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Mediated electrochemical oxidation of phenol in continuous feeding mode using Ag (II) and Ce (IV) mediator ions in nitric acid: A comparative study

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Abstract

Mediated electrochemical oxidation (MEO) process is one among the latest treatment technologies for the destruction of toxic organic pollutants under ambient temperatures and at atmospheric pressure. The process is a further extension of the conventional electrochemical treatment for the removal of toxic organics with powerful mediator oxidants in acidic medium. In this report the experimental results of using silver and cerium as mediator ions were compared with respect to their electro-oxidation behavior within the limitations of each mediator metal ion and their destruction efficiencies were compared for destructing phenol in continuous feeding mode. The following conclusions were drawn: (i) the optimum nitric acid concentration was found to be 8 and 3 M and the optimum temperature was found to be 60 and 80 °C for silver and cerium electro-oxidations, respectively; (ii) in the case of Ag (II)-MEO of phenol the maximum destruction efficiency achieved was 98% at 70 °C based on CO_2 evolved; (iii) for Ce (IV)-MEO of phenol the maximum destruction efficiency achieved was 93% at 90 °C based on CO_2. The results may provide baseline information on the use of suitable mediator metal ion in treating the target organic wastes by MEO process.

Keywords: Mediated electrochemical oxidation; Silver; Cerium; Nitric acid; Phenol; CO_2

1. 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 toxic organic pollutants and has been identified by the United Nations Environmental Programme as one of the promising future technologies for use in the developing nations [1]. In this process a mediator metal ion capable of exhibiting redox behavior in an acidic medium is used as an oxidant for the mineralization of toxic organic wastes and the reduced form of the oxidant is regenerated electrochemically in a closed cycle. DEO processes have been employed for the destruction of various organic compounds [2]. In these processes the organic compounds are oxidized to CO_2 and H_2O 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 in DEO processes. 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 [3], and hence the reduced electrode activity. But 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 present in the higher oxidation state. After the oxidation of organics, the reduced mediator ion is re-oxidized *in situ* by the electrochemical cell in a closed circuit and thus cycled infinitely [4–10].

The MEO processes with various mediator metal ions like silver, cerium, manganese, cobalt, iron, etc., were investigated and reported by many researchers. Farmer et al. have reported the oxidation of ethylene glycol and benzene with silver [11] as the mediator ion and destruction of chlorinated organics in presence of cobalt mediator [12]. Galla et al. [13] have investigated the destruction of pesticides using silver mediator in

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nitric acid medium. Varela et al. [14] have described the cerium mediated electrochemical oxidation of organic wastes in pilot plant system. Turner [15] 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 l^{-1}. Steele [4] has reviewed the early stages of the silver-MEO process. Nelson [16] has reviewed the cerium-MEO process and explained their larger sized electrochemical cell and portable plant installation. In the above reports the MEO process was carried out using larger sized plants and commercial systems were documented but the influences of various operating parameters such as the metal ion (oxidant) concentration, the operating temperature, the feed concentration of the organic compound, the oxidant solution recirculation flow rate, the cell voltage, etc., for mediator oxidant production and organic destruction were not discussed in detail due to the commercial significance of the process.

Although several metal ions have been used in MEO process silver and cerium are the extensively studied mediator ions for pilot and larger set ups. But in most of the reported works only the final destruction efficiencies were mentioned. Also it was observed from our previous experiments that the role of the mediator ion was not just to transfer the electron from the electrode surface to the organic molecule to be mineralized but the following factors are critically important for effective mineralization of the organics: (i) the concentration of the metal ion, (ii) the water oxidation by the oxidized metal ion and hence the stability of the oxidized species, (iii) the temperature of the system, (iv) the acid electrolyte concentration, (v) the amount of CO formation and (vi) the ability of the system for the destruction of a wide range of toxic organic wastes, etc. In our previous reports, the destruction of phenol using low concentration of Ag (II) mediator in continuous feeding mode and a batch reaction using Ce (IV) mediator in nitric acid were documented [7,8]. But the real application of the MEO process lies in its ability to treat organics in continuous feeding mode. Therefore, the comparative study of the silver and cerium MEO systems based on the electrochemical mediator oxidant production and its subsequent use for destructing a model organic pollutant in continuous feeding mode gets significance and has not been reported in the literature. The electro-oxidation studies for silver and cerium in nitric acid medium were carried out using a divided electrochemical cell to reveal the dependence of various parameters on the real conversion rates and their subsequent usage for destructing phenol in continuous feeding mode was carried out. Since the final products of mineralization are CO_2 and water, the course of the destruction process was monitored by measuring the volume of CO_2 evolved as reported by many authors [13,17,18–20].

