

摘 要

本研究利用人工製備磁性過氟辛酸鋁(magnetic perfluorooctylalumina, MPFOA)結合臭氧反應處理德基水庫原水，以探討磁性催化劑製備情形與處理原水反應機制和處理後水中有機物質之官能基分佈情形。

本研究採集中台灣地區德基水庫之飲用水水源為探討之水體，藉由 XAD-8 樹脂分離出五種天然有機物質，水中有機物分離成腐植酸(29.5%)、黃酸(19.5%)、疏水性中性物(37.9%)、疏水性鹼性物(2.9%)以及親水性物質(10.2%)等五種有機物。

製備磁性催化劑(MPFOA)之特性可利用掃描式電子顯微鏡/能量分散光譜儀(SEM/EDS)、超導量子干涉磁量儀(SQUID)、X光單晶繞射儀(XRD)以及傅利葉轉換紅外線光譜(FTIR)來鑑定。MPFOA具有吸附臭氧及有機物的能力，亦可增加臭氧在水中的溶解度及穩定度，故在臭氧化過程中添加MPFOA可提高臭氧對有機物質破壞之效率。在整個臭氧反應中皆利用即時監測偵測氧化還原電位(ORP)、水中溶解臭氧(DO₃)及pH即時數據資料，以供來討論臭氧反應機制並建立臭氧與添加催化劑反應之模擬Nernst方程式。

根據傅立葉轉換紅外線分光光譜儀和碳-13核磁共振光譜儀來探討原水經由臭氧反應與添加MPFOA後之官能基變化情形。本研究分

析結果發現水中部份官能基因臭氧添加 MPFOA 反應後而被破壞，有
提昇臭氧反應性之趨勢。

關鍵字：磁性過氟辛酸鋁、催化劑、天然有機物質、臭氧、傅立葉轉
換紅外線分光光譜儀、碳-13 核磁共振光譜儀

Abstract

This study the magnetic perfluorooctylalumina (MPFOA) is used to enhance the efficiency of ozonation on the treatment of the eutrophic raw water of Te-Chi Reservoir. The investigation includes the preparation of the magnetic catalyst, miasmic study on the ozonation of the raw water and the variation of functional groups upon the ozonation.

The water samples were collected from Te-Chi Reservoir which provides major domestic water supply in metropolitan central of the Taiwan area. The organic contents of water samples were extracted and classified into humic acids (HAs, 29.5 %), fulvic acids (FAs, 19.5 %), hydrophobic neutrals (37.9 %), hydrophobic bases (2.9 %) and hydrophilic fractions (10.2 %) by using of XAD-8 resins.

The characteristics of MPFOA can be identified by the scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS), Superconducting quantum interference device (SQUID), X-ray powder diffraction (XRD) and Fourier-transform infrared spectrophotometer (FTIR). MPFOA has the more ability to adsorb ozone and organic matters, and furthermore to increase the ozone dissolving rate and stability. Therefore, the ozonation with MPFOA can raise the decomposition efficiency of toward to organic matters. During ozonation process, the ORP, DO₃, and pH values were monitored and

connected to an on-line oscilloscope to investigate the ozonation mechanisms. The data also used to establish the Nernst equation and simulate the possible ozonation mechanisms the presence of catalyst.

The profile of functional groups during the ozonation was examined by both FTIR and ^{13}C NMR spectra. The variation of functional groups can represent the destruction by ozonation and ozonation with MPFOA in this study.

Keywords: magnetic perfluorooctylalumina (MPFOA), catalyst, NOMs, ozonation, FTIR, ^{13}C NMR

Contents

Chapter 1 Introduction.....	1
1.1 Introduction	1
1.2 Objectives.....	5
Chapter 2 Literature Review.....	6
2.1 Natural organic matters in reservoir.....	6
2.2 Application of ozone.....	7
2.2.1 <i>Advanced oxidation processes (AOPs)</i>	7
2.2.2 <i>Two-stage ozone reactions</i>	8
2.2.3 <i>Hydroxyl radicals measurement in ozonation</i>	10
2.2.4 <i>The catalytic ozonation</i>	11
2.3 Magnetic technology.....	12
2.3.1 <i>Magnetic particles and magnetic separation</i>	12
2.3.2 <i>Magnetic application</i>	13
2.4 Modeling.....	14
2.5 Change of functional groups.....	15
Chapter 3 Material and Methods.....	18
3.1 Experimental design.....	18
3.2 Methods and instruments.....	21
3.2.1 <i>Sampling site</i>	21
3.2.2 <i>Extraction procedure</i>	22
3.2.3 <i>Ozonation system</i>	26
3.2.4 <i>On-line oscilloscope monitors equipment</i>	28
3.3 Analysis Methods.....	29
3.3.1 <i>Basic water quality analysis</i>	29

