

DOCTORAL THESIS

Catalytic advanced oxidation processes for degradation of environmental emerging contaminants

Law, Cheuk Fung Japhet

Date of Award:
2019

[Link to publication](#)

General rights

Copyright and intellectual property rights for the publications made accessible in HKBU Scholars are retained by the authors and/or other copyright owners. In addition to the restrictions prescribed by the Copyright Ordinance of Hong Kong, all users and readers must also observe the following terms of use:

- Users may download and print one copy of any publication from HKBU Scholars for the purpose of private study or research
- Users cannot further distribute the material or use it for any profit-making activity or commercial gain
- To share publications in HKBU Scholars with others, users are welcome to freely distribute the permanent URL assigned to the publication

Abstract

In recent years, the increasing release of trace organic chemicals to the aquatic environment have been problematic to both the ecosystem and the human society. These trace organic chemicals, regarded as emerging contaminants, include different categories of chemicals, which are either deemed to be safe for human consumption or they are naturally occurring compounds. As a newly recognized class of emerging contaminant, artificial sweeteners are proven to be one of the most ubiquitous classes of emerging contaminants in environmental waters. Its transformation to different suite of TPs during water treatment processes generated more toxic influence than the parent compound is problematic.

The realization of the widespread of emerging contaminants, together with their ambiguous fate and impact to the environment have led to the development of advanced oxidation processes that can effectively attenuate this wide range of contaminants. In this work, several catalytic advanced oxidation processes were studied. On one hand, it aimed to evaluate their effectiveness on the removal of the artificial sweetener – acesulfame; and on the other hand, to shed lights on the future development of catalytic advanced oxidation processes.

In the first part of this thesis, the photo-Fenton treatment was evaluated on its potential to effectively remove acesulfame together with the produced transformation products, and the post-treatment toxicity screening. The photo-Fenton treatment was found to be effective in removing both the parent compound and the transformation

products, without leading to an increase in toxicity, which is largely related to the effective removal of the transformation products.

In attempt to reduce the reliance on UV irradiation, newly synthesized carbon and nitrogen co-doped TiO₂-based photocatalyst was applied to capture the simulated sunlight for the degradation of acesulfame. The heterogenous photocatalytic treatment was found to involve several different oxidative reactive species for both degradation and transformation by using several scavengers to alter the degradation profile. Unexpected transformation product was also formed upon treatment in actual water matrix, suggesting the impact of water constituents to the transformation of emerging contaminants. Toxicity results indicated the inability to achieve detoxification, suggesting that a more effective degradation process was needed.

To accelerate the degradation process, and enhance the performance at neutral pH, the use of redox mediators for Fenton/Fenton-like system was evaluated. Developed novel Fenton-like system involving copper(II) as transition metal ion, persulfate as oxidant and mercaptosuccinic acid as redox mediator led to effective removal of different contaminants. Elucidation of the proposed oxidation mechanism suggested the role of each components of the system, and the generation of different reactive species for degradation as indicated by the different acesulfame transformation profile obtained. The implementation of redox mediators to Fenton/Fenton-like system was beneficial and an effective approach.

In short, this work presents several kinds of catalytic advanced oxidation process and shed lights on improving the degradation performance with directions for the future development of better and more effective water treatment processes.

Table of Contents

Abstract	ii
Acknowledgements	iv
List of Tables.....	xi
List of Figures	xii
List of Abbreviations and Symbols.....	xxi
Chapter 1 Introduction.....	1
1.1. Emerging contaminants.....	1
1.1.1. Background.....	1
1.1.2. Artificial sweeteners as Emerging Contaminants	3
1.2. Advanced Oxidation Processes (AOPs).....	5
1.2.1. Introduction and two-steps mechanism of AOPs	5
1.2.1.1. Catalytic AOPs	7
1.2.2. Application of AOPs.....	14
1.3. Aim of thesis work	16
1.4. References.....	18
Chapter 2 Photo-Fenton treatment of acesulfame and ACE-TPs removal.....	24
2.1. Introduction.....	24
2.2. Results and Discussion.....	27