The objectives of the present investigation were to compare the kinetics of electro-oxidation of silver (I) and cerium (III) in nitric acid medium using a laboratory scale electrochemical cell, to find the influencing parameters under which a maximum conversion could be obtained and to compare the mineralization efficiencies of produced Ag (II) and Ce (IV) mediator ions taking phenol as the target organic pollutant under various metal ion concentrations and temperatures.

2. Experimental

2.1. Materials

Cerium (III) nitrate hexahydrate (99%) from Sigma–Aldrich, silver (I) nitrate (99.8%) from Junsei Chemical Co. Ltd., Japan, phenol (99%) and nitric acid (60%) from Sam Chun Chemicals, Korea were used as received.

2.2. Methods

The electro-oxidation of silver and cerium was carried out in a divided electrochemical cell fabricated in our laboratory using IrO_2/Ti DSA (mesh) anode and Ti (mesh) cathode each with the geometrical surface area of 4.0 cm^2 (effective surface area: 2.6 cm^2). The electrodes were kept separated by a proton exchange membrane (Nafion® 324). The membrane used was of low resistivity and able to pass a current density of ca. 5 kA m^{-2} [15]. The anode and cathode compartments of the cell were coupled to the analyte and catholyte vessels, respectively, and the electrolyte solutions were circulated through anodic and cathodic compartments repeatedly at the flow rate of 100 ml min^{-1} using peristaltic pumps till the required conversion was reached. The schematic diagram of mediated electrochemical oxidation system is reported previously [8]. The anolyte vessel was charged with 50 ml of the metal salts (silver (I) nitrate or cerium (III) nitrate) in nitric acid solution and catholyte vessel with only nitric acid. All the experiments were carried out under a constant cell voltage of 2.5 V. The temperature of the solutions was maintained using a thermostatic controlled water bath. During the passage of current, Ag (I) was oxidized to Ag (II) and Ce (III) was oxidized to Ce (IV) at the anode and nitric acid was reduced to nitrous acid at the cathode. At the catholyte, the NO_x gases evolved from nitrous acid decomposition was re-oxidized to NO_2 by continuous passage of atmospheric oxygen, which then solubilizes in water to form nitric acid. During the electrolysis samples were collected at different time intervals and the concentration of the formed Ag (II) and Ce (IV) was estimated as reported previously [7,8,21]. The current efficiency was calculated as the ratio between the current realized from Ag (I) or Ce (III) conversion to current supplied to the cell during the interval.

Under the optimum conditions of the cell for metal ion oxidation, phenol mineralization was carried out in continuous addition mode using a syringe pump. The phenol solution of known concentration was constantly fed at the rate of 0.05 ml min^{-1} into the anolyte reservoir up to 60 min. Phenol was oxidized into CO_2 and water, while the metal oxidant was reduced. The reduced metal ion was continuously regenerated *in situ* by the electrochemical cell. The CO_2 formed was brought out by passing a carrier gas (nitrogen; 500 ml min^{-1}) and the concentration of CO_2 evolved was measured using an infrared CO_2 analyzer (Anagas CD 98, Environmental Instruments). The mineralization efficiency of the process was calculated as the ratio between the accumulated CO_2 volume and the theoretical stoichiometric volume.

