오존을 이용한 질산용액 내 Cerium nitrate의 Ce^{3+}/Ce^{4+} 산화환원반응 연구

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A study on Ce^{3+}/Ce^{4+} redox reaction of cerium nitrate in nitric acid solution by using ozone

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Introduction

Relatively large quantity of organic liquid wastes containing complex and non-degradable agents is generated from the chemical decontamination companies. With increasing the utility of chemical decontamination, safe and effective treatment for waste reduction and final disposal is required. Various oxidation process which involve chemical, electrochemical and photochemical treatments have been investigated in many countries for the destruction of non-degradable organic wastes[1].

Mediated electrochemical oxidation(MEO) and ozone mediated oxidation, which operates at ambient temperature and pressure, have been intensively developed in USA and Europe for the safe and effective destruction of toxic or hazardous non-degradable wastes because of its powerful destroying capability, applicability on mixed wastes, and controllability of the process[2, 3].

In MEO and ozone mediated oxidation process, Ce^{4+}, Ag^{2+}, Fe^{3+} and Co^{2+} as mediators are oxidized by electric and ozone, turn into strong oxidants decomposing organic wastes in electrolytes, and then reduced at the same time. These metallic ions are regenerated by oxidation again. With this regeneration mechanism, MEO and ozone mediated oxidation dissolve the wastes continuously. The organic wastes are completely decomposed and turn into carbon dioxide and water in the end of reaction by these processes.

This study was performed with the aim of evaluating the Ce^{3+}/Ce^{4+} redox potential behavior in nitric acid electrolyte by ozone mediated oxidation, which trivalent cerium(cerous) is oxidized tetravalent cerium(ceric) by ozone and reduced simultaneously with decomposition of organic wastes. Ce^{3+}/Ce^{4+} redox potential was measured by using glassy redox electrode.

Experiments

In this work, cerium(Ⅲ) nitrate was oxidized by ozone in pyrex cylindrical reactor, of which dimensions are 5cm in diameter and 50cm in height. The connecting tubes and valves are teflons or stainless steels for resistance on ozone. Ozone was continuously sparged into the reactor through the diffuser to effectively oxidize cerium nitrate. Ozone gas was generated with ozone generator(Ozonetech Co. Ltd., OG100-1212R). The ozone product was 100g/hr.

The quantity of incoming ozone was controlled by flow meter from 100ml/min to 1,000ml/min. Dissolvent solutions(300ml), which were prepared by 0.01, 0.1 and 1M $Ce(NO_3)_3 \cdot 6H_2O$(Sigma-Aldrich Co) to 1, 2 and 3M HNO_3 solutions, was placed in the reactor.

The oxidation reactions of cerium(Ⅲ) nitrate were followed by measuring redox potential of Ce^{3+}/Ce^{4+} in the dissolvent solution taken out at appropriate time intervals. The Ce^{3+}/Ce^{4+} redox potentials were measured pH/ISE meter(Orion Co. Ltd., Model 720A) using Ag/AgCl reference electrode and glassy redox electrode under different reaction conditions, quantity of ozone, concentration of cerium nitrate and nitric acid.

Results

Fig. 1 presents calibration curves of Ce^{3+}/Ce^{4+} redox potential, measured at 25℃, 3M HNO_3 in three mixed solution containing different ratios of ceric and cerous. The Ce^{3+}/Ce^{4+} redox potentials were calculated using Nernst equation. In calibration curves, values of RT/nF(mV) and E^O(mV) are presented in Table 1.

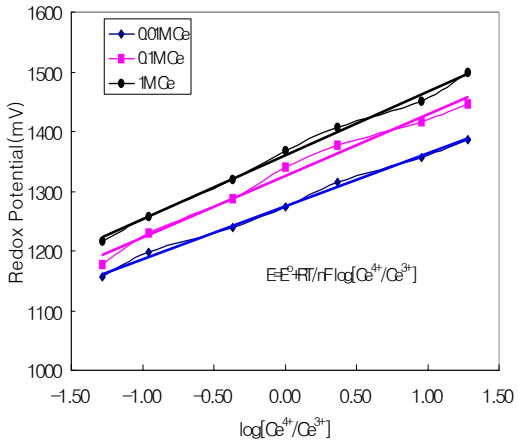

Fig. 1. Redox potential of solutions containing different ratios of ceric and cerous(25℃, 3M HNO_3).

