UVC Photo-Fenton Decomposition behavior of oxalic waste depending on H_2O_2 and iron catalyst for NPP chemical decontamination

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1. Introduction

This is a study on the decomposition of oxalic acid waste generated from the NPP chemical decontamination. The previous study on UVC photo-Fenton decomposition of oxalic acid (Jinhee Kim, wonzin Oh et al, NET 51, 2019) showed that the type of UV lamp and the irradiance density in terms of applied UVC energy irradiation/per volume,[kw*irradiation time/L] are important factors in simulation of the decomposition performance. The decomposition behavior of oxalic acid were studied as a function of H_2C_2 and iron catalyst concentration using a medium pressure UV lamp. Furthermore, the concentration ratio of H_2O_2 and iron catalyst was also investigated experimentally.

2. Methods and Results

2.1 Method

A : Cylindrical SUS reactor
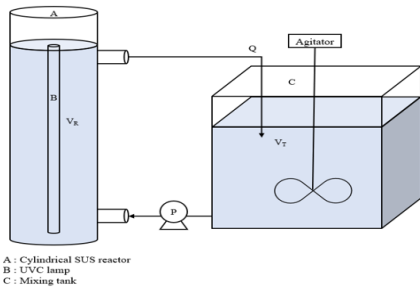B : UVC lamp
C : Mixing tank

Figure 1 Photo-reactor schematic for photo-Fenton treatment

The Fig 1 showed the experimental system for UVC Photo-Fenton decomposition of the oxalic waste. The decomposition behavior of oxalic waste depending on the amount of UVC energy applied were studied by varying the amount of hydrogen peroxide and iron(2+) catalyst together with its ratio. Table 1 showed the typical experimental condition in the study. As an iron catalyst FeCl2 was used in study. Residual concentration of H2C2O4 with reaction time was measured by TOC analyzer (TOC-V CPH, SHIMADZU, JAPAN).

2.2 Materials

Ferrous chloride (FeCl2-4H2O, Min. 99%), oxalic acid (H2C2O4-2H2O, Min. 99.5~100.2%), and hydrogen peroxide (H2O2, Min. 28%) were purchased from DAEJUNG company Korea. The size of UV reactor was 3L, waste volume 6L, Circulation rate 400ml/min, Reactor residence time 240 (min).

2.3 Results

In the previous study, the UVC decomposition behavior of oxalic acid was shown to be a first-order reaction of the oxalic acid concentration depending on the applied UVC energy density as follows:

- dC_Ox / dη = k* C_Ox, ic: C_Ox(0) = Co_Ox
C_Ox(η) = Co_Ox*exp(-0.693/kh*η),
where kh = 0.693/k is half decomposition energy density………………………………….. (1)

The table 1 and Fig 2 is an typical example of experimental condition and its simulation result using Eq(1) which shows that the decomposition reaction constant in terms of kh is 3.2[kJ/L] and R^2 is 0.99.

C_H2O2 =80 mM/L , Co_ox = 40[mM/L] , C_Fe(2+)=2 mM/L, with a random sampling time interval .

Time [min]	Roh_UV= Kw*T/V,[kJ/L]	pH	C_H2C2O4 [mmol/L]	Residual (%) by TOC	C_Fe2+ [mmol/L]	C_H+ [mmol/L]	TOC PPm	Residual[%] by Oh's model with Th=3.2
time[min]	Roh_UV			Resd_TOC[%]				Resd_Model[%]
0.00	0	2.08	32.9	100.0	2	8.31	788.5	100.00
10.00	3.96	2.12	14.6	44.5	2	7.58	350.6	42.42
20.00	7.92	2.25	12.9	39.4	2	5.62	310.5	17.99
40.00	15.84	2.49	12.3	37.5	2	3.23	295.6	3.24
60.00	23.76	2.52	11.1	33.6	2	3.01	265.3	0.58
90.00	35.64	2.56	9.6	29.2	2	2.75	230.5	0.04
120.00	47.52	2.60	8.2	24.8	2	2.51	195.6	0.00
150.00	59.4	2.72	6.9	21.0	2	1.9	165.5	0.00
180.00	71.28	2.85	6.1	18.4	2	1.41	145.2	0.00
240.00	95.04	3.04	4.8	14.5	2	0.91	114.3	0.00