Table 1
The formation yields of Ag (II) and Ce (IV) for various initial concentrations of Ag (I) and Ce (III) in 8 and 3 M nitric acid, respectively (electrolysis time, 60 min; cell voltage, 2.5 V; temperature, 25 °C for Ag and 80 °C for Ce; solution recirculation flow rate, 100 ml min^{-1})

Initial concentration of Ag (I) or Ce (III) (M)	[Ag (II)] (M)	[Ce (IV)] (M)
0.10	0.038	–
0.25	0.06	0.24
0.50	0.07	0.45
0.75	–	0.63
1.00	0.13	0.76
1.25	–	0.72

3. Results and discussion

3.1. Electro-oxidation of silver (I) and cerium (III)

The factors which influence the electro-oxidation of a metal ion in an electrochemical cell are the concentration of the metal ion, concentration of the acid electrolyte, temperature, flow rate of the solution recirculation and cell current. The flow rate of the solution recirculation and the cell voltage were fixed based on the mass transfer coefficients calculated from trial experiments. The effect of initial concentration of silver and cerium on the conversion yield is shown in Table 1. It can be seen from the Table 1 that under the same cell voltage and recirculation flow rate the jump in concentration (ΔC) of the Ce (IV) species was found to be high compared to Ag (II). This very small increase in the concentration of Ag (II) (when the initial Ag (I) concentration is increased from 0.5 to 1.0 M) restricts its employable initial solution concentration to 0.5 M, which is also found economical to the silver system. Whereas for cerium this could be further increased and initial concentrations up to 1.0 M were found to be the optimum working concentration. This is due to the fact that the water oxidation reaction by Ag (II) was quite high at high Ag (II) concentrations. From the above results 0.5 M Ag (I) and 1 M Ce (III) were chosen as the optimum working range for all further experiments. The parameters that largely affect and differentiate the silver and cerium mediator ions during electro-oxidation were the nitric acid concentration in the anolyte and the system temperature.

3.1.1. Effect of nitric acid concentration

The oxidation studies of Ag (I) and Ce (III) in various nitric acid concentrations were carried out at a fixed metal ion concentration and the effect of acid concentration on the oxidation rate and stability of the produced oxidant ion were found. The effect of acid concentration on silver (I) oxidation was studied for the nitric acid concentrations 3, 6, 8 and 10 M with 0.5 M Ag (I) at 25 °C. The cell voltage was 2.5 V and the solution circulation flow rate was 100 ml min^{-1}. The plots of Ag (II) formation vs. time at various acid concentrations are shown in Fig. 1. It can be seen in the figure that the concentration of Ag (II) increased with reaction time for increasing nitric acid concentrations. This was due to the high stability of the brown colored [Ag (NO$_3$)]$^+$ complex at higher acid concentrations [22]. The highest conversion of Ag (II) was obtained for 10 M nitric acid. The concentration of Ag (II) attained steady state nearly at 30 min for the acid concentrations 3 and 6 M due to the simultaneous water oxidation reaction by the Ag (II) ion whereas for 8 and 10 M the same was observed at around 60 min. This clearly shows that the stability of the formed Ag (II)–nitrate complex is increased at higher acid concentrations as reported by Sequeira et al. [22]. Although at 10 M nitric acid the conversion was found to be high, 8 M nitric acid was chosen as the optimum concentration for silver system because of the nearly same conversion rate at 60 min.

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^{-1} recirculation flow rate at 80 °C. Fig. 2 shows the formation yields of Ce (IV) at different nitric acid concen-

