MONASH University

Stormwater Disinfection Using Electrochemical Oxidation

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Abstract

Excessive urban stormwater runoff causes different aspects of environmental issues including flood, pollutant migration, deterioration and contamination of natural waterways. Meanwhile, water scarcity is becoming a significant problem in many places around the world. Stormwater as an alternative water source has drawn increasing attention in fit for purpose usage (such as irrigation, toilet flushing and even for the recreational purpose). Stormwater harvesting lies under the paradigm of Water Sensitive Urban Design (WSUD). Stormwater harvesting has multiple ecological, social and economic benefits. However, stormwater harvesting is not widely applied at present due to a lack of reliable disinfection technologies to treat stormwater to regulatory standards.

This thesis investigates the feasibility of using electrochemical oxidation (ECO) for stormwater disinfection. Treatment performance, energy consumption, disinfection mechanism, system operational durability and disinfection by-products level were assessed using both synthetic stormwater and real stormwater collected from different catchment sites in different rainfall events.

Commercial dimensional stable anode (ruthenium and iridium doped titanium electrode) was used for the preliminary lab-scale study to test stormwater disinfection using ECO technology. The results showed that effective disinfection could be achieved with very low energy consumption; e.g. the current density of 1.74 mA/cm^2 achieved total disinfection in 1.3 minutes, using only 0.018 KWh per ton of stormwater treatment. Chlorination through chloride oxidation was found to be the key process dominating the disinfection performance despite the low chloride concentration in the synthetic stormwater used in the study (9mg/L). This study also showed that the disinfection by-product level after the treatment is well below the Australian Drinking Water Guidelines. However, the rapid operational performance deterioration suggests that dimensional stable anode (DSA) is not suitable for stormwater application due to its low resistance to server oxygen production during the disinfection process.

An anode selection study showed that boron doped diamond (BDD) electrode is a suitable type of anode for stormwater ECO disinfection because of its comparable effective treatment performance to DSA and good durability potential. Presence of chloride was also found to be essential to effective disinfection using this type of anode.

In the third study, real stormwater water was collected from different catchment sites during different rainfall events to verify the ECO disinfection performance of indigenous *E. coli* present in real stormwater as compared to synthetic stormwater (*E.coli* spiked). Disinfection performance of other stormwater pathogens such as *Campylobacter*, *Enterococci* and *C. perfringens* were also assessed. ECO disinfection was effective to achieve disinfection below the detection limit within 30 minutes of operation for all tested pathogens in all collected stormwater samples. Initial stormwater chloride concentration was found to be significant to the treatment performance. The disinfected stormwater had disinfection by-products (DBPs) well below the Australian Drinking Water Guidelines. DBPs level in treated stormwater was positively correlated to the pH of influent stormwater. ECO disinfection achieved total disinfection (below the detection limit) even on gram positive and spore bacteria in their 95^{th} percentile concentration in pre-treated stormwater.

Overall, this thesis demonstrates that electrochemical oxidation can be a promising stormwater disinfection technique to achieve regulatory water re-uses targets. It discusses the implications for the practical implementation of the technology and identifies areas for future research in regards to the optimisation of the technology.

Declaration

This thesis describes my research performed at the Department of Civil Engineering Monash University during the candidature period from September 2012 to March 2017. This thesis is prepared in accordance with the requirements stated in Section 1.9 of Monash Graduate Research Thesis Examine Policy. This thesis is submitted to Monash University in total fulfilment of the requirements for the degree of Doctor of Philosophy.

I hereby declare that in Chapter 3 and 4 of this thesis, the anode surface analysis using Scanning Electron Microscope (SEM) was done by Zhouyou Wang (PhD. candidate in Chemical Engineering at Monash). I analysed the results and performed data interpretation. In Chapter 3 and 4, the *E. coli* characterisation using the optical microscope and the Transmission Electron Microscope (TEM) was done by Dr. Xiangkang Zeng (former PhD. candidate in chemical engineering at Monash). The result analysis and data interpretation of this part were performed by myself. In addition, both the experiment and the data analysis of the anode surface X-ray Photoelectron Spectroscope (XPS) test in Chapter 5 were performed by Dr. Thomas Gengenbach who is the senior research scientist at the Scientific and Industrial Research Organisation (CSIRO) in Australia. While the rest part of this thesis (experimental work, data analysis and thesis writing) was performed by myself. My supervisors: Professor Ana Deletic, Associate Professor David McCarthy and Associate Professor Xiwang Zhang also contributed to this entire thesis in project design, experimental design and critical thesis revising. The extent of their overall contribution in this thesis is about twenty percent. Otherwise, I declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

Wenjun Feng

November 2017

Ana Deletic (Main Supervisor)

November 2017

List of Publications

Journal Papers

Feng, Wenjun; McCarthy, David; Wang, Zhouyou; Zhang, Xiwang; Deletic, Ana, Electrochemical oxidation for stormwater disinfection: A feasibility investigation. (Submitted to *Water Research*).

Feng, Wenjun; Deletic, Ana; Wang, Zhouyou; Zhang, Xiwang; Gengenbach, Thomas; McCarthy , David, Electrochemical oxidation disinfects urban stormwater: major disinfection mechanisms and longevity tests. (Submitted to *Environmental science & technology*).

Wenjun Feng, McCarthy, David; Henry, Rebekah; Zhang, Xiwang; Deletic, Ana, Electrochemical Oxidation for stormwater disinfection: How does real stormwater chemistry impact on pathogen removal and disinfection by-products level? (Under internal review by supervisors)

Declaration of Publications and authorships

In accordance with Monash University Authorship Policy, the following declarations are made:

This thesis includes three journal papers (two have been submitted, one is to be submitted). Chapter 3, Chapter 4 and Chapter 5 present journal papers co-authored with Ana Deletic, David McCarthy and Xiwang Zhang. Additional co-authors are Zhouyou Wang, Xiangkang Zeng in Chapter 3 and Chapter 4, Thomas Gengenbach in Chapter 4 and Rebekah Henry in Chapter 5. My contribution to the work involved the following:

Chapter	Publication Title	Publication Status	Nature and Extent of Candidate's Contributions
3	Electrochemical oxidation for stormwater disinfection: A feasibility investigation.	Under review (*Water Research*)	Conception, design of the project Analysis and interpretation of data Drafting the paper 75%
4	Electrochemical oxidation disinfects urban stormwater: major disinfection mechanisms and longevity tests.	Under review (*Environmental science & technology*)	Conception, design of the project Analysis and interpretation of data Drafting the paper 60%
5	Electrochemical Oxidation for stormwater disinfection: How does real stormwater chemistry impact on pathogen removal and disinfection by-products level?	Under internal review by supervisors	Conception, design of the project Analysis and interpretation of data Drafting the paper 65%

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the student's and co-authors' contributions to this work. In instances where I am not the responsible author, I have consulted with the responsible author to agree on the respective contributions of the authors.

Wenjun Feng

November 2017

Ana Deletic (Main Supervisor)

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Table of Content

Glossary of terms and abbreviations

AOP	*Advanced oxidation process*
BDD	*Boron-doped diamond electrode*
C. perfringens	*Clostridium perfringens*
CFU	*Colony-forming unit*
COD	*Chemical oxygen demand*
CT	*A CT value is the product of the concentration of free chlorine and the contact time required to achieve a certain degree of disinfection*
DBP	*Disinfection by-product*
DSA	*Dimensional stable anode*
E. coli	*Escherichia coli*
EC	*Electrical conductivity, µs/cm*
ECO	*Electrochemical oxidation*
EDX	*Energy dispersive X-ray detector*
EMC	*Event-mean concentration of a target pollutant during rainfall*
E_{unit}	*Unit energy consumption - the energy required to achieve the 3-log disinfection for one tone of stormwater, KW·h/1000kg*
HAAs	*Haloacetic acids*
Hvols	*Halogenated organic compounds*
I_d	*Current density, mA/cm^2*
K	*E. coli decay rate, MPN/min*
MPN	*Most probable number*
PCO	*Photo-catalytic oxidation*
PFU	*Plaque-forming unit*
r_s	*Coefficient of correlation calculated using Spearman's Rank test*
SEM	*Scanning electron microscope*
T_{90}	*The time required to achieve the first one log reduction during a disinfection process*
TEM	*Transmission electron microscope*
THMs	*Trihalomethanes*
TOC	*Total organic carbon*
WSUD	*Water sensitive urban design*
XPS	*X-ray photoelectron spectroscopy*
XRD	*X-ray powder diffraction*

Chapter 1: Introduction

Chapter 1 Introduction

1.1. BACKGROUND

Urbanisation increases the fraction of impermeable surface within our living environment. As a result, surface runoff is increased during a rainfall event posing higher flood risks. Climate change may act to facilitate this effect as the intensity and frequency of rainfall in some areas are heightened. In addition to reducing the serviceability of our urban environment, high stormwater flows lead to increased levels of pollutants being discharged into waterways, resulting in ecological deterioration.

Urban water has been traditionally managed through large centralised water supply and treatment facilities, requiring extensive costs and energy inputs for their construction, operation and ongoing maintenance[1]. In the event of a system failure, a large portion of the service area may be affected. The use of alternative water sources (managed by decentralised facilities) for non-potable fit for purpose uses is gaining mounting interest and becoming more publicly accepted[1-2] as people become more environmentally aware.

By treating and recycling stormwater at the local scale, both these issues can be addressed. In general, the benefits of stormwater harvesting are reduction of excessive surface runoff and flooding, mitigation of pollution transport into receiving waters during a rainfall event, providing an alternative water source for fit for purpose use, reduction of potable water usage.

