

論文 / 著書情報  
Article / Book Information

題目(和文)	TOCおよびCOD測定によるフェノールの促進酸化処理の評価
Title(English)	Study on Advanced Oxidation Process of Phenol based on TOC and COD Measurements
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

(博士課程)  
Doctoral Program

## 論文要旨

THESIS SUMMARY

専攻: 物質電子化学 専攻  
Department of  
学生氏名: 叶 (葉) 嘯  
Student's Name

申請学位 (専攻分野): 博士 (工学)  
Academic Degree Requested Doctor of  
指導教員 (主): 北村 房男  
Academic Advisor(main)  
指導教員 (副):  
Academic Advisor(sub)

要旨 (英文 800 語程度)  
Thesis Summary (approx.800 English Words)

Water treatment is quit important for the survival and development of human beings. And advanced oxidation process (AOP), which is a set of chemical treatment procedures designed to remove organic materials in water or waste water by oxidation reactions with hydroxyl radicals ( $\cdot\text{OH}$ ), is one important method used for water treatment. In my research, ozone ( $\text{O}_3$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was utilized for AOP treatment to treat the waste water containing low concentration of phenol, which is one kind of important industrial raw materials. After the treatment, the sample solutions were evaluated by total organic carbon (TOC) and chemical oxygen demand (COD).

My doctoral thesis consists of seven chapters. In Chapter 1, background and objectives of this research were described.

In Chapter 2, the meaning of TOC and COD and the mechanism of TOC and COD measurements were introduced in detail. In my lab, I use UV/persulfate oxidation to decompose all the organics into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Based on the electrical conductivity of water, TOC of water samples can be measured automatically. On the other hand, In COD measurement, sample solutions were oxidized by  $\text{KMnO}_4$  (with  $\text{H}_2\text{SO}_4$  and  $\text{AgNO}_3$ ) at  $100^\circ\text{C}$  for 30 min. Then by detecting the concentration of  $\text{MnO}_4^-$ , the COD values were calculated automatically. In this chapter, the mechanism of ozone generation was also introduced. Ozone was produced by water electclysis with the anode coated by  $\text{PbO}_2$ . The mass flow rate (mg / min) was measured and in this research the mass flow rate was kept at 0.60 mg / min.

In Chapter 3, we discussed how residual  $\text{H}_2\text{O}_2$  (after AOP treatment) affects the COD measurement and how to solve this problem.  $\text{H}_2\text{O}_2$  reacts with the oxidant (e.g.,  $\text{KMnO}_4$ ) utilized in COD analysis, resulting in the overestimation in COD measurement. Using  $\text{Na}_2\text{CO}_3$  as catalyst for the decomposition of  $\text{H}_2\text{O}_2$  under a heated condition ( $95^\circ\text{C}$  for 2 h),  $\text{H}_2\text{O}_2$ -derived COD of oxalic acid (OA) solution could be brought successfully to less than submicromolar. However, the overdose of acid ( $\text{H}_2\text{SO}_4$ ) added for neutralizing the  $\text{Na}_2\text{CO}_3$ -containing OA solution was found to cause new interference in COD measurement. It is considered that in strong acid solutions the decomposition of  $\text{KMnO}_4$  may be accelerated during COD analysis, leading to its overestimation. The results suggest that a suitable decomposition of residual  $\text{H}_2\text{O}_2$  as well as a suitable control of acidity (to neutrality) of the sample solution subjected to COD analysis is essentially necessary for the correct COD estimation.

In chapter 4, we discussed the ozonation and AOP treatment of phenol solution. At first 1.50 mM phenol solutions were treated by  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$  or  $\text{O}_3/\text{H}_2\text{O}_2$ . According to TOC removal, it is impossible to oxidize phenol by  $\text{H}_2\text{O}_2$  at room temperature without any catalyst. And by using  $\text{O}_3$ , about 30% TOC was removed in 180 min. However, due to the low reaction rate between  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  in acidic solution ( $\text{pH} = 3$ ), when  $\text{H}_2\text{O}_2$  was added to this system, comparing with ozonation, there was few advanced effect detected. When pH was adjusted to about 11, it was found that the TOC removal was increased

to 67.2% in 180 min. Since  $\text{HO}_2^-$  formed at high pH can react with  $\text{O}_3$  rapidly to generate OH radical, AOP can oxidize phenol faster than ozonation at high pH. Then at optimum conditions, it was found that phenol solution could be oxidized by ozone or AOP, but it was difficult to remove TOC and COD completely. I plotted the relationship between TOC and COD, and it seems that the transformation of TOC and COD is related to the mechanism of phenol oxidation. There are three stages for ozonation and AOP treatment of phenol and different stage shows different slope in the plots of TOC vs COD. Depending on the mechanism of oxidation and the figure of TOC vs COD (or TOC/COD vs time), maybe which kinds of organics exist in the solution could be speculated. However, oxidation of phenol is so complicated that it is difficult to make this theory clearly, so I selected several intermediates (such as maleic acid, oxalic acid) which were reported to be formed during phenol oxidation by peroxone and tried to find the relation between the mechanism of oxidation and TOC/COD

In Chapter 5 and Chapter 6, AOP treatment of oxalic acid and malic acid was evaluated. At optimum conditions, Oxalic acid (0.75 mM) was oxidized completely in 120 min. By calculating the experimental value of TOC/COD, it was found that the oxalic acid was oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  directly and during the AOP treatment, just oxalic acid existed in the solution. On the other hand, during the AOP treatment, TOC and COD of malic acid solution were decreasing continuously and experimental values of TOC/COD changed from 0.55 to 0.77, and finally reached to 1.50. Each organic has theoretical value of its own TOC/COD and the TOC/COD value of solution changes with different organics. According to the mechanism of oxidation, I think that by using TOC/COD value, it is possible to speculate the organics existing in aqueous solution.

In Chapter 7, I described the general conclusions of this research.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note: Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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