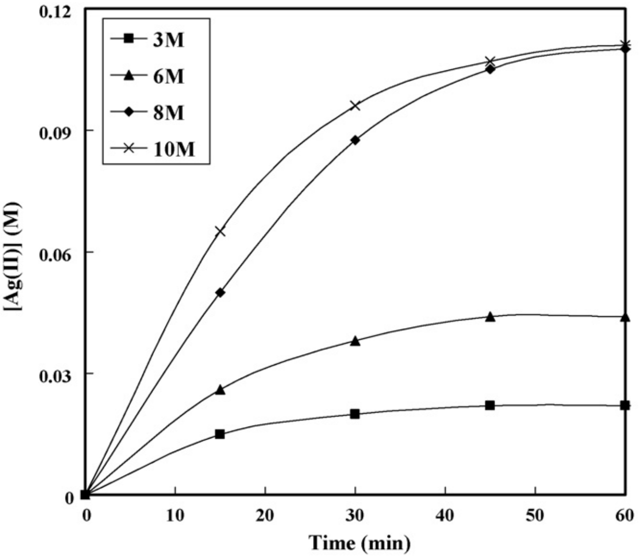

Fig. 1. Silver (II) formation vs. time at various nitric acid concentrations at 25 °C ([Ag (I)]$_{\text{initial}}$ = 0.5 M).

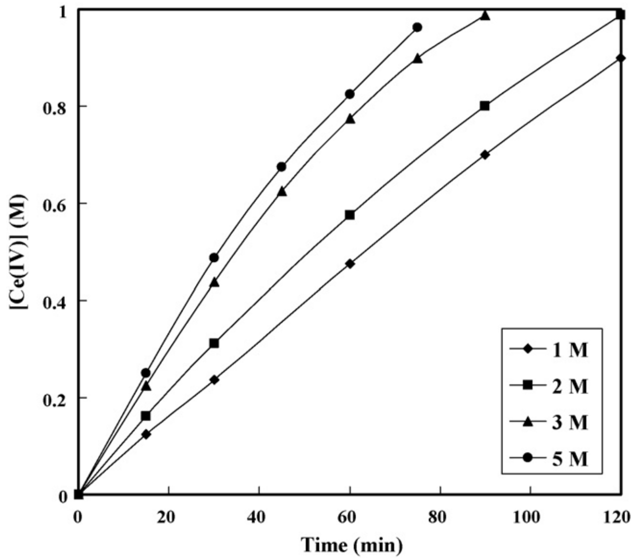

Fig. 2. Ce (IV) formation vs. time at various nitric acid concentrations at 80 °C ([Ce (III)]$_{\text{initial}}$ = 1 M]).

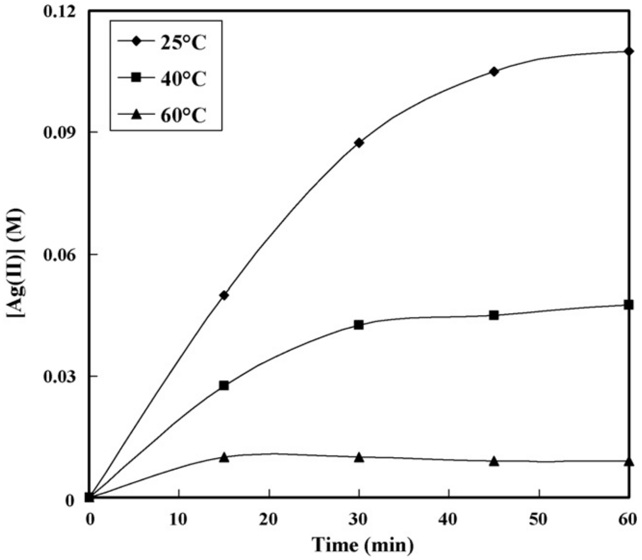

Fig. 3. Silver (II) formation vs. time at various temperatures ([Ag (I)]$_{initial}$ = 0.5 M; [HNO_3] = 8 M).