Stormwater harvesting can be achieved using Water Sensitive Urban Design[1, 3] (WSUD) technologies. WSUD is a water management idea developed in the late 1990s. It aims to integrate the urban water cycle with urban planning and design[3]. In response to this, water sensitive cities should access to a diversity of water sources underpinned by a diversity of centralised and decentralised infrastructure, to provide ecosystem services for the built and natural environment, and comprises socio-political capital for sustainability and water sensitive behaviours[3].

Commonly used WSUD technologies for stormwater management include constructed wetland, biofiltration system, vegetated swales, infiltration system and porous pavement. WSUD technologies act to capture, infiltrate, and treat stormwater flows. Among WSUD technologies, stormwater biofiltration systems (also known as raingardens and bioretentions) are regarded as the most advanced for stormwater harvesting due to their high treatment performance, self-sustainability and reliability[4].

Stormwater harvesting has not been widely adopted in real practice due to the excessive level of microbes presenting in treated stormwater using current natural system based WSUD technologies. For example, stormwater biofilters demonstrated good performance for reducing sediments[5-6], nutrients[7-8], metals[9] and even micro-pollutants[10]. Contrasty, well-designed stormwater biofilters could only provide in average one log inactive of the incoming *E.coli*[11-12]. Considering the high *E. coli* inflow concentration (geometric mean of 35,961 MPN/100mL)[13], the treated stormwater has residual concentration well exceeded the guideline value (<10 CFU/100mL) for non-potable uses[13]. Therefore, stormwater harvested using current WSUD technologies could only be used for restricted irrigation[13]. This has become the major barrier to wide adoption of stormwater harvesting.

In response to this, a new stormwater disinfection technology that complies with WSUD principles needs to be developed. Stormwater usually comes in high quantity over a short period and subjects to the pattern of intermitted dry and wet events. Therefore, the stormwater disinfection technologies should be highly effective, low cost, and reliable, while using minimal energy and chemicals.

1.2. ELECTROCHEMICAL OXIDATION FOR DISINFECTION

Electrochemical oxidation (ECO) refers to the oxidation process occurring on the anode side in an electrolytic cell. Target chemicals such as organics could be oxidised either through direct (direct electron uptake from the anode) or indirect (oxidised by anode produced intermediates such as free chlorine or hydroxyl radicals) processes[14].

ECO has been well studied and utilised for treating organic pollutants in wastewaters[14-17]. Recently, application of this technology for disinfection has also been studied in wastewater, ballast water and surface water treatment[18-21]. Compared to other treatment technologies, such as chlorination, photo-catalytic oxidation, ozonation and UV irradiation, ECO can be operated without chemical addition and under lower capital and operational cost[22]. Therefore, ECO has a promising potential for disinfection of stormwater.

The ECO studies done for wastewater and surface water found that sufficient chloride ion and optimum operational current are essential for achieving effective disinfection performance through free chlorine production and hydroxyl radical production, respectively. However, stormwater has very low chloride concentration (e.g. the statistical mean concentration is 11.4 mg/L in Australia)[13] compared to the tested surface water and wastewater (118 mg/L to 10 g/L)[19-21, 23-25]. In addition, stormwater has low electric conductivity; usually between 50-500 µS/cm[26-29]. Therefore, it is speculated that very likely the findings made in the past ECO studies will not be directly transferable for its application to stormwater.

The aim of this Ph.D. thesis is to understand the feasibility of using ECO system as stormwater disinfection technology. The key objectives are to assess the disinfection performance, energy consumption and longevity of ECO system under stormwater operational condition. The influence of stormwater chemistry on disinfection performance and disinfection by-products are also to be studied.

1.3. SCOPE OF THE RESEARCH

In the first instance, current Water Sensitive Urban Design (WSUD) technologies for stormwater harvesting are reviewed to define the need for new technology for stormwater disinfection. A screening selection is then conducted by evaluating the treatment performance, system configuration, system operation and energy consumption of some cutting-edge disinfection technologies. Electrochemical oxidation (ECO) is selected as the stormwater disinfection technology

in this research. Therefore, this research aims to assess the feasibility of using ECO for stormwater disinfection and to gain knowledge to inform future application.

Synthetic stormwater represents the 'typical' stormwater property is used to understand the ECO disinfection performance of lab strain *E. coli*. Two different anode types: dimensional stable anode (DSA) and boron doped diamond (BDD) anode are used for the disinfection performance study. DSAs are metal oxides coated titanium anodes that have good ability to produce free chlorine for disinfection from oxidising chloride ion presenting in water[18]. Boron doped diamond (BDD) anode achieves disinfection mainly through hydroxyl radical production. The disinfection rate, energy consumption, disinfection mechanism and disinfection by-products (DBPs) are compared between selected DSA and BDD.

A longevity study is conducted to evaluate the disinfection performance of selected DSA and BDD over accumulated usage. Continuous *in-situ* operation of these two ECO systems at a catchment site simulates the accumulated usage. The disinfection performance with respect to accumulated operational time is then evaluated for both anodes. This study also investigates the mechanism of deterioration observed on DSA.

The ECO disinfection performance of multiple microbe species is evaluated using stormwater collected from different stormwater catchment sites. The influence of stormwater chemistry to the disinfection performance and DBPs level is studied based on the collected stormwater samples.

1.4. OUTLINE OF THESIS

This thesis consists of seven chapters. An overview of each of the chapter is provided below:

Chapter 1 – Introduction: The introduction will justify the main research topic and present the overall aim, that is, emphasise the importance of developing Electrochemical Oxidation (ECO) system for stormwater disinfection.

Chapter 2 – Literature review: The review of the literature provides the current knowledge on stormwater treatment performance using biofiltration system as the current most advanced stormwater harvesting practice. Available disinfection technologies are also reviewed to assess their feasibility for stormwater treatment. A detailed review of electrochemical oxidation, which is selected as the next generation technology for stormwater disinfection, is provided.

Chapter 3 – Feasibility study of using electrochemical oxidation for stormwater disinfection: This chapter focuses on assessing the feasibility of using electrochemical oxidation for stormwater disinfection. It firstly investigates the stormwater disinfection performance and energy consumption of ECO under different operational currents. It attempts to elucidate the mechanism governing stormwater disinfection and the impact of the chloride ion on treatment performance. The observation of disinfection performance deterioration of DSA is reported and the possible deterioration mechanism is studied. Finally, the ECO disinfection performance of indigenous microbes and the DBPs are evaluated using stormwater samples collected from different stormwater catchment sites.

Chapter 4 – Anode material selection for stormwater ECO disinfection: This chapter investigates the disinfection mechanism of selected DSA and BDD using synthetic stormwater. To understand the anode deterioration issues identified in Chapter 3, the disinfection performance over the accumulated *in-situ* operation time is evaluated for both DSA and BDD anodes.

Chapter 5 – Performance validation of ECO stormwater disinfection using BDD Anode: This chapter investigates the performance of the ECO disinfection process using actual stormwater of varying quality. It investigates the effect of stormwater composition on disinfection performance of indigenous *E. coli* and DBPs level in treated stormwater. The E. coli removal efficiency is also compared with that of selected pathogen indicators and microorganisms.

Chapter 6 – Recommendations for the application of electrochemical oxidation for stormwater disinfection: This chapter draws together the findings from the different laboratory studies. Lessons and knowledge gaps are identified and recommendations are made to inform further studies pertaining to advancing the technology for stormwater disinfection.

Chapter 7 – Conclusions and future work: This chapter provides a discussion of the strength and constraints of this research, presents conclusions and provide recommendations for future research.

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Chapter 2: Literature Review

Chapter 2 Literature Review

2.1. INTRODUCTION

This chapter starts with a literature survey discussing the need for developing an adequate technology for stormwater disinfection. The quality of raw stormwater and the treatment performance of current water sensitive urban design (WSUD) technologies on various stormwater pollutants (sediments, nutrients, heavy metals and pathogens) are reviewed. The quality of treated stormwater using different WSUD technologies is then compared with several guidelines (AGWR-SHR, 2009[1]; ANZECC, 2000[2]; NHMRC, 2001[3]) to highlight the technology gap that exists in order to treat stormwater for suitable end-uses.

An overview of available water disinfection technologies currently used in wastewater and drinking water treatment industries is then presented. The potential translation of these technologies for stormwater treatment was assessed. Electrochemical oxidation (ECO) was selected as a potential technology based on its reported high efficiency, low operational cost and low disinfection by-product level.

Therefore, in the third part of this chapter, a general review was presented to understand the reaction mechanism, impact of anode material, impact of operational conditions and disinfection performance as reported in previous studies employing ECO systems.

2.2. STORMWATER HARVESTING USING CURRENT WSUD TECHNOLOGIES

Stormwater is rainwater runoff from catchment surface[4]. It contains different types of pollutants; the level of these pollutants varies depends on catchment condition, local climate and specific rainfall event[1]. Raw stormwater treated using WSUD technologies could be used fit for purpose. In order to evaluate the possibility of using harvested stormwater for irrigation, recreation and even potable uses, the corresponding required degree of treatment is summarised in Table 2-1 (nutrients and metals) and Table 2-2 (pathogen).