Table 1. Standard potential of the Ce^{3+}/Ce^{4+} couple and RT/nF at different concentration.

Cerium nitrate Concentration	E^O(mV)	RT/nF(mV)
0.01	1274.9	88.36
0.1	1325.3	103.55
1	1359.7	107.32

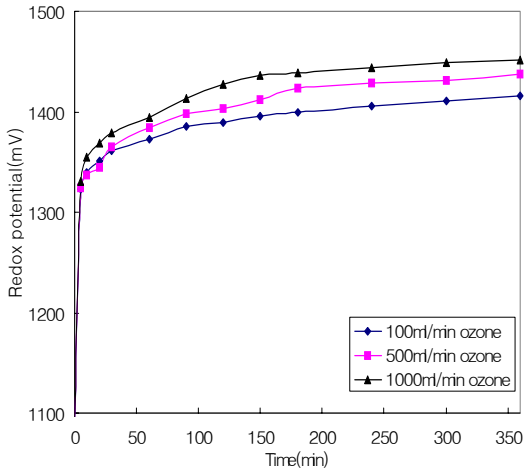

Fig. 2. Effect of flow rates of ozone on redox potential at 25℃, 1M $Ce(NO_3)_3$ - 3M HNO_3.

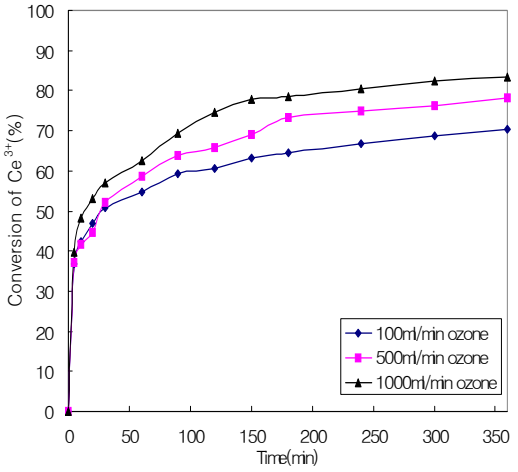

Fig. 3. The oxidation efficiency of different flow rates of ozone.

Dependencies of the redox potentials on quantity of ozone and change of ceric ratio in solution are displayed in Fig. 2 and Fig. 3. The color of solutions was changed to yellowich with increasing reaction time. A shift to high values of potential with increasing injection quantity of ozoen was observed that trivalent cerous is rapidly oxidized to tetravalent ceric with increasing injection quantity of ozone.

When injection quantity of ozone was maintained constantly, dependence of the redox potentials on concentration of cerium nitrate is displayed in fig. 4. Under reaction condition with 100ml/min ozone and 3M HNO_3, redox potentials were increased was observed with increasing concentration of cerium nitrate. Conversions of around 70% to tetravalent ceric were obtained in all of three solution(Fig. 5).

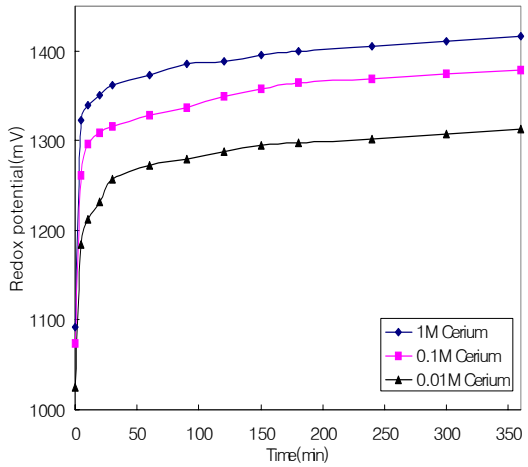

Fig. 4. Effect of concentrations of cerium nitrate on redox potential at 25℃, 3M HNO_3.and 100ml/min ozone.

