

Modeling of Organic Destruction by Cerium Mediated Electrochemical Oxidation Process

Vasily V. Kokovkin, Sang Joon Chung, Il-Shik Moon*

Department of Chemical Engineering, Sunchon National University

(ismoon@sunchon.ac.kr*)

Introduction

The mediated electrochemical oxidation process is an emerging technology for the destruction of organics, which uses an electrochemical cell to generate the oxidizing species at ambient temperatures (below 100°C) and at atmospheric pressures. Since MEO technology is still in the stage of development the complete process understanding require good modeling approach. The organic destruction in the MEO process can be carried out either in a batch or in a continuous mode. The continuous process in real applications is used mainly for minimizing the oxidant usage by simultaneous regeneration, and more organic materials can be destroyed in a continuous process than in a batch process.

In this report we propose two kinetic models for organic destruction in the continuous process [1]. First model is based on a simple first order oxidation reaction kinetic and mass balance equations. We apply this model to find the rate constants from the best fit to experimental data. The rate constant temperature dependence was used to calculate the thermodynamic parameters of the organic destruction activation process. The model was also tested for a long term organic feeding process to investigate the tendency of CO₂ evolution and the remaining organic concentration, and appropriate experiments were carried out. Second model takes into account several destruction processes assumed to be independent. In this extended model, the parameters are the appropriate rate constants and partial quantities of total organic destroyed.

Results and Discussion

The whole experimental procedure of organic addition in our experiments consists of two parts. In the first, the organic is added at particular time with simultaneous destruction, and in the second, after the organic feed is stopped, destruction only takes place. The modeling is concerned with the first part of the procedure.

Thus, the total time of organic addition is divided into n small intervals (Δt) during which it is assumed that the quantity of organic is added as one portion (ΔQ) i.e., equal portion of organic addition in equal interval of time. The quantity ΔQ may be defined as the product of concentration and volume of feed solution ($\Delta Q = C_{\text{feed}} \cdot \Delta V_{\text{feed}}$) or as that of MEO solution after addition and dilution ($\Delta Q = \Delta C \cdot V_{\text{MEO}}$). Using the second definition, the mathematical expressions for concentration of the organic added and remaining in the MEO solution are represented in Table. Note that the meaning of

V_{MEO} value was omitted because of its constancy from the expressions to get them simplified.

Table 1. Modeling Terms of Organic Concentration Calculations for Continuous Process of Organic Destruction

Step No.	Total time	Amount of organic compound		
		Added	Remained	Summation of GP
0	Δt	ΔC	ΔC	ΔC
1	$2\Delta t$	$2\Delta C$	$\Delta C + \Delta C \exp(-k \Delta t)$	$\Delta C(1 - \exp(-k2\Delta t)) / (1 - \exp(-k \Delta t))$
2	$3\Delta t$	$3\Delta C$	$\Delta C + \Delta C \exp(-k \Delta t) + \Delta C \exp(-k 2\Delta t)$	$\Delta C(1 - \exp(-k3\Delta t)) / (1 - \exp(-k \Delta t))$
3	$4\Delta t$	$4\Delta C$	$\Delta C + \Delta C \exp(-k \Delta t) + \Delta C \exp(-k 2\Delta t) + \Delta C \exp(-k 3\Delta t)$	$\Delta C(1 - \exp(-k4\Delta t)) / (1 - \exp(-k \Delta t))$
...
m-1	$m\Delta t$	$m\Delta C$	$\Delta C + \Delta C \exp(-k \Delta t) + \Delta C \exp(-k 2\Delta t) + \Delta C \exp(-k 3\Delta t) + \dots + \Delta C \exp[-k(m-1)\Delta t]$	$\Delta C(1 - \exp(-km\Delta t)) / (1 - \exp(-k \Delta t))$
..
n-1	$n\Delta t$	$n\Delta C$	$\Delta C + \Delta C \exp(-k \Delta t) + \Delta C \exp(-k 2\Delta t) + \Delta C \exp(-k 3\Delta t) + \dots + \Delta C \exp[-k(n-1)\Delta t]$	$\Delta C(1 - \exp(-kn\Delta t)) / (1 - \exp(-k \Delta t))$

As can be seen in Table 1, at the step $N=0$ some quantity of organic is added which is assumed to be not reacting in that moment, and its concentration becomes ΔC . In the step $N=1$, a new portion of organic is added, and now, this is present in the system (ΔC) with the previously added and partly unreacted organic ($\Delta C \exp(-kt)$). The concentration of the remaining organic is shown in the fourth column. In this column we can see the expressions for the consequent steps. But these expressions are too complex for large N values, and the procedure can be simplified if we consider that the expression for unreacted organics is a geometrical progression. Final sums of these calculations are given in the fifth column.

