Plug Flow 반응기에서 Ce(IV)에 의한 EDTA의 분해

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Destruction of EDTA by Ce(IV) in Plug Flow Reactor

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Introduction

Mediated Electrochemical Oxidation (MEO) process is a non-combustion process which operates at ambient conditions and has the capacity to mineralize organics into CO_2 and water. Currently, few research groups are involved in developing MEO process with different mediated couples towards the commercial scale [1, 2]. In our previous investigations evaluated the destruction efficiencies of different organics in MEO process with Ce(IV) as the mediator with or without regeneration by the electrochemical cell [3-6].

MEO process is usually carried out in a batch or continuous mode. The main disadvantage of MEO process in batch mode is ineffective usage of MEO solution components and as a consequence it has a low productivity of organic destruction. In the continuous process organic is added during definite time interval long enough to destruct high quantity of organics. But, as our previous investigations showed two problems had to be addressed. First was to provide high residence time for each newly introduced portion of organic into the reactor and the second was to optimize the circulation regime of reactor on the basis of separate processing each organic portion.

Here the results are presented on EDTA destruction in continuous process without cerium regeneration.

Experimental

MEO solution was prepared using electrochemical cell as described earlier [4, 5] from 1M cerium(III) nitrate (TERIO Corp. China) dissolved in 3M nitric acid solution. EDTA destruction studies were carried out in a continuous process at temperatures 70, 80 and 95℃.

In this study schematic diagrams of plug flow reactor for destruction of EDTA are presented in Figure 1.

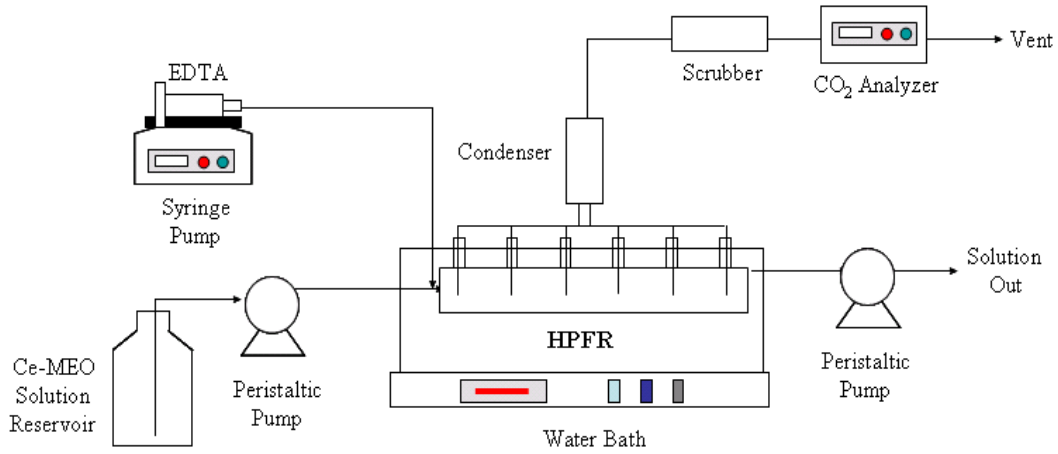

Figure 1. Schematic diagram of plug flow reactor for destruction of EDTA in MEO process

Suitable analytical methods were developed to check the concentrations of reactants, and final products of oxidation reaction. MEO destruction process is accompanied by Ce(IV) reduction. Samples at different time intervals were taken in the reactors and at the outlet and the remaining concentration of Ce(IV) was checked by titration with ammonium iron (II) sulfate hexahydrate (Samchun Pure Chemical Co. Ltd. Korea).

The efficiency of organic destruction was also checked by TOC analyzer (TOC-5000A, Shimadzu) in samples taken at the outlet of the reactors.

Results and Discussion

According to the stoichiometry EDTA would destruct in MEO process in the following manner:

$$2NaEDTA + 40Ce(IV) + 10H_2O \quad 10CO_2 + 40Ce(III) + 38H^+ + N_2 + 2Na^+ \cdots\cdots (1)$$

During the process, significant amounts of gaseous products (CO_2 and N_2) are formed inside the reactor, which causes mixing of solution layers. The plug flow reactor was especially constructed to study the effect on EDTA destruction efficiency.

The influence of the following parameters as residence time in reactor, mixing procedure and temperature were studied on EDTA destruction efficiency.