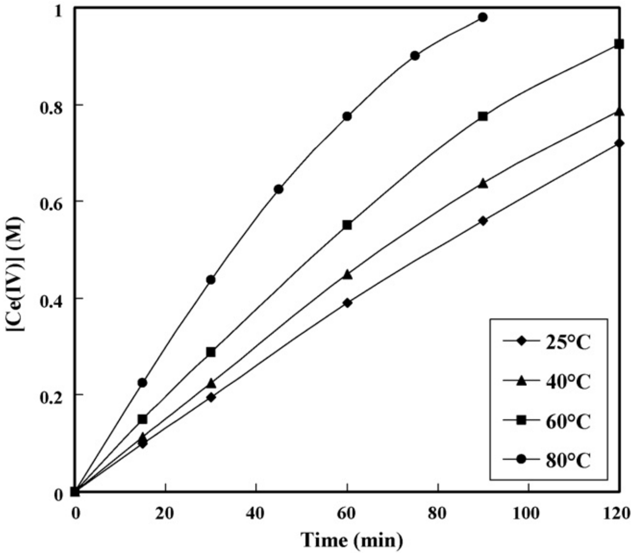

Fig. 4. Ce (IV) formation vs. time at various temperatures ([Ce (III)]$_{initial}$ = 1 M; [HNO_3] = 3 M].

trations (1–5 M). By increasing the concentration of nitric acid from 1 to 5 M, the yield of Ce (IV) was found increased significantly. Wei et al. [21] and Pleecher and Valdes [23] 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 [24]. Therefore, the increase in the conversion may be considered to arise from the sole contribution of increase in the nitric acid concentration. Also, it was observed that the current efficiency increased with increasing nitric acid concentration. The highest current efficiency of 90% was obtained for the concentration 5 M nitric acid.

3.1.2. *Effect of temperature*

As the metal ion oxidations are strongly dependent on the temperature in electrochemical processes, the effect of temperature on electrochemical oxidation of Ag (I) and Ce (III) was studied at 2.5 V and 100 ml min^{-1} solution flow rate. The oxidation of 0.5 M Ag (I) in 8 M nitric acid was carried out at different temperatures. The formation of Ag (II) with respect to the reaction time at different temperatures is shown in Fig. 3. It can be seen that as the temperature was increased from 25 to 60 °C the concentration of Ag (II) in the solution was decreased from 0.11 to 0.01 M. This significant decrease in the Ag (II) concentration may be due to the increased rate of water oxidation by Ag (II). The temperature dependence of Ag (II) on the oxidation kinetics of water was reported by Lehmani et al. [25]. The reduction of Ag (II) by water can be represented as follows [22].

$$4AgNO_3^+ + 2H_2O \rightarrow Ag^+ + O_2 + 4HNO_3$$

Therefore, increase in temperature results in decrease of Ag (II) concentration. The effect of temperature on the electrochemical oxidation of 1 M Ce (III) in 3 M nitric acid was studied in the range 25–80 °C. The Ce (IV) formation with time at various temperatures is shown in Fig. 4. It can be seen from the figure that the rate of Ce (IV) formation increased with the increase in solution temperature. When the logarithm of rate of oxidation was plotted against the reciprocal of the absolute temperature 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^{-1}. Horbez and Storck [26] have reported that for cerium oxidation in sulfuric acid medium with platinum coated titanium electrode if the operating cell voltage is above 1.1 V vs. SCE (saturated calomel electrode) then the evolution of oxygen is inevitable and occurs parallel to 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. [21] (16.3 kJ mol^{-1}) and Sedneva [27] (32.2 kJ mol^{-1}) for Ce (III) oxidation in nitric acid using cyclic voltammetric data. Also the current efficiencies were increased with increase in the temperature. Therefore, for Ce (III) oxidation 90 °C can be taken as the optimum working temperature for obtaining maximum conversion with high coulombic efficiency.

3.2. *Mineralization of phenol*

Mineralization of phenol was carried out in continuous feeding mode with *in situ* regeneration of the mediator ions (silver and cerium oxidants) in nitric acid to compare the properties of silver and cerium mediator ions in terms of destruction efficiencies and to find the optimum conditions for each metal ion system for obtaining maximum destruction yield. It was observed from our earlier experiments that the mediator ion concentration and temperature were the two important factors that influence the destruction reaction.

