

東海大學環境科學與工程學系碩士班

碩士論文

利用磁性金屬臭氧催化劑降解水中消毒副產物

The Assembly of Magnetic Metal Ozone Catalyst to
Decompose Disinfection of Byproduct

研究生：呂理維 撰

指導教授：張鎮南 博士

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摘要

本研究採集天然水樣為供應大台中地區飲用水水源的德基水庫，利用 DAX-8 樹脂將原水樣品分離成五種有機成分，分別為腐植酸(10.8%)、黃酸(25.4%)、疏水性中性物質(23%)、疏水性鹼性物質(4.1%)和親水性物質(34.9%)。磁性 $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{CoO}_x$ 催化顆粒利用溶膠凝膠法製成應用於催化臭氧反應上。而顆粒上的 pH_{pzc} 為 1.87，一開始先利用商業性腐植酸作為降解對象，找出在不同的 pH 值上的最佳降解效果。在 pH 4 時，比較於臭氧反應，催化臭氧反應有明顯的降解效果，而所得到的 K_d 值為 $0.214(\text{s}^{-1})$ 。香豆素作為捕捉氫氧自由基的物質，也是觀察在催化臭氧反應下氧化直接與間接反應的途徑，實驗數據顯出直接/間接的比率為 37/63 在 pH 4 的條件之下，而 pH 7 時為 39/61，pH 10 29/71。催化臭氧反應在降解腐植酸的數據 A_{254} ，在 pH 4 為 88.6%，在 pH 7 為 82.6%，在 pH 10 為 81.8%。催化臭氧反應其在酸、中、鹼都以間接氧化反應為主。

關鍵字：天然腐植酸、臭氧反應、催化臭氧反應、氧化還原電位、氫氧自由基。

Abstract

This study collected natural water samples from Te-Chi Reservoir which provides the water source to the metropolitan Taichung area. The organic contents of raw water sample were extracted and classified into hydrophobic neutrals (HPON, 23%), humic acids (HAs, 10.8%), fulvic acids (FAs, 25%) hydrophobic bases (HPOB, 4.1%) and hydrophilic fractions (HPI-F, 34.9%). Magnetic $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{CoO}_x$ was synthesized by sol-gel methods as catalysts in ozonation. The catalysts was indicated with the pH_{zpc} of 1.87. Initially, decomposition of commercial humic acid in different pH levels, (pH 4, 7 and 10) was investigated. The acidic condition was found have high decomposition rate (K_d , 0.214 S^{-1}). The coumarin as a hydroxyl radical scavenger was investigated the contribution of direct/indirect oxidation mechanisms in deionized water by sole ozonation and catalytic ozonation in different pHs. Experimental data indicated the contribution of direct/indirect reactions were 37/63% in pH 4, 39/61% in pH 7 and 29/71% in pH 10 by catalytic ozonation, respectively. The indirect oxidation would be the major reaction mechanisms in the catalytic ozonation. The catalyst

ozonation reduction rates of A_{254} are 88.6% (pH 4), 82.6 (pH 7) and 81.8% (pH 10), which is significantly improved than that of ozone alone systems.

Keywords: NOMs, Ozonation, ORP, hydroxyl radicals, catalytic ozonation

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Nomenclature

NOM	Natural organic matter	天然有機物質
HS	Humus	腐植質
FA	Fulvic acid	黃酸
HA	Humic acid	腐植酸
DBP	Disinfection by-product	消毒副產物
THM	Trihalomethane	三鹵甲烷
HAA	Halogenated acetic acid	鹵化乙酸
AOP	Advanced oxidation process	高級氧化程序
·OH	Hydroxyl radicals	氫氧自由基
ORP	Oxidation reduction potential	氧化還原電位
HPO-F	Hydrophobic fraction	疏水性成分
HPI-F	Hydrophilic fraction	親水性成分
HPON	Hydrophobic neutrals	疏水性中性物質
HPOB	Hydrophobic bases	疏水性鹼性物質
HPOA	Hydrophobic acids	疏水性酸性物質
DBPFP	Disinfection by-product formation potential	消毒副產物生成潛能
¹³ C	¹³ C nuclear magnetic resonance spectroscopy	碳 ¹³ 核磁共振光譜儀
NMR		
FTIR	Fourier transform infrared spectrophotometer	傅利葉轉換紅外線光譜
AOM	Artificial organic matter	人為有機物質
TOC	Total organic carbon	總有機碳
COD	Chemical oxygen demand	化學需氧量
DO	Dissolved oxygen	溶氧
TDS	Total dissolved solids	總溶解固體
DI	Deionized	去離子
DO ₃	Dissolved ozone	溶臭氧
A ₂₅₄	Absorbance at 254 nm	254 nm 波長之吸光度
DOC	Dissolved organic carbon	溶解有機碳
SUVA	Specific ultra-violet absorbance	比吸光度
HPLC	High performance liquid chromatography	高效能液相層析儀
k _d	Self-decomposition constant of ozone	臭氧的分解速率常數
R	Gas constant (8.314 V-coulombs K ⁻¹ mol ⁻¹)	氣體常數
T	The absolute temperature (K)	絕對溫度
n	The number of electrochemical gram equivalent per gram mole exchanged during the redox reaction (equivalent mol ⁻¹)	轉移電子之莫耳數

pzc	point of zero charge	零電荷點
TEM	transmission electron microscopy	穿透式電子顯微鏡
XRD	x-ray Diffraction	X-光粉末繞射儀
NSA	nanoparticle size analyzer	奈米顆粒粒徑分析