Table 2-1 Summarised guideline values for irrigation using stormwater, recreation and potable usages

Pollutant	Unit	Irrigation[a]	Recreation[b]	Portable[c]
Total suspended solids - TSS	mg/L	-	-	-
Total phosphorus - TP	mg/L	0.8-12		-
Total nitrogen -TN	mg/L	25-125		-
Nitrate - NO_3^-	mg/L	-	10	50
Ammonium - $NH4^+$	mg/L	-	-	-
Aluminium - Al	mg/L	20	0.2	-
Cadmium - Cd	mg/L	0.05	0.005	0.002
Chromium - Cr	mg/L	1	0.05	0.05
Copper - Cu	mg/L	5	1	2
Iron - Fe	mg/L	10	0.3	0.3
Manganese - Mn	mg/L	10	0.1	
Nickel - Ni	mg/L	2	0.1	0.02
Lead - Pb	mg/L	5	0.05	0.01
Zinc - Zn	mg/L	5	5	-

[a]Trigger value guidelines for agricultural irrigation (AGWR-SHR, 2009)
[b]Water quality guidelines for recreational purpose (ANZECC, 2000)
[c]Health value guidelines for potable water (NHMRC, 2011)

Table 2-2 Australian guideline values for microbial quality of water for different uses

Guideline	Water use	Guideline value
Australian Drinking Water Guidelines (NHMRC, 2011)[3]	Potable use (drinking water)	0 *E. coli*/100mL
Australian Guidelines for Water Recycling Stormwater Harvesting and Reuse (AGWR-SHR, 2009)[1]	Non-potable use (public, open-space irrigation)	>1.5 log10 reduction of viruses and bacteria[a] >0.8 log10 reductions of protozoan parasites[a] E. coli<10 colony forming units (CFU)/100mL
Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC/ARMCANZ, 2000)[2]	Primary contact (swimming, bathing and other direct water-contact sports)	<150 faecal coliform/100mL <35 *Entrerococci*/100mL 0 pathogenic free-living protozoan
	Secondary contact (boating and fishing)	<878 *E. coli*/100mL <1000 faecal coliform/100mL <230 *Enterococci*/100mL

[a:] This reduction is based on a normal raw stormwater concentration

By comparing the raw stormwater quality (Table 2-3, Table 2-4) with the required water quality for general irrigation, recreational and potable uses, stormwater without any treatment basically does not satisfy any of these fit for purpose usage due to the excessive concentration of heavy metals and the presence of substantial microbes. Therefore, it is essential to provide treatment for harvested raw stormwater before it could be used for any end-uses.

Table 2-3 Summarised physicochemical characteristics of raw stormwater

	Characteristics	Unit	AGWR-SHR Data[1]				Other Resources
			Mean	Percentile			
				5th	50th	95th	
Physico-chemical	Electri conductivity[a]	µs/cm	-	-	-	-	few hundreds
	pH	-	6.35	5.50	6.33	7.27	5.7-7.0[5]
	Suspended solids	mg/L	99.73	19.01	77.24	254.47	47-779[5]
	Turbidity	NTU	50.93	7.98	40.74	127.79	9.1-172[5]
	Bicarbonate - as $CaCO_3$	mg/L	35.21	29.99	35.04	40.97	-
	Chloride	mg/L	11.40	9.75	11.35	13.20	-
Nutrients	Ammonia	mg/L	1.135	0.102	0.793	3.281	0.20[6]
	Oxidised nitrogen	mg/L	0.680	0.132	0.592	1.523	0.87[6]
	Total dissolved nitrogen	mg/L	3.28	0.68	2.59	8.22	1.84[6]
	Total nitrogen	mg/L	3.09	0.62	2.51	7.46	2.17[6], 1.1-5.3[5]
	Total organic carbon	mg/L	16.90	11.99	16.60	22.80	19-33[5]
	Total phosphorous	mg/L	0.122	0.047	0.102	0.260	0.095-0.90[5]
Metals	Aluminium	mg/L	1.19	0.49	1.07	2.29	-
	Arsenic	mg/L	0.009	0.006	0.009	0.011	-
	Cadmium	mg/L	0.0198	0.0015	0.0127	0.0606	0.00066-0.015[5]
	Chromium	mg/L	0.009	0.002	0.008	0.017	0.014-0.077[5]
	Copper	mg/L	0.055	0.012	0.041	0.141	0.040-0.17[5]
	Iron	mg/L	2.842	1.126	2.674	5.100	2.8-11.3[5]
	Lead	mg/L	0.073	0.017	0.063	0.162	0.051-0.41[5]
	Manganese	mg/L	0.111	0.054	0.103	0.197	0.37[5]
	Mercury	mg/L	0.218	0.080	0.201	0.411	0.00052[5]
	Nickel	mg/L	0.009	0.004	0.009	0.017	0.040[5]
	Zinc	mg/L	0.293	0.080	0.272	0.570	0.26-0.73[5]

[a]Electric conductivity of stormwater has not been reported in existing literature, based our previous monitoring the value was around 10^2µs/cm

Table 2-4 Summarised microorganisms level in raw stormwater

Microorganisms	Unit	AGWR-SHR Data[1]				Other resources
		Mean	Percentile			
			5th	50th	95th	
Campylobacter	MPN/L	<2	<2	<2	<2	NT[a]-1000000[3, 7]
E. coli	CFU/100mL	35961	61	5800	240000	9-130000[7-10]
Enterococci	CFU/100mL	3095	26	740	12100	40-18400[7]
C. perfringens spores	CFU/100mL	322	<5	140	905	-
FRNA coliphage	PFU/L	55	<1	<1	180	-
Pseudomonas aeruginosa	CFU/L	-	-	-	-	1-11000000[3, 10-11]

[a]Microorganism was not detected

Stormwater treatment could be achieved using WSUD technologies. These technologies include vegetated swales, stormwater pond, infiltration system, stormwater constructed wetland and stormwater biofiltration, etc[12-13]. These stormwater management facilities varying from neighbourhood to regional scales can provide different levels of stormwater treatment.

Assessment of the treatment performance of these WSUD technologies on stormwater pollutant removal is essential for understanding the fit for purpose usage of harvested stormwater and for defining the technology gap that exists in order to further improve the water quality for higher end-uses. The specific stormwater treatment performance of stormwater biofilters, stormwater constructed wetlands and vegetated swales are reviewed as three typical examples of WSUD technologies.

Stormwater biofilter is vegetated trench with soil based filter media underlying. The size of this facility is normally 2% of its serving catchment area[14]. During the rainfall event, stormwater is delivered into the system through either surface flow or constructed pipe system. Stormwater flows over the vegetated surface receiving preliminary treatment of coarse sediments. Stormwater percolating through the filter media will undergo a series treatment processes such as physical filtration, chemical adsorption and biological degradation[12, 15]. Active chemical compound with good cation exchangeability such as zeolite and perlite are usually added to the soil-based filter media to enhance the adsorption of soluble pollutants. In long term perspective, vegetation converts trapped pollutants such as nutrients and metals into biomass[16]. This process reduces the pollutant concentration in the filter media and prevents leaching due to pollutants accumulation. Biofiltrated stormwater could infiltrate into the surrounding environment or be collected in a drainage pipe installed at the bottom of the biofilter with the lined surface.

Stormwater constructed wetland, in general, is a vegetated body of shallow water. In practices, it consists of a litter trap for gross pollutant removal, an inlet zone for sedimentation of coarse particles and a macrophyte zone with vegetation for further treatment[12, 17]. The vegetation increases the effective treatment surface area and hence increases the retention time for treatment. Particulate pollutants will be removed through filtration and sedimentation. Nutrients and metals are treated mainly through biodegradation by bacteria (such as nitrifiers and denitrifies) and biological uptake by vegetation. Comparing to other WSUD technologies, wetland also provides storage for treated stormwater and habitat for local flora and fauna.

Vegetated swale and filter strip mainly function as a preliminary treatment facility for sediments removal during the conveying process of stormwater to the near water body or other WSUD facilities[12-13]. They are mildly sloped grass channels. The surface roughness increases the stormwater retention time and enhances stormwater filtration for sediments removal.

Table 2-5 Summarised stormwater quality harvested using common WSUD technologies

	Pollutant - outflow	Unit	Biofilters	Wetlands	Swales filter strips
Nutrient	Total suspended solids - TSS	mg/L	0.003-6.6[18-20]	1.5-22[12]	10-40[12]
	Total phosphorus - TP	mg/L	0.03-0.16[20-21]	0.2-0.4[12]	0.1-0.6[12]
	Total nitrogen -TN	mg/L	0.65-2.0[20, 22-23]	0.8-9[12]	1-2.5[12]
	Nitrate - NO_3^-	mg/L	0.02-0.6[20, 22-23]	0.36[12]	0.5-1[12]
Heavy metal	Ammonium - NH4+	mg/L	0.02-0.08[12, 20]	0.6[12]	-
	Aluminium - Al	mg/L	0.2-1[16]	-	-
	Cadmium - Cd	mg/L	<d.t.[a16]	-	5-6[12]
	Chromium - Cr	mg/L	<d.t.-0.002[16]	-	7-10[12]
	Copper - Cu	mg/L	0.004-0.01[16]	0.7-7[12]	5-27[12]
	Iron - Fe	mg/L	0.2-0.81[16]	-	140-690[12]
	Manganese - Mn	mg/L	0.004-0.07[16]	-	-
	Nickel - Ni	mg/L	0.0025-0.01[16]	-	52-53[12]
	Lead - Pb	mg/L	<d.t.-0.003[16]	-	7-80[12]
	Zinc - Zn	mg/L	0.007-0.03[16]	0.031[12]	11-94[12]
Microbe	*E. coli*	MPN/100mL	26-2000[24-27]	-	-
	Total coliform	MPN/100mL	386-4500[12]	200-12000[12]	300000[12b]
	Enterococci	MPN/100mL	78-400[24, 28]	-	-
	Campylobacter	MPN/L	0.91-2.81[24]	-	-
	C. perfringens	Orgs/100mL	0-77[24, 28]	-	-

[a]Below the detection limit

[b]Leaching (negative removal) observed for microbes

The treated stormwater quality using these three WSUD technologies are summarised in Table 2-5. In terms of nutrient and heavy metal removal, stormwater treated using biofilters and wetland generally meets the standard for non-restricted irrigation[1] and recreational usage[2]. Biofilters are even able to reduce nutrients and heavy metals down to the potable water quality[3]. However, none of these WSUD technologies could eventually treat stormwater to satisfy any of these fit for purpose uses when the effluent concentration of microbes is considered. Although biofilters outperformed other two WSUD technologies in nutrients, heavy metals and microbial removal, stormwater treated using biofilters have *E. coli* concentration that is still one to two orders higher than the specified value for non-restricted irrigation (<10CFU/100mL)[1].