3.3.2 Absorbance at wavelength of 254 nm.....	30
3.3.3 Dissolved organic carbon (DOC).....	30
3.3.4 Hydroxyl radicals determination.....	32
3.3.5 Preparation of magnetic superparamagnetic perfluorooctanoic acid-type catalyst.....	34
3.3.6 Scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS).....	37
3.3.7 Superconducting quantum interference device (SQUID).....	38
3.3.8 X-ray powder diffractometer (XRD).....	38
3.3.9 Fourier Transform Infrared Spectrometer (FTIR).....	39
3.3.10 Carbon-13 Nuclear Magnetic Resonance (CPMAS ¹³ C NMR).....	39
Chapter 4 Results and Discussion.....	41
4.1 Water quality of Te-Chi Reservoir.....	41
4.2 Characteristics of preparation magnetic perfluorooctylalumina (MPFOA) catalyst.....	50
4.2.1 Specific surface area.....	50
4.2.2 Magnetic particle patterns.....	50
4.2.3 Magnetization curves.....	53
4.2.4 Crystal structure of magnetic particles.....	54
4.2.5 The characteristics and recycling test of MPFOA catalyst.....	56
4.2.6 The dose of catalyst.....	58
4.3 The investigation of ozonation mechanisms.....	60
4.3.1 Hydroxyl radicals measurement.....	60
4.3.2 Ozonation and catalytic ozonation mechanisms.....	62

4.4 Modeling of ozone and catalyst reactions.....	66
4.5 Change of functional groups during ozonation.....	69
Chapter 5 Conclusions and Suggestions.....	77
5.1 Conclusions.....	77
5.2 Suggestions.....	79
References.....	80
Appendix.....	89
Appendix I.....	89
Appendix II.	93

List of Tables

Table 3.1 Summary of the reagents and equipments for NOMs water separation from Te-Chi Reservoir by resin extraction process.....	24
Table 3.2 ORP analysis conditions by the Digital storage Oscilloscope.....	28
Table 3.3 Basic water quality analysis items and methods.....	29
Table 3.4 Summary of the reagent and equipment for DOC test.....	31
Table 3.5 Summary of the calibration equation for DOC.....	32
Table 3.6 Summary of the calibration equations for coumarin.....	34
Table 4.1 The water quality parameters of Te-Chi Reservoir raw water in recent years (1998-2006).....	43
Table 4.2 The percentage distribution of Te-Chi Reservoir NOMs (% of DOC) in recent years (2001-2006) and compare to literature.....	47
Table 4.3 The EDS spectra of atomic percent of the intermediates (a, b, c) along the preparation of MPFOA.....	53
Table 4.4 Abbreviated tables of group frequencies for NOMs organic groups obtained by Lin <i>et al.</i> (2001), Hafidi <i>et al.</i> (2005) and Kanokkantapong <i>et al.</i> (2006).....	70

List of Figures

Figure 3.1 The experimental design and analysis process of this study.....	20
Figure 3.2 The water sampling location of Te-Chi Reservoir, which supply water for domestic water in Tai-Chung area, central Taiwan, ROC.....	21
Figure 3.3 The flowchart of separated five NOMs categories (HAs, FAs, hydrophobic bases, hydrophobic neutrals and hydrophilic fractions) from Te-Chi Reservoir raw water by resin separation process.....	25
Figure 3.4 Schematic diagram of the 5-liter ozonation system equipped with a mixer and three monitor sensors (pH, ORP and dissolved ozone) connected with oscillographic recorder. Ultraviolet detector (Cary 50) connected with the optical fiber probe for monitoring the change of A_{254} in ozonation system.....	27
Figure 3.5 Schematic diagram of experimental system for the preparation experiments. The system contains: nitrogen purge injector, mixer, the thermometer and heating plate.....	37
Figure 4.1 The percentage of five species (HAs, FAs, hydrophobic bases, hydrophobic neutrals and hydrophilic fractions) of organic fractions extracted from Te-Chi Reservoir in 2006.....	45
Figure 4.2 The SUVA value (A_{254}/DOC) of raw water and five fractions (HAs, FAs, hydrophobic bases, hydrophobic neutrals and hydrophilic fractions) extracted from Te-Chi Reservoir in 2006.....	49
Figure 4.3 The SEM pictures and EDS spectra of the preparation steps of MPFOA. (a) $\text{Fe}_3\text{O}_4/\text{SiO}_2$, (b) $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Al}(\text{OH})_3$ and (c) MPFOA.....	52
Figure 4.4 Magnetization curves of various magnetic particles.....	54