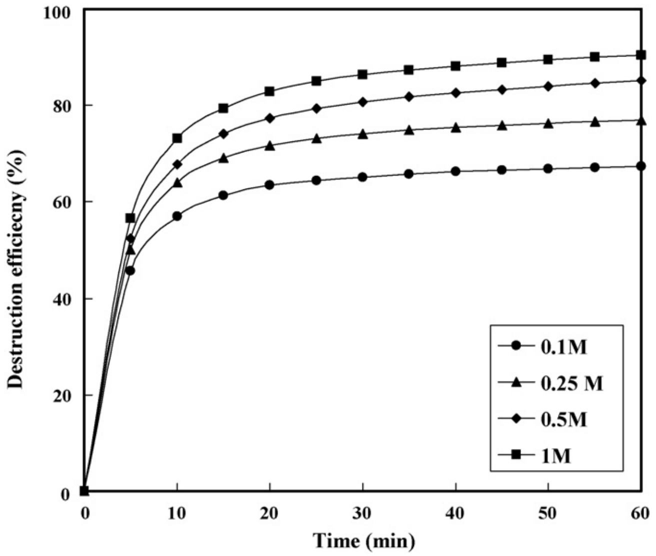

Fig. 5. Phenol destruction efficiencies vs. time for various initial concentrations of Ag (I) in 8 M nitric acid at 60 °C ($[\text{Phenol}]_{\text{feed concentration}} = 10{,}000$ ppm; phenol addition started when Ag (II) formation reached the steady state).

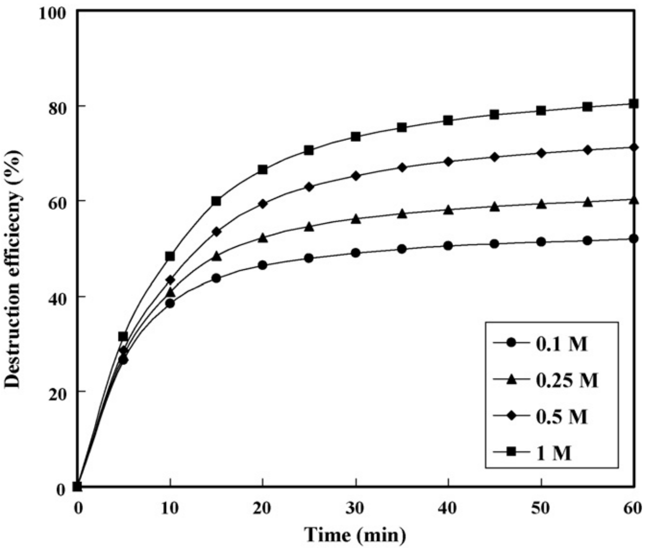

Fig. 6. Phenol destruction efficiencies vs. time for various initial concentrations of Ce (III) in 3 M nitric acid at 80 °C ($[\text{Phenol}]_{\text{feed concentration}} = 10{,}000$ ppm; phenol addition started after 96% conversion of Ce (III) to Ce (IV)).

3.2.1. *Effect of mediator ion concentration*

In the MEO process the metal ion acts as a mediating species and promotes the transfer of electrons from anode to the organic molecules to be destroyed. The concentration of the mediator ion decides two important things in the overall process. One is the coulombic efficiency of the electrochemical process and the other is the destruction efficiency of the organic oxidation process. The destruction efficiency of organic oxidation and the coulombic efficiency of the overall process could be increased by increasing the metal ion concentration [7]. The destruction efficiencies of phenol obtained with various initial concentrations of Ag (I) in 8 M nitric acid at 60 °C is given in Fig. 5. It is seen from the Fig. 5 that the destruction efficiency increases significantly from 67% to 90% when the initial concentration of Ag (I) is increased from 0.1 to 1.0 M. This is due to the fact that at the high initial concentration of Ag (I) the conversion to Ag (II) is high and hence the higher destruction efficiency. But the difference in destruction efficiencies between 0.5 and 1.0 M Ag (I) was only 5%. Therefore, for all further phenol destruction experiments 0.5 M Ag (I) was used as the optimum working concentration.