Chandrasena *et al.* tested pathogen removal performance of stormwater biofilters under laboratory scale using free phase *E.coli* only[25]. The outflow concentration of *E. coli* was found to be highly proportional to the inflow concentration, with an overall removal ranged between 1 to 2 log reductions. The proportion of biofilter antecedent water volume in outflow varied the *E.coli* outflow concentration significantly, which shows long term treatment within biofilters played an important role in the overall pathogen removal performance. Net leaching of *E.coli* was also detected in Chandrasena's experiment when a relatively low inflow concentration event occurred within a short period after a very high inflow concentration event. In 2012, Chandrasena *et al.* tested pathogen removal performance of biofilters under a field scale using ten faecal microorganisms including: indicators and pathogenic bacteria, protozoa and viruses[24]. Although a design of submerged zone showed enhanced pathogen removal performance compare to other design configurations, removal of bacteria (with mean value close to 1 log reduction), protozoa (mean value close to 0.8 log reduction) and viruses (mean value lower than 0.5 log reduction) were still consistently lower than the standard required for non-restricted irrigation2. In 2012, a similar lab scale biofilter study was done by Li *et al.*, 3 indicators (*Clostridium Perfringens*, E. coli and F-RNA coliphages) were used to evaluate the pathogen removal performance of different configured biofilters under different operational conditions[28]. For all configurations tested, mean removal of 3 log reduction was achieved for *C. perfringens* and F-RNA coliphages. This indicated a promising removal of these two types of indicators by biofilters. However, for *E.coli*, which is a more commonly concerned indicator for pathogenic bacteria, the outflow concentration varied between 450 MPN/100mL and 22,000 MPN/100mL. For the biofilter designed with a permanent saturated zone with added carbon source, 2 log reduction could be achieved under normal operational conditions and only 0.6 log reduction could be achieved when biofilters dosed after an antecedent dry weather period.

It is clear that the quality of stormwater treated using current natural system based WSUD technologies does not even satisfy the standard for non-restricted irrigation, not even mention for recreational or potable uses. Therefore, development of new WUSD technologies for further

disinfection of stormwater becomes a primary consideration in order to enable the treated water to be used for a wider range of non-potable applications.

2.3. OVERVIEW OF CURRENT WATER DISINFECTION TECHNOLOGIES

The disinfection technology that could be potentially applied for stormwater treatment should satisfy the WSUD principles, that is, they should be operated under zero or minimum energy input, are efficient, sustainable and environmental friendly in their performance. Therefore, the following sub-sections look into the treatment performance, operational cost and disinfection by-product level of current disinfection technologies.

2.3.1. Chlorination

Chlorination has being commonly used for potable water disinfection since the early 20th century[29-30]. It was recognised as one of the most innovative technology at the time when it came into practice. This disinfection method is highly valued because of its high efficiency[31-32], good residual effect and low cost[32-34], hence it is still irreplaceable in large scale water treatment system such as municipal potable supply.

However, the negative side of this technology came to prominence almost simultaneously. Residual chlorine in treated water is harmful to phytoplankton and zooplankton in the environment[29-30, 32-33, 35]. Chlorine also causes significant damage to gills of fishes by oxidising haemoglobin which eventually causes malformation or failure of the respiratory system[36-37].

Another main concern from using this technology comes from potable water treatment. Residual chlorine in water increases the incidence of bladder, rectal and colon cancer; this harmful impact on human health has been widely proved by large numbers of epidemiology studies and experiments[38-41]. Chlorine is added to water (0.2-1mg/L) usually as hypochlorous acid and hypochlorite, because of their strong oxidation ability. Besides microorganisms, they can also readily react with Natural Organic Matters (NOM), such as humic acid and fulvic acid. Trihalomethanes (THMs), which can be formed through this reaction, is a group of halogenated organic compound disinfection by products

(DBPs) credited for its carcinogenic effect. Table 2-6 shows a summary of DBPs from chlorination and their concentration in normal potable water supply[42].

Table 2-6 Halogenated disinfection by-product formed in chlorination process (source from Fawell *et al.*, 1997[43], Cumming *et al.*, 1992[44], Richardson *et al.*, 2012[45])

Disinfection by-products:	**Concentrations (µg/L)**	
	Median	Maximum
THMs[a]		
Chloroform	25	240
Bromodichloromethane	9.5	90
Chlorodibromomethane	1.6	36
Bromoform	<0.2	7.1
HAAs[b]		
Dichloroacetic acid	15	74
Trichloroacetic acid	11	85
Bromochloroacetic acid	3.2	49
Monochloroacetic acid	1.3	5.8
Dibromoacetic acid	<0.5	7.4
Monobromoacetic acid	<0.5	1.7
HANs[c]		
Dichloroacetonitrile	2.1	10
Bromoacetonitrile	0.7	4.6
Bromochloroacetonitrile	0.6	1.1
Dibromoacetonitrile	<0.5	9.4
Trichloroacetonitrile	<0.02	0.02
Haloketones		
1,1,1-Trichloropropanone	1	8.3
1,1-Dichloropropanone	0.4	2.5
Others		
Chlorate	161	9180
Chloral hydrate	2.1	25
Chloropicrin	0.4	3.7
MX[d]	0.005	0.067
Cyanogen chloride	0.62	-
Halonitriles	0.4	3.7

[a]: Trihalomethanes, [b]: Haloacetic acids, [c]: Haloacetonitriles,
[d]: 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone

Nieuwenhuijsen *et al.* reviewed the adverse impact of chlorination DBPs on human reproductive outcomes in 2000[46]. Substantial epidemiology studies indicated chlorination generated halogenated organic compound, especially THMs and HAAS, is a significant incentive to intrauterine growth retardation (IUGR)[47-52], spontaneous abortion and congenital malformations[47, 51-53], in which the foetal central nervous system and the respiratory system are most likely to be affected[49, 54-56].

2.3.2. Chlorine Dioxide

Chlorine dioxide has been used as an alternative oxidant to chlorine over the past few decades[30]. It has a stronger oxidation ability and longer residual effect compared to chlorination[30]. Most of the studies showed pure chlorine dioxide could reduce the formation of traditional DBPs such as THMs and HAAs in disinfection process; therefore it has been recognised as one of the safest and most efficient alternatives[30]. There are also some disadvantages associated with this technology in practice, particularly involving its high cost. The cost of using this technology is usually 5-10 times more expensive than chlorination[57]. The production of chlorine dioxide using chlorine and sodium chloride is process intensive[58]. Chlorine dioxide is explosive; safety measures and regulations must be applied during transportation and use of this chemical[30]. Commercially available chlorine dioxide usually contains a small amount of chlorine introduced into the production reaction and this can potentially introduce traditional halogenated organics (THMs, HAAs and HANs etc.) during water disinfection. Hua et al. demonstrated that prior Ozonation of waste water can eliminate THMs and other DBPs formation resulting from the residual chlorine in post chlorine dioxide treatment[58]; however, this directly increases the cost of using this technology and makes the treatment process less convenient. Although routinely concerned halogenated organics were not reported in chlorine dioxide oxidation[30, 45, 57], increase of unknown total organic halogen (uTOX) formation was detected[58], so the potential environmental and health impact of this technology still remains unclear[30].

2.3.3. Ozonation

Ozone is a strong oxidant that can react with a variety of organic matters including waterborne microbes[30]. This technology can also be coupled with UV radiation to generate advanced oxidation process (AOP), which can yield an enhanced disinfection performance[59]. Ozonation, as a single process, is good at controlling the taste, colour and odour of water[30]. Moreover, as a strong oxidant, ozone is able to oxidise a variety of micro-organic pollutants including pesticides, THMs and HAAS, etc.[30, 60-61]. However, this technology does not provide sufficient residual effect, which makes it impossible to be used in large scale water supply system[30]. Bromoform and other brominated by

products are the main health concern arising from using this technology, however, there is no epidemiological information available for the application of this technology[29-30, 62]. Unknown organic by products and the consequent uncertain health impact are, perhaps, another disadvantage regarding ozonation[30].

