

The Applicability of pH Measurement as an Indicator for Estimation of Oxalic Acid Concentration

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1. Introduction

The key factor is less radioactive waste in applying the chemical decontamination method to remove the corrosion oxide film on the surface of NPP system. For this, the oxalic acid($H_2C_2O_4$) is widely used as a reducing agent, and thus oxalic acid waste liquid is generated[1]. To decompose the oxalic acid, a method of applying advanced oxidation processes(AOPs) has been studied, and UV/ H_2O_2 treatment has been generally applied[2].

In the UV/ H_2O_2 treatment, excessive H_2O_2 dose causes a scavenge effect that consume OH radicals[3], and thus an appropriate H_2O_2 dose estimate is required depending on the concentration of the treated target. However, during decomposing the oxalic acid by UV/ H_2O_2 treatment, it is difficult to measure the concentration of oxalic acid immediately. Therefore, a measure for immediate concentration estimation is needed to estimate the appropriate amount of H_2O_2 dose depending on the concentration of oxalic acid.

In this study, pH was selected as an indicator to estimate the concentration of oxalic acid. To determine suitability as an indicator, it was confirmed that the pH depending on the concentration of oxalic acid with ferrous ion was appropriately fitted with the concentration of hydrogen ion according to the acid dissociation constant(pKa) of the oxalic acid. In addition, it was confirmed that pH in the decomposition of oxalic acid by UV/ H_2O_2 was fitted with this model to assess whether it is applicable in the actual decomposition process.

2. Experiments

2.1 Fitting of pH depending on the concentration of oxalic acid

The oxalic acid has acid dissociation equilibrium as shown in the following equation, and it can estimate the concentration of hydrogen ion depending on the oxalic acid concentration.



We confirmed how well the hydrogen ions concentration depending on the oxalic acid concentration(from the above equation) fitted the pH value of the mixed solutions of various concentration oxalic acid with 2 mM $FeCl_2$. The oxalic acid concentration was set as 5, 10, 15, 20, 25, 30 mM and MATLAB was used for pH calculation.

2.2 Applicability in oxalic acid decomposition process

In order to confirm the applicability of the model formula to the actual oxalic acid decomposition process, pH of the oxalic acid containing ferrous ion was measured over time in the UV/ H_2O_2 treatment. The solution was prepared by mixing 2 mM ferrous chloride and 30 mM oxalic acid. For the UV/ H_2O_2 treatment, 120 W amalgam lamp was used. After injection of 30 mM H_2O_2 , the UV lamp was operated with 200 mL/min circulation using the peristaltic pump. The decomposition was carried out for 1 hour, and the change behavior of oxalic acid concentration and pH over time was observed. To investigate decomposition behavior of oxalic acid, Total Organic Carbon(TOC) was measured using TOC analyzer(TOC-V CPH, SHIMADZU, JAPAN)

3. Results

Fig. 1 shows that the comparison of pH by calculated from the acid dissociation constant and pH by measurement of the mixed solutions of various concentration oxalic acid with 2 mM FeCl₂. The results show that there is no significant difference between the pH calculated from the acid dissociation constant of pure oxalic acid and pH by measurement of the mixed solutions although 2 mM FeCl₂ is present. Also, as shown in Fig. 2, the pH calculated from the oxalic acid concentration over time in UV/H₂O₂ and the measured pH were not significantly different. However, there was a difference at the low concentration, which is considered to be the influence of residual Cl⁻ ion after decomposition.

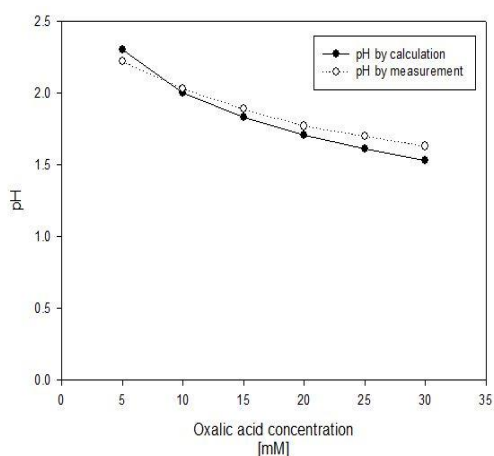


Fig. 1. Comparison of pH by calculation and by measurement depending on oxalic acid concentration.

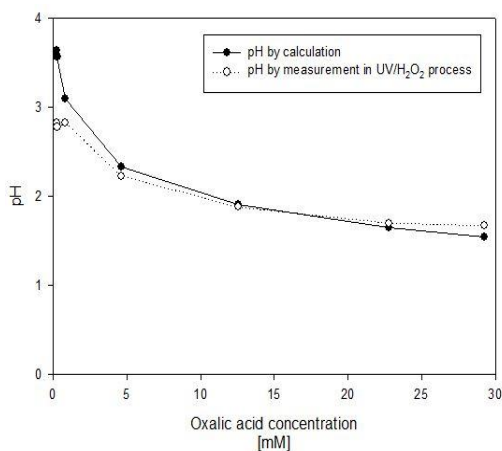


Fig. 2. Comparison of pH by calculation and by measurement in UV/H₂O₂ process.

4. Conclusion

It was investigated whether pH is suitable as an indicator for estimation of oxalic acid concentration. We obtained the following conclusion from the experimental results:

1. The oxalic acid containing Fe²⁺ ion follows hydrogen dissociation behavior similar to the acid dissociation equilibrium of pure oxalic acid
2. In the UV/H₂O₂ process to decompose oxalic acid, immediate concentration estimation is possible by measuring pH at concentration range above 5 mM.

5. Acknowledgement

This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20141510300310).

REFERENCES

- [1] Nagase, Makoto, et al., "Low corrosive chemical decontamination method using pH control, (I) basic system", *Journal of nuclear science and technology*, 38(12), 1090-1096 (2001).
- [2] Quici, Natalia, et al., "Oxalic acid destruction at high concentrations by combined heterogeneous photocatalysis and photo-Fenton processes", *Catalysis today*, 101(3-4), 253-260 (2005).
- [3] Wang, G. S., et al., "Characteristics of natural organic matter degradation in water by UV/H₂O₂ treatment", *Environmental technology*, 27(3), 277-287 (2006).