It was studied the influence of different liquid mixing methods like ultra-sonification, nitrogen gas bubbling and line mixing of MEO solution with EDTA on destruction efficiency. The concentration of Ce(IV), which can be reduced to Ce(III) by reaction with organics, is presented in Figure 2. It was shown that nitrogen bubbling and line mixing method gave highest EDTA destruction efficiency.

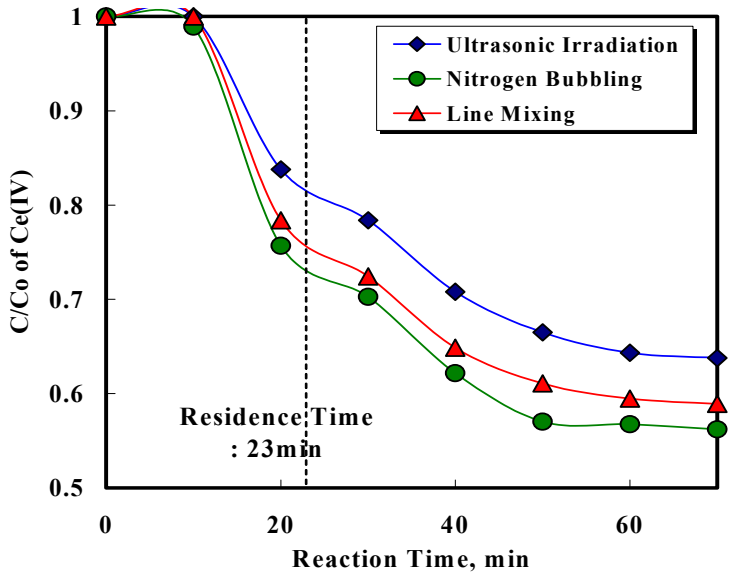

Figure 2. EDTA destruction efficiency with different mixing modes at 80℃

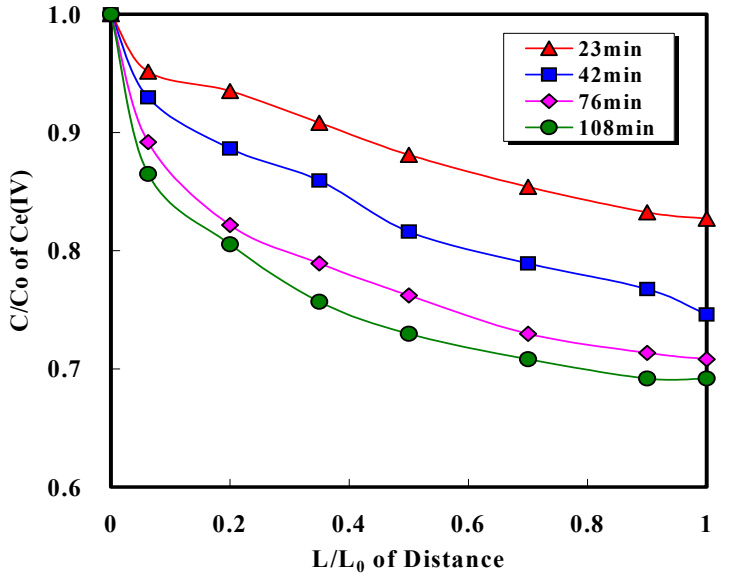

Figure 3. EDTA destruction efficiency with different residence time at 80℃

Residence times for HPFR were calculated by following equation:

$$t = -\frac{1}{k} \times \ln \frac{C}{C_0} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

Where k = $7.0 \cdot 10^{-4} s^{-1}$ obtained in our previous experiments, C/C_0 = relative EDTA concentration.

As can be seen from the Figure 3, EDTA destruction efficiency rises with the residence time rising. So, taking high enough residence time for plug flow reactor, it is possible to get desired destruction efficiency of process (much more than 95%).

Conclusions

Results of ethylenediaminetetraacetic acid (EDTA) destruction process in a continuous mode were presented. The destruction of EDTA by MEO process was studied in horizontal plug flow reactor. It was shown that the higher residence time of reactor and temperature of solution, then, there was the higher EDTA destruction efficiency. The horizontal type of plug flow reactor gave the desired efficiency (more than 95%) of overall mineralization process.

Acknowledgements

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