2.3.4. Ultra-violation (UV) Irradiation

UV irradiation has been widely applied in some small scale disinfection system or used in the tertiary treatment process. UV, normally with an optimum wavelength between 250-270nm[63], is added into the water as an energy source. This irradiation is strong enough to penetrate the cell wall of bacteria or the protein capsid of a virus and it directly destroys the genetic material (DNA and RNA), hence it eliminates reproduction of pathogen[30, 64]. There is no chemical used during the treatment process and no disinfection by product formed[30, 65]. UV disinfection minimises the contact or disturbance introduced into water and it has become a good alternative to chemical disinfection technologies. Another advantage of UV disinfection is the short retention time. For a properly designed system, under the practical condition, it only takes less than 10 seconds to achieve up to 4 log reduction of bacteria[66]. There are some existing limitations of using UV disinfection. Clarity of the water is very important to the treatment performance as it directly determines the dissipation of UV energy penetrating into water[30, 63-64]. Inflow water with a TSS concentration higher than 30mg/L is not considered suitable for UV disinfection[63]. Also, because of the instantaneous irradiation disinfection, there is no residual effect left in water[30, 59, 63, 65]. Organisms can sometimes repair and reverse the destructive effects of UV through a "repair mechanism," known as photo reactivation, or in the absence of light known as "dark repair"[30, 63]. Although UV provides a broad-spectrum bactericidal effect[30], pathogens like fungal spores and protozoa are less sensitive to the UV irradiation[30, 66]. Therefore, a significantly increased dosage of UV is required for these pathogens[63]. Nowadays, researchers are also focusing on integrating UV with other traditional chemical treatment processes such as ozonation and Fenton reaction to overcome this shortcoming of UV used on its own[59, 67].

2.3.5. Advanced Oxidation Processes (AOPs)

Advanced oxidation process refers to a set of chemical reactions or processes that use in-suit produced hydroxyl radical as the main oxidant to achieve the degradation of organics and disinfection of bacteria and virus[59]. Hydroxyl radical (·OH) is the neutral form of hydroxide ion (OH^-), it has very strong oxidation ability as it tends to uptake one electron to become a more stable hydroxide ion. It is the strongest oxidant known in aqueous solution with an oxidation potential of 2.8eV. The extremely high oxidation ability ensures non-selective decomposition of most organic pollutants into carbon dioxide and water (known as total mineralisation of organics)[68]. Meanwhile, the residual effect of this chemical is minimum compared to most of other oxidants such as chlorine, ozone and hydrogen peroxide[59]. The strong oxidation ability, fast reaction rate and minimum residual effect of hydroxyl radical have made the advanced oxidation processes to be favoured by a large variety of water treatment applications requiring higher treatment performance and environmental sustainability.

Hydroxyl radical is formed in some typical examples of AOPs such as photo-Fenton reaction, UV/ozone reaction, electrochemical reaction, photo-catalysis, etc.[59, 67-69]. The disinfection pathway of hydroxyl radical is achieved through the oxidation of cell wall and cytoplasmic membrane. Saito *et al.*[70] showed the rupture of *Streptococcus sobrinus* cell wall to be a consequence of hydroxyl radical destruction after, rapid leakage of potassium ions and other intracellular material were detected. Sunada *et al.*[71] further showed lipopolysaccharides and peptidoglycan are the two targeting organics of hydroxyl radicals. Maness et al. suggested attack of phospholipid on the cytoplasmic membrane and the consequent respiratory system failure were the main mechanism for *E. coli* K12 disinfection[72]. In contrast, Matsunaga *et al.*[73] suggested decomposition of Coenzyme A (CoA) is a key disinfection mechanism for *L. acidophilus*, *S. cerevisiae* and *E. coli*. They also demonstrated the disinfection performance was inversely proportional to the thickness and complexity of the cell wall. Meanwhile, some other reactive oxygen species generated in AOPs such as $O_2^{\bullet-}$ and $\bullet OOH$ also contribute to some extent to the disinfection performance; however, the detail disinfection mechanism of these oxidants still remains uncertain[74].

2.3.5.1. Photo-catalytic oxidation (PCO)

Semiconductor photo-catalytic oxidation (PCO) is a commonly used advanced oxidation process that relies on the *in-situ* production of hydroxyl radicals and other reactive oxygen species[68]. Over the past 30 years, the application of this technology attracted tremendous research interest from scientists and engineers mainly due to its strong oxidation ability to refractory organics using just natural solar energy. Research and application of PCO have shown successful disinfection and removal of a variety of chemicals in wastewater treatment such as alkanes, aliphatic alcohols, aliphatic carboxylic acids, alkenes, phenols, aromatic rings, dyes, halogenated alkanes, alkenes, surfactants and other emerging organic micro-pollutants[75].

Several pilot scale PCO treatment systems have been installed and tested over the past ten years[76-77], among which the PSA (The Plataforma Solar de Almeria) facility installed in Spain is one of the successful examples in operation. PSA as the largest PCO system in Europe belongs to Centro de Investigaciones Energéticas Medioambientales y Tecnológicas (CIEMAT) and was built under the initiative of Spain government. A pilot system built up with 32 m^2 compound parabolic trough solar collector (CPC) and 300 L tubular reactor was operated for detoxification and disinfection of industrial waste water using either mobilised or immobilised Titanium Dioxide catalyst[78].

Although there are a variety of semiconductors used as the catalyst for the photo-catalytic oxidation such as $TiO_2, ZnO, Fe_2O_3, CdS, ZnS$ and etc., TiO_2 has been generally recognised as the most commonly used photo-catalyst because it is cheap, non-toxic, chemically and thermally stable[77]. In addition, the band gap wave length of this semi-conduct (380nm) overlaps with the UV spectrum of natural sunlight (300nm to 390nm), which ensures that solar irradiation is able to drive the catalytic reaction[75, 77, 79]. The second advantage of using Titanium Dioxide comes from its relatively inert chemical property against photo degradation compared to other semiconductors[75]. There are three different crystal structures of TiO_2 corresponding to three different titanium dioxide crystals: anatase, brookite and rutile. All these crystals are structured with basic TiO_6 octahedrons. The way in which TiO_6 octahedrons are packed differentiates the physical and chemical properties of those crystals.

Commercially available Degussa® P25 TiO_2 powder has been practically used for the photo-catalysis oxidation due to its remarkable higher photo-catalytic activity and lower price. P25 is a composite of anatase/rutile mixture with a ratio of 7:3, which is made up of 30nm TiO_2 particles with specific area of 55 ± 5 m^2/g[80]. Lonnen *et al.* tested the photo-catalytic disinfection of protozoan, fungal and bacterial microbes using a P25 coated immobilised reactor under a simulated solar irradiation condition[81]. The results showed that at least 4 log reduction could be achieved for protozoan, fungi and bacteria after 8 hours of continuous simulated solar irradiation. In contrast, spores of *Bacillus subtilis* showed resistance to the photo-catalytic disinfection where only 1.7 log reduction was achieved under similar operating conditions[81].

2.3.5.2. Electrochemical Oxidation

Electrochemical Oxidation (ECO) and other electrochemical processes have been studied for more than 200 years since electrolysis of water and electroplating were discovered in the early 19th century[82].

ECO refers to the reactions occurring on the anode side of an electrolytic cell due to the uptake of electrons (e^-) and the consequent oxidation of reducible chemicals[83]. This reducible chemical could be either organic or inorganic. ECO is always associated with electrochemical reduction which happens at the same time but on the cathode side of the electrolytic cell. Conventionally, current is defined as the movement of positive electrons (e^+) from a higher potential terminal to a lower potential terminal. In the actual situation, this is equivalent to the movement of electrons (e^-) from a lower potential terminal (cathode) to a higher potential terminal (anode). Thus, it can be idealised that anode is an electron acceptor initiating oxidation reaction and the cathode is an electron donor, which initiates the corresponding reduction reaction. Hydrolysis of water will be a good example of this, where negatively bonded oxygen atom is oxidised to free oxygen on the anode and a positively bonded hydrogen atom is reduced to free hydrogen on the cathode. This direct electron transfer on the anode (e.g. oxygen evolution) is called the direct anodic oxidation[83].

Besides electrons, there are also some electron-generated species such as hydroxyl radicals (•OH) and other reactive oxygen species ($O_2^{\bullet -}$, $\bullet OOH$ and H_2O_2)[83-85]. these mediated species have a stronger oxidation ability compared to direct anodic electron uptake, which eventually leads to a total mineralisation of organic matters into carbon dioxide and simple inorganics[83, 85]. Therefore they have been more studied for decomposition of organic matters and water disinfection.

As an application, ECO has been regarded as very a promising technique for organics removal and disinfection from wastewaters[86-89].

2.4. FEASIBILITY OF ELECTROCHEMICAL OXIDATION FOR STORMWATER DISINFECTION

2.4.1. Mechanism of Electrochemical Oxidation

Electrochemical oxidation (ECO) is a resultant process of organic decomposition, which can be achieved either through electrochemical conversion or Electrochemical combustion depending on the type of anode material used[90-91]. Therefore, ECO can occur through two pathways, as discussed below.

Comninellis *et al.* (1994)[90] explained these different mechanisms of ECO based on two limiting situation: active and non-active anodes. Active anodes are usually made of a material that is not in its highest available oxidation states (e.g. pure metals, and low oxidation state metal oxides). Because they are not in the highest available oxidation state, opportunities exist for the anode material to be oxidised first before oxidation of organic matter[83]. The redox couple MO_X/MO_{X+1} (lower oxidation state and higher oxidation state of metal oxides) becomes the catalyst and continuously transfers the oxidation from chemisorbed oxygen to organics. In this case, electrochemical conversion dominates the oxidation mechanism, whereby chemisorbed active oxygen on anode lattices selectively decompose refractory organics into smaller organic compounds. Active anode materials usually have a high electrochemical activity for aromatic ring opening but they don't have enough activity to provide further oxidation of organics. This becomes applicable when

decomposition of non-biodegradable organics into biodegradable organics is required, as it will be much more economical to achieve the following decomposition using conventional treatment process. Unlike active anode material, non-active anode material only acts as a sink to remove electrons and does not participate in any oxidation reaction because they are already in their highest oxidation states and cannot be further oxidised. In this situation, physisorbed hydroxyl radicals (MO_x•OH) will initiate a non-selective combustion of organics. This Electrochemical combustion is able to totally decompose organics into carbon dioxide or other simple inorganics with a high current efficiency.