The destruction efficiencies of phenol with various initial concentrations of Ce (III) in 3 M nitric acid at 80 °C are given in Fig. 6. It is seen from the figure that as the initial concentration of Ce (III) increased the destruction efficiency of phenol was found increased. The increase in the destruction efficiency between 0.1 and 1.0 M Ce (III) was found to be ca. 35%. Whereas the differences in destruction efficiency between 0.5 and 1.0 M Ce (III) is around 15%. Unlike silver system the cerium mediated phenol oxidation requires relatively a high initial concentration of the metal ion to obtain the same destruction efficiency in spite of higher temperature. This may be due to the fact that Ag (II) oxidizes water molecules and get reduced to Ag (I) and therefore even at low concentrations it produces more free radicals, which effectively oxidize the organic molecules into CO_2. Therefore, it can be concluded that for silver mediated oxidation 0.5 M Ag (I) and for cerium system 1 M Ce (III) were found to be the optimum initial concentrations to obtain the maximum organic destruction and coulombic efficiencies.

3.2.2. *Effect of temperature*

The effect of various temperatures on the destruction efficiencies of phenol calculated from CO_2 evolved for silver mediated oxidation is shown in Fig. 7. At room temperature (25 °C) the destruction efficiency of phenol was found to be only 65%. The destruction efficiency increased as the temperature increased. The increase in the destruction efficiency between the room temperature and 70 °C is ca. 33%. At 70 °C the liquid phase COD

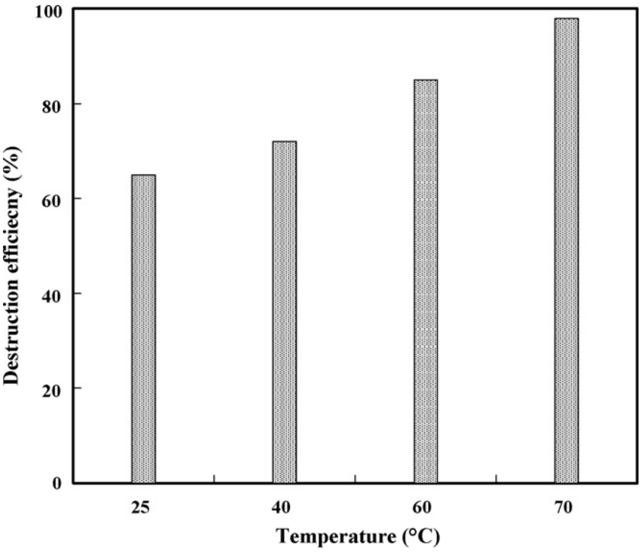

Fig. 7. The final destruction efficiencies of phenol at different temperatures obtained with silver mediated MEO process ($[\text{Ag (I)}]_{\text{initial}} = 0.5$ M; $[\text{HNO}_3] = 8$ M; $[\text{Phenol}]_{\text{feed concentration}} = 10{,}000$ ppm; phenol addition started when Ag (II) formation reached the steady state).

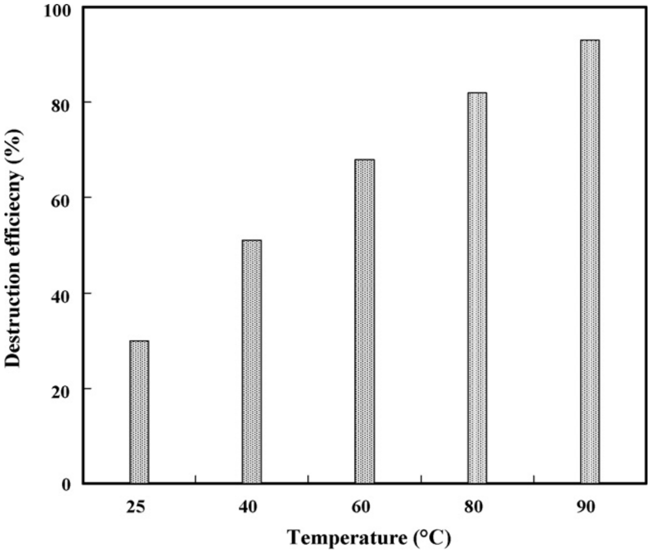

Fig. 8. The final destruction efficiencies of phenol at different temperatures obtained with cerium mediated MEO process ([Ce (III)]$_{\text{initial}}$ = 1 M; [HNO_3] = 3 M; [Phenol]$_{\text{feed concentration}}$ = 10,000 ppm; phenol addition started after 96% conversion of Ce (III) to Ce (IV)).