Figure 4.5 X-ray diffraction (XRD) patterns with the radiation source of Cu K α for various magnetic particles: (a) Fe ₃ O ₄ particles; (b) Fe ₃ O ₄ /SiO ₂ particles; (c) Fe ₃ O ₄ /SiO ₂ /Al(OH) ₃ particles and the final product of (d) MPFOA particles.....	56
Figure 4.6 The FTIR spectrum of (a) Perfluorooctanoic acid (PFA), (b) Original MPFOA, (c) Reused MPFOA and (d) 5 th Reused MPFOA. The main functional C-F bonds located between 1,100 to 1,250 cm ⁻¹	58
Figure 4.7 The ORP profiles of ozonation (blank) with the dose amount of 0, 0.5, 1.0, 2.0, 3.0 and 4.0 g/L of MPFOA.....	59
Figure 4.8 The maximum OH radicals (mg/L) in pure water during saturated ozone. The initial coumarin concentration (65 mg/L) indicates the maximum amount of OH radical (1.6 mg/L) in the reactor.....	61
Figure 4.9 The analytic value on-line monitored data (a) ORP and DO ₃ , (b) OH radicals during the ozonation and catalytic ozonation of pure water.....	63
Figure 4.10 The on-line monitored data (a) ORP and OH radicals, (b) pH and DO ₃ during the ozonation and catalytic ozonation of Te-Chi Reservoir raw water.....	65
Figure 4.11 The Nernst model simulation of A ₂₅₄ during ozonation and catalytic ozonation of Te-Chi Reservoir raw water.....	68
Figure 4.12 FTIR spectrums of Te-Chi Reservoir raw water during (a) before ozonation (Raw water), (b) after ozonation (Raw water + O ₃) and (c) after ozonation with MPFOA (Raw water + O ₃ + MPFOA).....	72
Figure 4.13 ¹³ C NMR spectra of Te-Chi Reservoir raw water (a) before ozonation (Raw water), (b) after ozonation (Raw water + O ₃) and (c) after ozonation with MPFOA (Raw water + O ₃ + MPFOA).....	75
Figure 4.14 ¹³ C NMR spectra of humic acid from Te-Chi Reservoir raw water (a)	

before ozonation (Humic acids), (b) after ozonation (Humic acids + O₃)
and (c) after ozonation with MPFOA (Humic acids + O₃ + MPFOA)...76

Nomenclatures

¹³ C-NMR	¹³ C nuclear magnetic resonance	碳-13 核磁共振光譜儀
A ₂₅₄	Absorbance at 254 nm	254 nm 波長之吸光度
AOP	Advanced oxidation process	高級氧化法
COD	Chemical oxygen demand	化學需氧量
DO	Dissolved oxygen	溶氧
DO ₃	Dissolved ozone	溶臭氧
DOC	Dissolved organic carbon	溶解有機碳
FAs	Fulvic acids	黃酸
FTIR	Fourier transform infrared spectrophotometer	傅利葉轉換紅外線光譜儀
HAs	Humic acids	腐植酸
HPLC	High performance liquid chromatography	高效率液相層析儀
MPFOA	Magnetic perfluorooctylalumina	磁性過氟辛酸鋁
NOMs	Natural organic matters	天然有機物質
OH radical	Hydroxyl radical	氫氧自由基
ORP	Oxidation reduction potential	氧化還原電位
SUVA	Specific ultra-violet absorbance	比紫外光吸光度
SEM/EDS	Scanning electron microscopy with energy dispersive spectroscopy	掃描式電子顯微鏡/能量分散光譜儀
SQUID	Superconducting quantum interference device	超導量子干涉磁量儀
TDS	Total dissolved solids	總溶解固體
XRD	X-ray powder diffractometer	X 光粉末繞射儀