Comninellis *et al.* (1994)[90] established a comprehensive model for both electrochemical conversion and combustion with respect to active and non-active metal oxide anodes. There are four assumptions made for this model under simultaneous oxygen evolution with the participation of water:

- the active species (physisorbed or chemisorbed oxygen) in both organics oxidation and oxygen evolution are the same;
- there is no chemisorption of organics onto the anode surface;
- the oxidation of organics is a first order reaction with respect to both reactive oxygen species and organics;
- oxygen evolution is a first order reaction with respect to the active species (physisorbed or chemisorbed oxygen)

This comprehensive model assumed a common first step for both kinds of anode material:

$$MO_x + H_2O \longrightarrow MO_x(\bullet OH) + H^+ + e^- \quad (1)$$

In equation (1), MO_x is a metal oxide, $(\bullet OH)$ is the physisorbed hydroxyl radical. Water molecule will be oxidised first to form physisorbed hydroxyl radicals onto the metal oxide anode surface. And this initial reaction happens within both the active and non-active anode. When the metal oxide (anode material) has a higher available oxidation state, physisorbed hydroxyl radicals will then interact strongly with the anode material to form a higher state of metal oxide (MO_{x+1}):

$$MO_x(\bullet OH) \longrightarrow MO_{x+1} + H^+ + e^- \quad (2)$$

Equation (2) only happens on active anode, where MO_{x+1} represents metal oxide containing chemisorbed oxygen in lattices. Then the further oxidation of organics (R) and evolution of oxygen are actually initiated by the MO_X/MO_{X+1} redox couple instead of hydroxyl radicals (3).

$$MO_{x+1} + R \longrightarrow MO_x + RO \quad (3)$$

$$MO_{x+1} \longrightarrow MO_x + \frac{1}{2}O_2 \quad (4)$$

The oxidation of organics competes with the consumption of higher oxide species. Oxygen is produced during the process according to equation (4).

In contrast, the non-active anode surface does not interact with physisorbed hydroxyl radicals, which results in the direct electrochemical combustion of organics (5). Reactions 5, 6 and 7 occur simultaneously:

$$MO_x(\bullet OH) + R \longrightarrow MO_x + CO_2 + H_2O + H^+ + e^- \quad (5)$$

$$MO_x(\bullet OH) \longrightarrow MO_x + \frac{1}{2}O_2 + H^+ + e^- \quad (6)$$

$$2MO_x(\bullet OH) \longrightarrow 2MO_x + H_2O_2 \quad (7)$$

The activity of side reactions (4, 6, and 7) significantly depends on anode material used. In general, the lower the side reaction activity, the higher the current efficiency will be. Although organics oxidation can be made to occur below the oxygen evolution potential (to maximise the current efficiency), the overall treatment efficiency is reduced significantly due to the limited kinetics[90]. In the absence of oxygen evolution, the anode will be passivated due to the accumulation of some refractory species; these materials can only be oxidised under high applied voltage with simultaneous oxygen evolution[90-91]. Moreover, some side reactions also produce weak oxidants such as H_2O_2 and O_3, which can provide multi-oxidation pathways to enhance the overall treatment reliability with respect to different pollutants. It is desirable to achieve a good balance between oxidation efficiency and energy efficiency. This can be achieved through a proper anode material selection and optimisation of other system parameters.

2.4.2. Electrochemical Oxidation Systems

During the last decade, improvement in electrochemical oxidation (ECO) technology in the field of wastewater treatment was mainly possible through integration with other processes[83-84, 92]. The efficiency of organics oxidation or microbial disinfection can be significantly enhanced when ECO is used as an intermediate process for the production of other oxidants; resulting in higher reaction kinetics. Electro-Fenton reaction [69, 84, 93] and ECO assisted chlorination[83, 94] are the most promising combinations. These integrated processes however actually rely on traditional oxidants such as hydrogen peroxide molecule and free chlorine. Because of the operational complexity of these systems and unavoidable chemical residuals, these technologies are considered as not applicable for stormwater treatment, therefore extensive information on this subject will not be presented in this review paper. From now on, all parameters considered are either significant ECO system configuration parameters or stormwater related parameters that might have a significant effect on the ECO process.

2.4.2.1. Anode material

According to the Cominellis's model[90], anode material impacts significantly upon the ECO mechanism through its interaction with hydroxyl radicals and oxygen evolution. Oxygen overvoltage is a chemical property of anode material; it determines the minimum required voltage to produce oxygen from hydrolysis of water[95]. In order to eliminate the energy consumption from this side reaction, an anode material with high oxygen overvoltage is desirable. A range of electrodes were tested for different applications over the last few decades including polypyrrole, granular activated carbon, graphite, Activated Carbon Fibre (ACF), glassy carbon, pure Platinum, DSA (Dimensional Stable Anode, usually made of metal oxides coated titanium substrate) and Boron Doped Diamond (BDD) thin film. ECO had not been utilised under practical water treatment scale until efficient and stable anode materials have been developed[92]. These promising materials are non-active BDD electrode and active Dimensional Stable Anode (doped or undoped metal oxides of Pb, Ti, Ru, Ir, Sn and Sb on Titanium substrate). BDD electrode is recognised as the best anode material for ECO in

water treatment despite its incredibly high cost. Merits of this material include high oxygen overvoltage, hydroxyl radical production and good durability[83, 92, 96-98].

Panizza *et al.*[99] conducted a comparison of treatment performances of Methyl red using different anode materials including Si/BDD, Ti/PbO_2, Pt and Ti/Ti-Ru-Sn ternary oxide (DSA). The experiment was done in a parallel plate electrode cell with Na_2SO_4 as supporting electrolyte. A centrifugal pump was used to circulate the flow to achieve both mixing and continuous treatment. The total oxidation of COD was found only when BDD and PbO_2 were applied as anode material due to their higher rate of hydroxyl radical production. Ternary metal oxide was only able to provide a partial decomposition of methyl red, which resulted in a very low treatment performance of COD. A strong relationship between anode material and treatment performance was shown in this experiment (Figure 2-1).

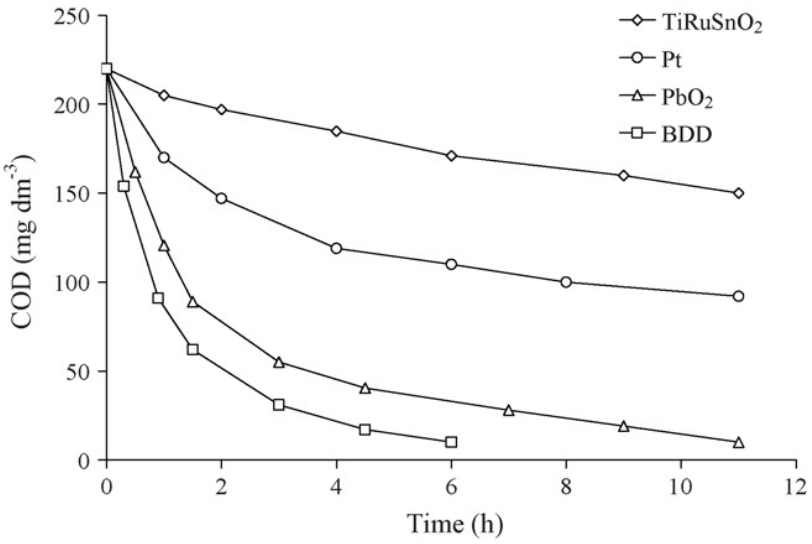

Figure 2-1 Comparison of the trend of COD during the oxidation of 200mg/dm^3 of methyl red in 0.5M Na_2SO_4 at different anodes. Conditions: *I*=500mA; flow rate=180 L/h[99]

BDD and PbO_2 performed better over Platinum and ternary oxide for COD removal. It should be noted that treatment performance was evaluated based on the total decomposition of organics since COD was used as the only targeting pollutant. This result is however limited in its scope in the instance where total mineralisation is not necessarily required, such as disinfection or pre-treatment

of some refractory organics for post-biodegradation. Disinfection, which might have a different oxidation mechanism, will possibly show a different pattern of sensitivity to anode materials.

Another experiment conducted by Lacasa *et al.*[100] can be used to support the above hypothesis. Electrochemical Denitrification was carried out using both BDD and Dimensional Stable Anode (DSA) anodes in a low concentration chloride electrolyte ($NaCl = 0.085M/L$). The results showed a similar oxidation removal performance of nitrate for both BDD and DSA anodes. This result is very different from those using COD or total organics as the targeting pollutant, which further reveals the treatment performance of different anode materials is pollutant specific: it is not always necessary to evaluate the anode performance based on total mineralisation of organics. Meanwhile, although the overall oxidation performance was found to be the same between BDD and DSA, reaction by-products during the oxidation process were found to be different when different anode materials were used. Under a low chloride concentration condition (which might be the case in stormwater applications), the formation of perchlorate was only found in the water treated using BDD. Hence the use of BDD for drinking water production is not recommended. Finally, Lacasa *et al.*[106] concluded that in the case of BDD, the oxidation reaction is initiated by hydroxyl radicals and associated ozone while in the case of DSA, it is mainly due to the direct electron transfer onto the anode.

