Lee, S.J. Chung, S. Balaji, V.V. Kokovkin, I.S. Moon, Destruction of EDTA using Ce (IV) mediated electrochemical oxidation: A simple modeling study and experimental verification, Chemosphere 68 (2007) 1067–1073.

[17] M. Matheswaran, S. Balaji, S.J. Chung, I.S. Moon, Silver mediated electrochemical oxidation: Production of silver (II) in nitric acid medium and in situ destruction of phenol in semi batch process, J. Ind. Eng. Chem. 13 (2007) 231–236.

[18] S.J. Chung, S. Balaji, M. Matheswaran, T. Ramesh, I.S. Moon, Preliminary studies using hybrid mediated electrochemical oxidation (HMEO) for the removal of persistent organic pollutants (POPs), Water Sci. Technol. 55 (2007) 261–266.

[19] M. Matheswaran, S. Balaji, S.J. Chung, I.S. Moon, Mineralization of phenol by Ce (IV) mediated electrochemical oxidation in methanesulphonic acid medium: A preliminary study, Chemosphere, accepted for publication.

[20] V.V. Kokovkin, S.J. Chung, S. Balaji, M. Matheswaran, I.S. Moon, Investigation of electrochemical cell current requirements for toxic organic waste destruction in Ce(IV)-MEO process, Korean J. Chem. Eng. 25(5) (in press).

[21] S. Balaji, S.J. Chung, M. Matheswaran, I.S. Moon, Cerium(IV) mediated electrochemical oxidation process for the destruction of various organic pollutants in batch and continuous organic feeding modes, Korean J. Chem. Eng. 25(6) (in press).

[22] Z. Chiba, Mediated electrochemical oxidation of mixed wastes, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-112669 April, 1993.

[23] J.C. Farmer, F.T. Wang, R.A. Hawley-Fedder, P.R. Lewis, L.J. Summers, L. Foiles, Electrochemical treatment of mixed and hazardous wastes: oxidation of ethylene glycol and benzene by silver(II), J. Electrochem. Soc. 139 (3) (1992) 654–661.

[24] S. Balaji, S.J. Chung, R. Thiruvenkatachari, I.S. Moon, 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, Chem. Eng. J. 126 (2007) 51–57.

[25] Il Shik Moon, Electrochemical cell for hybrid mediated oxidation of organic wastes, Korea Patent 10-2005-0045983, May 31, 2005.

[26] A.D. Turner, Organic destruction using the silver(II) process, Membr. Technol. 142 (2002) 6–12.

[27] C.A.C. Sequeira, D.M.F. Santos, P.S.D. Brito, Mediated and non-mediated electrochemical oxidation of isopropanol, Appl. Surf. Sci. 252 (2006) 6093–6096.

[28] J. Varela, S. Oberg, T.M. Neustedter, N. Nelson, Non-thermal organic waste destruction: characterization of the cerox system 4, Environ. Prog. 20 (4) (2001) 261–271.

[29] T. Tzedakis, A. Savall, Electrochemical regeneration of Ce(IV) for oxidation of *p*-methoxytoluene, J. Appl. Electrochem. 27 (1997) 589–597.