Note that Table 1 presents the results of calculations of the unreacted organic in the system during the addition only. If the organic addition is stopped, however, the calculation for concentration changes may be obtained according to first order kinetics after the last portion is added in to the system. The only unknown parameter is the k value. Setting k values in the expected range, numerical calculations may be made with Microsoft Excel program.

Evolution of CO₂ from the system can be calculated as the difference between the reactant added and the reactant remaining in each step using first order kinetics. It should be emphasized here that if a carrier gas with constant flow rate is used to bring out all CO₂ formed during the reaction.

In the real applications, however, long time feeding is needed (hours, days etc.). It means that the MEO solution should not accumulate the organic substance. The organics should be completely and constantly destructed upon feeding. Therefore, in the destruction process, some steady state regime should come into existence. From our short term experiments, it was found that a steady state was not reached in 30 minutes. So the model was tested for much longer time periods.

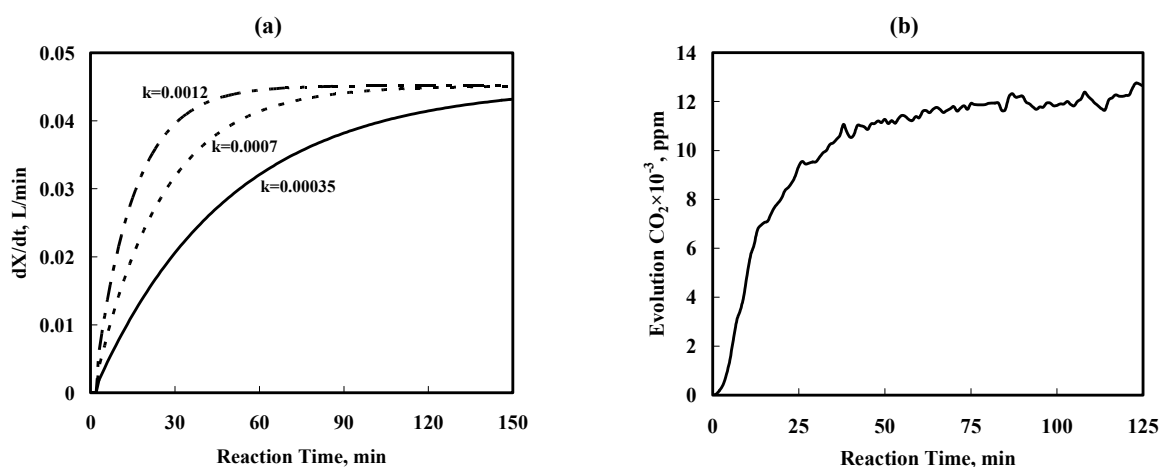


Figure 1. Modeling curves for three destruction processes with $k=3.5 \cdot 10^{-4}$; $7.0 \cdot 10^{-4}$ and $1.2 \cdot 10^{-3} \text{ s}^{-1}$ at 3 ml/min feeding rate of 2.5 % EDTA (a); experimental curve for CO₂ evolution during 2.5% EDTA destruction at 80 °C (b).

Figure 1 (a) presents the modeling curves for long time feeding (2.5 hours) for three processes of CO₂ evolution, having k values of $3.5 \cdot 10^{-4}$; $7.0 \cdot 10^{-4}$ and $1.2 \cdot 10^{-3}$ at 3 ml/min feeding rate of 2.5 % EDTA. As can be seen in the figure 1, the steady state really comes after 40 min for the process with $k=1.2 \cdot 10^{-3}$ and after 100 min with $k=7.0 \cdot 10^{-4}$. However, for $k=3.5 \cdot 10^{-4}$, the steady state was not reached up to 2.5 hours. This process may need much more time for reaching a steady state.

These findings led us to conclude that the proposed model satisfactorily predicted the steady state condition for organic feeding and simultaneous destruction. Subsequent experimental results were conformed to the model predictions.

In the present report, the modeling of the continuous feeding process was described, and further experiments are currently being investigated for longer durations. These experimental results seem to open up a new perspective for the destruction of large quantities of organics in the continuous mode MEO process.

Conclusion

Two models were proposed for calculating the remaining organic in MEO solution during a continuous process of organic addition followed by destruction and hence CO₂ produced. The models were based on pseudo-first order kinetics and mass balance equations. The remaining organic was calculated by using geometrical progression. The models predicted a steady state for the destruction process during a simultaneous organic feeding. It showed a way for large organic destruction in a long time MEO process treatment. Experimental results confirmed that the modeling predictions were accurate.

Acknowledgements

This work was funded by Core Environmental Technology Development Project for Next Generation (Eco-Technopia-21) of Korea Institute of Environmental Science and Technology (KIEST).

References

1. S.Balaji, V.V. Kokovkin, Sang Joon Chung, Il-Shik Moon, Modeling of EDTA destruction by cerium(IV) mediated electrochemical oxidation process. Environmental Science and Technology, 2006, (Submitted)