Another electrochemical microbial disinfection experiment was conducted by Jeong *et al.*, [101]. They showed that DSA has a much stronger ability to oxidise chloride compared to BDD [101]. It should be noted that this study was undertaken to determine a case specific oxidation ability of different anode materials rather than the contribution arising from oxidation of chloride.

In addition to the chemical mechanism, the biocidal mechanism might be important for the final disinfection performance during electrochemical oxidation. A good example of this would be the disinfection or germ minimisation by electrochemically produced oxygen. Although active anode materials such as DSAs have higher activity of oxygen evolution (due to the lower oxygen evolution voltage compared to BDD), this conventional disadvantage in organics decomposition has a germicidal effect on anaerobic microbes[92].

During the recent decades, BDD electrode was routinely favoured by most of the researchers because of its low oxygen evolution and high hydroxyl radical production, which leads to complete decomposition of organic matters into carbon dioxide (mineralisation). In contrast, commercially available Dimensional Stable Anode (DSA) has very limited ability in complete decomposition of organic matter.

However, it is to be noted that DSA can partially oxidise some sensitive chemicals such as aromatic ring, chloride and etc.[83, 99, 101]. Although a higher production of oxygen from DSA is conventionally recognised as not energy efficient, this was determined based on organics removal performance. Considering the possible contribution of aeration to disinfection [92], the actual energy efficiency of this side reaction might be re-evaluated when this anode material is employed. In this chapter, different types of anode materials are reviewed so as to enlighten on how DSA can be used as a potential anode material for stormwater ECO disinfection. Of importance is the fact that although BDD can deliver a superior disinfection performance as compared to DSA, its use comes with a high operational cost. Hence, as long as the difference in disinfection performance between BDD and DSA lies within a practically acceptable range with a net positive benefit-cost ratio, DSA can be an attractive anode material. The reduction reaction happens at the cathode, as electrons are released. [83]. This becomes of importance when electro-reduction is the desired treatment process. A good example of the application of Electrochemical reduction would be the removal of heavy metals and hardness[83, 102]. Positively charged metal ions will eventually deposit on the cathode surface where they gain electrons. Hydrogen will be produced at the same time at the cathode. [103]. *Dhar et al.*[104] and *Drogui et al.*[105-106] reported the disinfection reaction to occur at the cathode as a consequence of hydrogen peroxide production.

However, due to the low concentration of hydrogen peroxide produced in this reaction and also the weak oxidation ability of this chemical, the cathodic disinfection reaction does not compensate for the more powerful anodic oxidation[92]. This signifies that a self-inert and durable

cathode material would be suitable for use (usually stainless steel or pure Titanium[83-84, 86-89, 97-98, 100-101, 103, 107]).

However, the deposition of $CaCO_3$, $Mg(OH)_2$, and other insoluble matters will occur on the cathode surface, especially when the discharged water has a high hardness[83, 92]. The deposited material can be redissolved by reversing the polarity under a regular interval basis[92, 108]. This cleaning method requires using an anode material for both electrodes. However, research shows that the lifespan of the anode will be reduced when subjected to frequent polarity reversal. Kraft compared the lifespan of different anode materials under regular polarity reversal[92]; the shortest lifespan of electrode tested was Ti/RuO_2, followed by IrO_2 coated electrode with a lifespan of about 3 months. Mixed RuO_2/IrO_2 coated electrode had a longer lifespan of one year under the experiment conditions. Promising result was shown in regards to the Platinum coated Ti anode, which is still running unaffectedly after 8 years of experimental simulation. Other cathode cleaning methods including ultrasonic cleaning[109] and mechanical cleaning[92] are also applicable but none of them are successful under long term operation with respect to polarity reversal[92].

2.4.2.2. Effect of electrode distance, applied voltage and operational current density

Mass transfer is a primary factor influencing the kinetics of any chemical reaction [82, 88, 110-111]. The distance between anode and cathode plays an important role in mass transfer during the ECO reaction [83, 96, 111-112].

In general, there are two types of mass transfer mechanisms in electrochemical oxidation[111-112]. The first one is diffusion, which is the movement of ions or molecules arising from a concentration difference. This process occurs near the anodic or cathodic surface[111, 113]. For example, a layer of concentrated oxidizing reagents will form right close to the anode surface (positive electrons, reactive oxygen species or hydroxyl radicals). On the other hand, reducing agents such as electrons, organic matters or micro-organism form a relatively more concentrated outer layer next to the inner layer (as shown in Figure 2-2). The Faster the diffusion exchange between these two layers, the faster will be the oxidation reaction. The second mass transfer mechanism is convection, which refers to the

movement of molecules or ions in the bulk solution. This process ensures an efficient movement of reactants to diffusion layers, where the reaction takes place. A limited convection mass transfer will result in a decreased concentration of the reactant (electrons, organics or microbes) at the outer diffusion layer of the anode relative to concentrations in the bulk solution. This happens when the diffusion process (that is, consumption of reactants) takes place at a faster rate than of the convection process (that is, movement within the bulk solution) [83, 114].

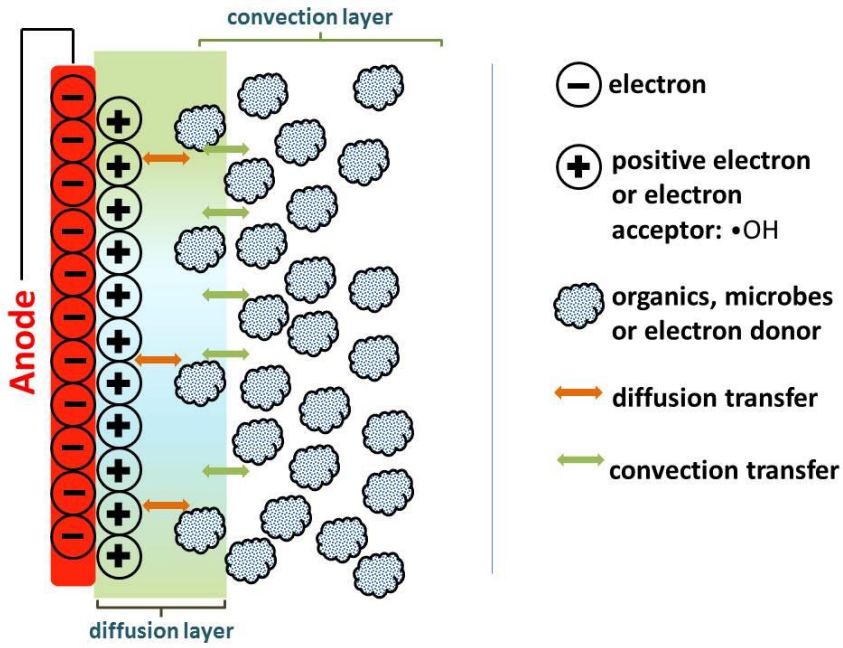

Figure 2-2 A schematic diagram of mass transfer (both diffusion and convection) happening on the anode side

This phenomenon is popularly known as "Concentration Polarisation", where the original current efficiency will be reduced due to the existed energy barrier of mass transfer. In this case, an additional energy or "over potential" is required to break through the energy barrier in order to force the reaction to maintain the previous rate. This operational "over potential" is greater than the voltage required thermodynamically for the ideal reaction to happen[115]. The relationship between the overpotential of an actual electrochemical reaction and the corresponding anode current can be explained by the Tafel equation[116]:

$$\eta(\Delta V) = aln\left(\frac{i}{i_o}\right) = aln(i) - aln(i_o) \quad (8)$$

Where "η" or "ΔV" is the anode over potential, "a" is the Tafel slope, which is a characteristic constant of the system, "i" is the actual anodic current density (mA/cm^2), "i_o" is the equilibrium diffusion exchange anodic current, which represents the ideal current when the anodic over potential is zero.

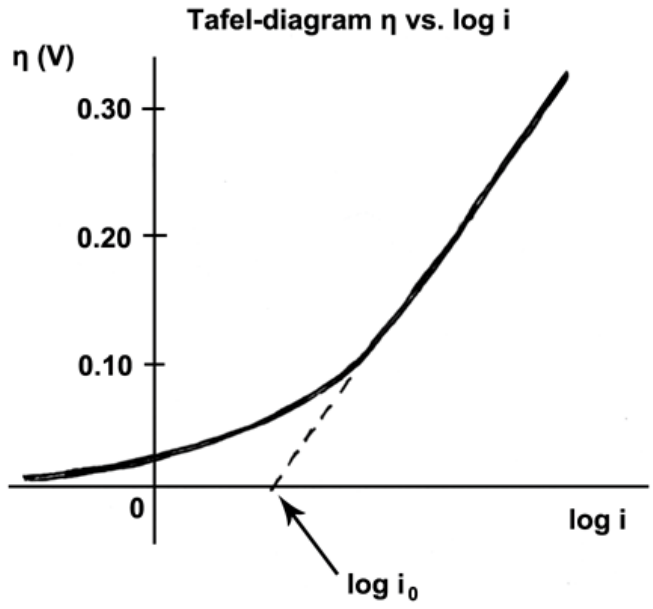

Figure 2-3 A qualitative plot of Tafel Equation[117]

Figure 2-3 is a qualitative expression of the relationship between the anodic "over potential" and current density under the real electrochemical oxidation. It is obvious that when the current density is increased (as a result of increased operational voltage, reduced system resistance or etc.), the system "over potential" will also increase. This means, more energy will be used to overcome the electrode polarisation, which results in a lower energy efficiency of ECO under the same power supply. The above model becomes relevant when the influence from electrode distance and system applied voltage are being studied. Zhang et al. optimised the ECO system for removal of COD from landfill leachate[112]. They found the electrode distance influenced the COD removal performance through its impact on the reaction mass transfer.