Table 1. Example of Oxalic Waste UVC Photo Fenton Decomposition Experimental Condition
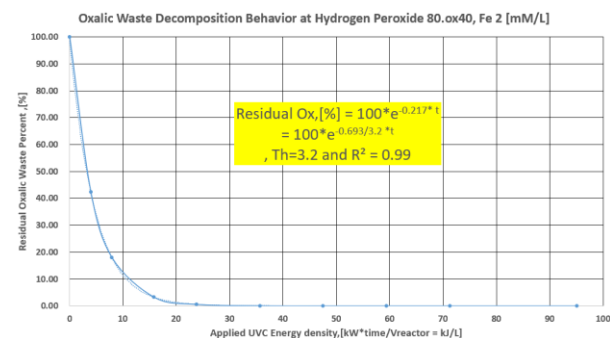

Fig. 2 UVC Photo Fenton Decomposition Performance Simulation Result of Table 1 Decomposition Condition
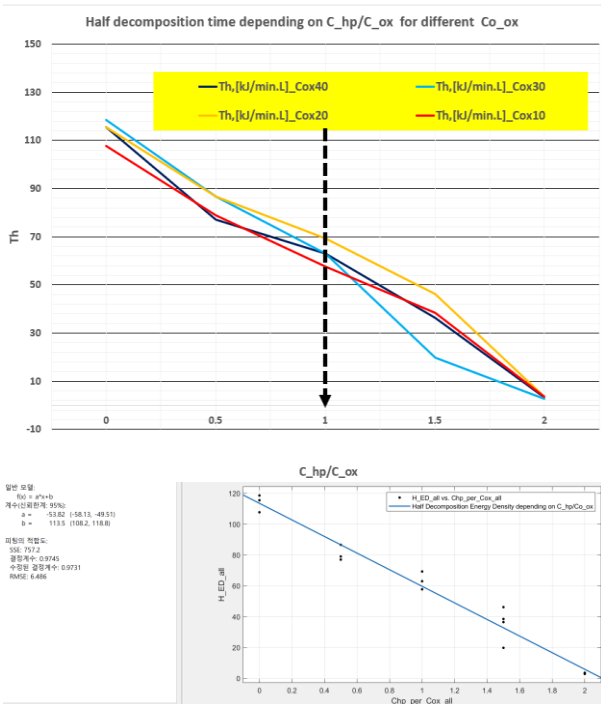
Fig. 3 Experimental result and its linear simulation of the applied energy density for half oxalate decom-position, kh[kJ/L], depending on $C\_H_2O_2/C\_Ox$ at Co_Ox of 10,20,30,40 [mM/L] and C_Fe of 2[mM/L]

The above figure shows that the decomposition behavior of oxalic acid Waste in terms of half energy density is linearly correlated with the ratio of hydrogen peroxide to oxalic acid concentration and the correlation equation is as follows:

Th,[kJ/L] = -53.82 * C_hp/C_ox +113.5 with R^2 of 0.97………………………………………………….(2)

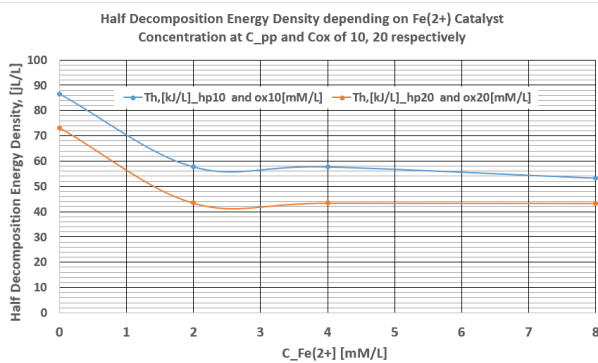Fig. 4 Effect of half decomposition energy density depending on Fe(2+) catalyst concentration at C_ox of 10 and 20 [mM/L]

The Fig. 4 shows that the decomposition half energy density is not affected of increase of Fe(2+) concentration more than 2[mM/L], while at C_Fe(2+)<2 [mM/L], the decomposition half energy

density increase by decrease of C_Fe(2+) up to almost two times.

4. Conclusion

The following conclusions were obtained for oxalate decomposition behavior by UVC Photo-Fenton depending on H_2O_2, $H_2C_2O_4$, and Fe^{2+} Concentration.

1. The decomposition rate in terms of half decomposition time constant of th was drastically increased depending on increase of the ratio of C-Hp/C-ox up to 2 where th approaches to zero.
2. The concentration of Fe^{2+} as a catalyst take a role to increase the decomposition rate of oxalic acid waste, but increase of Fe^{2+} concentration more than 2[mM/L] do not increase the decomposition rate.

ACKNOWLEDGEMENT

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