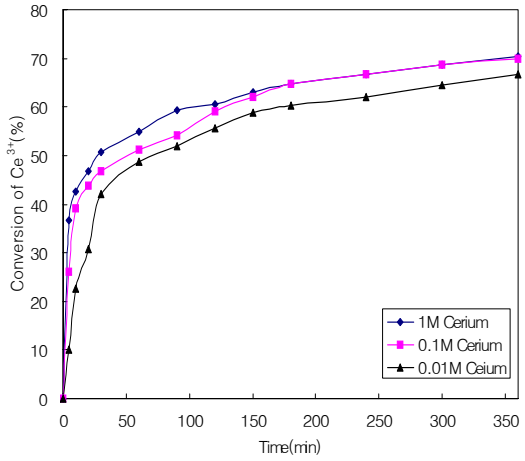

Fig. 5. The oxidation efficiency of different concentrations of cerium nitrate.

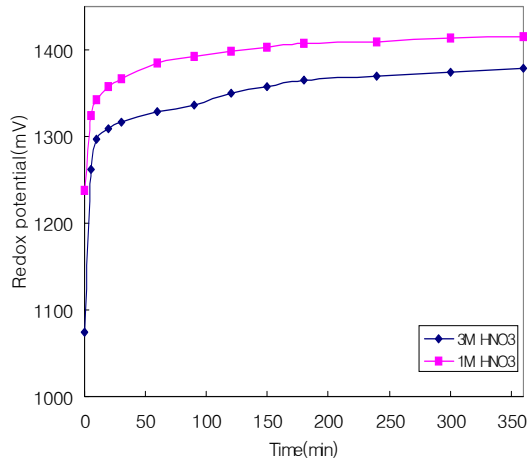

Fig. 6. Effect of concentrations of nitric acid on redox potential at 25℃, 3M HNO_3.and 100ml/min ozone.

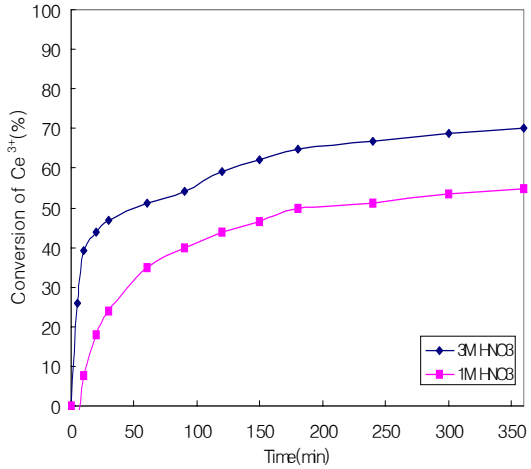

Fig. 7. The oxidation efficiency of different concentrations of nitric acid.

Fig. 6 presents the changes of redox potential on concentration of nitric acid and the conversion ratio of Ce^{3+} on concentration of nitric acid is displayed in Fig. 7. The redox potential of Ce^{3+}/Ce^{4+} was increased with increasing concentration of nitric acid that conversion ratio of Ce^{3+} to Ce^{4+} was more increased with increasing concentration of nitric acid than no contain nitric acid in solution. A shift to more positive values of potential with increasing concentration of nitric acid was observed that suggests the formation of nitrate complexes of the tetravalent ceric ion.

Discussions and Conclusions

Ce^{3+}/Ce^{4+} redox potential in ozone mediated oxidation for safe and effective destruction of non-degradable wastes at ambient temperature using cerium as a mediator was investigated to understand decomposition mechanism of non-degradable wastes. The conversion efficiencies of Ce^{3+} to Ce^{4+} were ultimately obtained over 65% because of nitrate complexation and hydrolysis of Ce^{4+} in diluted solution can lead to a decrease in the redox potential of the system[4, 5]. Around 50% conversion efficiencies, however, were obtained in a short time.

With increasing injection quantity of ozone, concentration of cerium nitrate and nitric acid, the conversion efficiency on ozone mediated oxidation was increased. Also from results, measuring of redox potential of on ratio of $Ce^{3+}$and Ce^{4+} can be used instead of complicate UV measuring. The works of optimization on ozone mediated oxidation need to conduct in the future.

Acknowledgements

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