2.2.1.	Optimization of the photo-Fenton system	27
2.2.1.1.	Effect of $[\text{Fe(II)}]_{\text{ini}}$	27
2.2.1.2.	Effect of $[\text{H}_2\text{O}_2]_{\text{ini}}$	28
2.2.1.3.	Effect of light intensity	30
2.2.1.4.	Performance in wastewater matrix	31
2.2.2.	Identification and toxicity evaluation of ACE TPs.....	33
2.2.2.1.	TPs identification and structural elucidation	33
2.2.2.2.	Time profiling of ACE TPs and its toxicity assessment.....	40
2.3.	Conclusions	49
2.4.	References	50
Chapter 3 – Photocatalytic oxidation of acesulfame using carbon and nitrogen co-doped TiO_2 photocatalyst.....		55
3.1.	Introduction	55
3.2.	Results and Discussion.....	58
3.2.1.	Optimization of operation parameters	58
3.2.1.1.	Adsorption of ACE by C,N- TiO_2 citrate	58
3.2.1.2.	Effect of C,N- TiO_2 citrate loading	60
3.2.1.3.	Effect of light source	63
3.2.1.4.	Application in actual water matrices	65
3.2.1.5.	Quencher test for identification of reactive species	66

3.2.2.	Evaluation of ACE TPs formation by C,N-TiO ₂ citrate photocatalytic oxidation.....	71
3.2.2.1.	Relationship between transformation products formation and the reactive species involved in ACE degradation	72
3.2.2.2.	ACE-TPs formation in actual water matrices.....	75
3.2.2.3.	Time profile study	79
3.2.3.	Toxicity assessment	83
3.3.	Conclusions.....	86
3.4.	References	88

Chapter 4 Redox Mediator-modified Fenton/Fenton-like system for emerging contaminants degradation.....92

4.1.	Introduction.....	92
4.2.	Results and Discussion.....	96
4.2.1.	Addition of redox mediators for Fenton treatment at neutral pH	96
4.2.1.1.	Effect of redox mediators to Fe(II)/H ₂ O ₂ system.....	96
4.2.1.2.	Comparison of redox mediators' effect towards Fe(II)/H ₂ O ₂ system 100	
4.2.1.3.	Performance in actual water matrices.....	102
4.2.2.	Degradation of contaminants by Cu(II)/PS/MSA system.....	103
4.2.2.1.	Degradation of selected model contaminants.....	104

4.2.2.2.	Optimization of operation parameters	105
4.2.3.	Analysis of reactive species and proposed oxidation mechanism	112
4.2.3.1.	Formation of Cu-MSA complex & participation of MSA in degradation system	112
4.2.3.2.	Inhibition test to determine specific reactive species	116
4.2.4.	Influential factors to the Cu(II)/Ox/RM system	122
4.2.4.1.	Influence of the structure of redox mediators on degradation.....	122
4.2.4.2.	Choice of oxidant	127
4.2.4.3.	Effect of dissolved O ₂	132
4.2.4.4.	Effect of pH	134
4.2.4.5.	Effect of water matrices.....	136
4.2.5.	Transformation of ACE in Cu(II)/PS/MSA system.....	138
4.2.5.1.	Comparison of ACE-TPs formation with traditional Fenton treatment	138
4.2.5.2.	Time profile monitoring of ACE-TPs and ACE transformation pathway in Cu(II)/PS/MSA system	140
4.3.	Conclusions	144
4.4.	References	145
Chapter 5 Experimental		151
5.1.	General Information	151

5.1.1.	Chemicals and Reagents	151
5.2.	Degradation Experiments.....	153
5.2.1.	Irradiation chambers	153
5.2.2.	Fenton and photo-Fenton treatment in Chapter 2	154
5.2.3.	Photocatalytic oxidation treatment in Chapter 3.....	155
5.2.4.	Modified Fenton/Fenton-like treatment in Chapter 4	156
5.3.	Instrumentation	157
5.3.1.	UHPLC-MS/MS – Quantitative Analysis.....	157
5.3.2.	UHPLC-QTOF-MS – Transformation products (TPs) identification and structural elucidation	158
5.3.3.	Instrument control, Data acquisition and analysis	159
5.3.4.	UV-Vis spectrophotometer analysis	159
5.4.	<i>Vibrio fishceri</i> bioluminescence inhibition assay (VFBIA) – Microtox bioassay	160
5.5.	References	161
Chapter 6 Conclusions and Future Outlook		162
6.1.	Thesis summary	162
6.2.	Future Outlook	164
	Output of Thesis Work.....	167
CURRICULUM VITAE		169