analysis indicated 99% COD removal. Balazs et al. [18] have reported that always there exists a difference between the CO_2 and TOC destruction efficiencies and the destruction efficiency calculated from CO_2 evolved is always less than the liquid phase TOC measured. It was found that the maximum destruction efficiency was achieved at 70 °C. This may be due to the fact that at higher temperatures even though the stability and the real concentration of liquid phase Ag (II) is lessened, the increase in the production of OH^* free radicals increase the organic oxidation ability of the system. So, at higher temperatures the concentration of silver (II) was observed to be decreased in the liquid phase (Fig. 3) whereas the destruction efficiency of phenol was found increased (Fig. 7).

In the case of cerium at higher temperature the rate of Ce (III) oxidation is increased and the water oxidation is less or very minimum as the concentration of Ce (IV) produced was found to be stable for a long time even for several days. The effects of different temperatures on the destruction of phenol were found with 1.0 M initial Ce (III) in 3 M nitric acid at 80 °C as shown in Fig. 8. It can be observed from the figure that the destruction is only 30% at 25 °C and then increases at higher temperatures. The maximum destruction efficiency of 93% was observed at 90 °C. It was concluded here that although Ce (IV) is highly stable at higher temperatures than Ag (II), in terms of organic destruction efficiency Ce (IV) is somewhat less powerful even at high concentration and temperature compared to silver (II) due to the lower redox potential of cerium redox couple than silver couple [4,16]. To tackle the problem of higher temperature employed during the organic mineralization in the case of cerium system and also to improve the current efficiency of the electrochemical oxidation and organic destruction efficiency, a mixed metal mediator system taking cerium with catalytic quantities of silver was carried out successfully in this lab and published recently [28].

4. Conclusions

The metal ions silver and cerium were electro-oxidized with good current efficiencies using an electrochemical cell with DSA electrodes. The metal ion oxidation rate was influenced by many factors, such as the metal ion concentration, concentration of the acid electrolyte, temperature, flow rate of the solution recirculation through the cell and the current density. It was found that at high acid concentration the stability of the Ag (II) ion was more but slowly undergoes reduction because of water oxidation reaction. But high temperature results in the fast depletion of Ag (II) concentration. In the case of cerium the Ce (IV) species was found to be stable even at higher temperatures and the rate of water oxidation was practically undetectable.

The results of phenol mineralization showed that the degradation rate of phenol was very effective by the silver and cerium-MEO processes. The optimum conditions obtained for the best degradation in silver mediated degradation were 0.5 M initial Ag (I), 8 M nitric acid, 70 °C for the phenol feed concentration of 10,000 ppm with the addition rate 0.05 ml min^{-1}. For cerium mediated phenol degradation the optimum conditions were found to be 1 M initial Ce (III), 3 M nitric acid, 90 °C for the same concentration and addition rates of phenol.

The advantages of the silver-MEO process for organic waste destruction are the lower operating temperature due to the high redox potential of the silver redox couple. The disadvantages are the precipitation of silver with chlorine containing organic compounds particularly at lower Ag (II) concentrations and the unwanted side reaction of water oxidation by Ag (II). Although the oxidizing ability of the cerium-MEO process is slightly less than silver-MEO process, Ce (IV) oxidant is highly stable and cerium does not undergo precipitation with chlorine containing organic compounds. Therefore, it can be concluded that the choice of the mediator ion depends upon the chemical composition of the organic waste to be treated and the boiling point of the organics present in the waste. A rough estimation shows that cerium process is somewhat economical than the silver-MEO process for practical applications. Although the MEO process is capable of completely destroying almost all the organic compounds the high energy consumption of this process compared to the currently used conventional methods may slow down its entry for commercial usage. But in the near future if strict environmental regulations are imposed world wide, this process will be an attractive and a potential candidate among the new technologies.

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