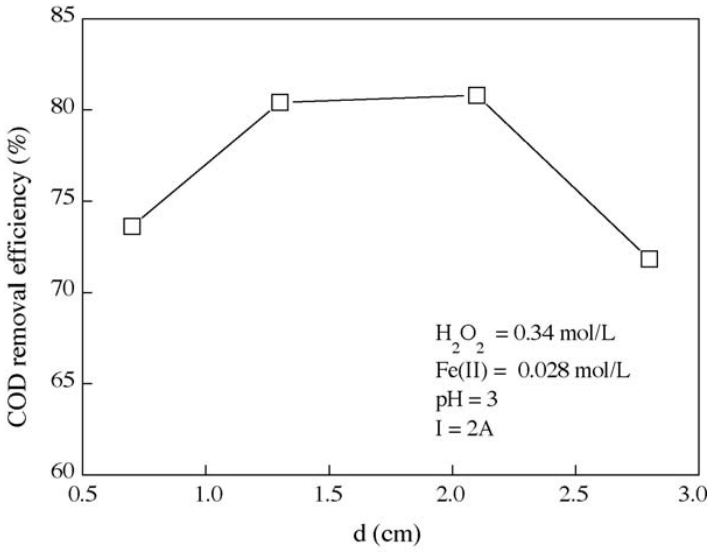

Figure 2-4 COD removal performance under different electrode distances under constant current supply[112]

Under the same applied system current (2A), when the electrode distance is greater than the "optimum distance" (1.5-2.0cm), the COD removal performance start to decrease (Figure 2-4). In this case, the performance is "diffusion limited" due to the decrease of the ions exchange capability between two diffusion layers as a result of an increase in system resistance. However, the relationship between the electrode distance and removal performance did not always follow this trend. For instance, a further decrease of the electrode distance caused a performance reduction in COD removal, which could be explained by the insufficient convection mass transfer under the rapid rate of diffusion. Concentration polarisation starts to occur at the two diffusion layers of the anode, and hence the anodic overpotential will eventually increase. Under a constant energy supply, this increased anodic overpotential used to overcome the energy barrier of polarisation consequently reduced the energy left for the actual ECO reaction. On the other hand, Zhang *et al.*[112] found that increasing the system current leads to a decreased rate of increase of COD removal performance: they attributed this to the "convection limited" mechanism. Not surprisingly, the current efficiency gradually decreased with respect to the increasing system current as shown in Figure 2-5. This was mathematically explained by the Tafel equation, where the anodic overpotential is positively correlated to the current applied.

The physical explanation of this phenomenon is the rate of convection is not sufficient to synchronise with the diffusion on the anode surface. The overall reaction becomes convection limited and under this situation, the further increase of the applied current eventually does not contribute to the reaction rate as efficiently as before.

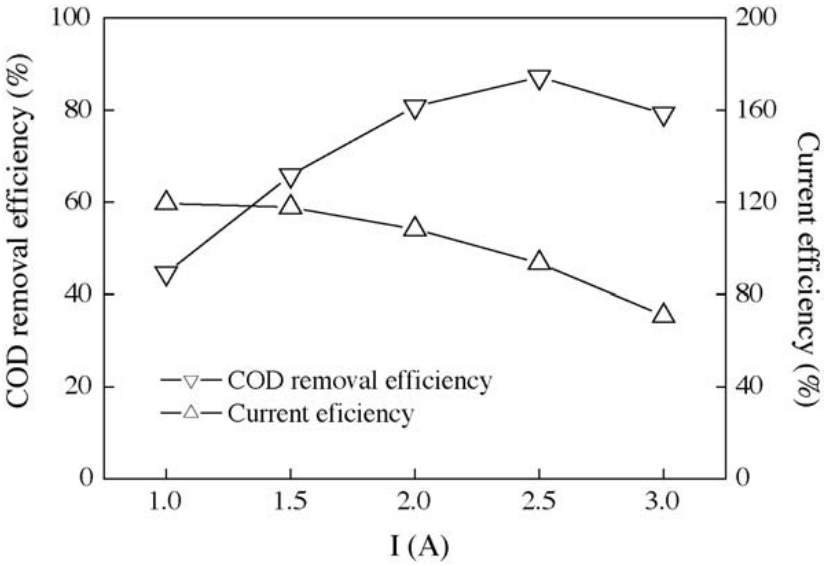

Figure 2-5: COD removal efficiency and current efficiency with respect to changing current[112]

Although the system current (mA) or the current density (mA/cm^2) on electrode surface are commonly used as one of the primary controlling parameters in some studies on electrochemical oxidation, it is not specific and appropriate to be analysed parallel with other mutually exclusive primary factors, especially under the multi-factorial uni-variate analysis[118]. That is because current or current density is a resultant expression of other primary system configurations and operational conditions, such as anode material, applied voltage, electrodes distance, solution electricity conductivity and oxidation rate etc. Most of the studies show increasing current density will lead to higher oxidation efficiency[96, 103, 119]. This is however due to the improvement of other primary related factors such as an increase in applied voltage, solution electricity conductivity or reduction of electrodes distance among others. When investigating the impact of primary system configurations and operational conditions on the disinfection performance, current density should be measured for

each experiment configuration during the operation this should then be integrated with multifactorial analysis as a supplementary factor or rather it can also be analysed as the system performance.

2.4.2.3. Effect of operational conditions

The effect of operational condition (water characteristics) on the treatment performance of ECO has been widely studied using lab synthetic water, surface water and wastewaters.

Treating water with higher electric conductivity has a stronger ability for ions exchange. Abd-Ellah *et al.*[120] showed clearly the mass transfer between two diffusion layers of the anode to be significantly enhanced in a more conductive electrolyte. Higher electric conductivity of the electrolyte or the bulk solution will also increase the energy efficiency of ECO by reducing the system resistance when a constant desired current is applied according to $P = I^2R$, which is a transformation of Ohm's Law for a circuit model.

Water chemistry has a significant influence on the ECO reaction. In particular, some ions may have significant positive or negative impact on the overall treatment performance. Data obtained from our unpublished field monitoring work of stormwater treatment system indicates that four major cations ($Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}$) and anions ($HCO_3^{-}, SO_4^{2-}, Cl^{-}$) are present in higher levels than other metal ions and anions. Kantrowitz and Woodham[121] also reported Calcium (Ca^{2+}), bicarbonate (HCO_3^{-}) and chloride (Cl^{-}) are the three major ions in stormwater runoff based on their monitoring data in Florida. The presence of substantial calcium and bicarbonate ions in stormwater is possibly caused by the dissolution of calcium carbonate and magnesium carbonate according to following chemical equations:

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2 \quad (9)$$

$$MgCO_3 + H_2O + CO_2 \longrightarrow Mg(HCO_3)_2 \quad (10)$$

Calcium carbonate is a fundamental constituent of rock and most of the concrete components such as permeable pavement and building façade. Magnesium carbonate is also a common compound in the natural environment. Since Stormwater runoff is usually exposed to the atmosphere over a large surface area, conditions are conducive for the above reactions. Hardness in natural stormwater is

similarly caused by Reaction (9) and (10). Results from our unpublished field monitoring further validated the above hypothesis, showing that the molar number of bicarbonate ions is very close to half of the sum of the molar number of both calcium and magnesium ions. Although there are currently no known studies that report on a decrease in ECO performance caused by the hardness of the medium, it is speculated that the high levels of bicarbonate ions in stormwater may have a negative impact on the ECO disinfection performance. Given that hydroxyl radical is one of the major oxidants in ECO treatment (using non-reactive anode), both Zhang *et al.*[122] and Guillard *et al.*[123] report a scavenging effect of hydroxyl radicals by carbonate and bicarbonate ions as shown in equation 11 and 12. This scavenging effect is due to the fact that the hydroxyl radical has a much higher reaction kinetics with carbonate/bicarbonate ion ($k=3.9 \times 10^8$) than it does with most organics[123].

$$CO_3^{2-} + \bullet OH \longrightarrow OH^- + CO_3^{\bullet -} \quad (11)$$

$$HCO_3^- + \bullet OH \longrightarrow H_2O + CO_3^{\bullet -} \quad (12)$$

Several studies indicate that chloride ion is favoured for by decomposition and disinfection using ECO[83, 90, 92, 100, 112, 124]. Chloride will be oxidised on the anode and become free chlorine after it loses an electron (Equation 13)[83]. Chlorine can also be further hydrolysed to hypochlorous acid, which is also a strong oxidant that is normally used in chlorination disinfection (Equation 14)[83]. Although both chlorine and hypochlorous acid have a lower oxidation ability compared to hydroxyl radical, this indirect oxidation usually has a much more efficient performance than the anodic oxidation[107]. The produced free chlorine has a longer life span than the hydroxyl radicals and can be readily transported throughout the bulk solution[83].

$$2Cl^- \longrightarrow Cl_2 + 2e^- \quad (13)$$

$$Cl_2 + H_2O \longrightarrow HClO + Cl^- + H^+ \quad (14)$$

Fang et *al.*[124] conducted an experiment of chloride-assisted electrochemical disinfection of MS2. They found that increasing the chloride concentration (achieved by the addition of sodium chloride in the solution) resulted in a significant improvement in the disinfection performance as shown in Figure 2-6.

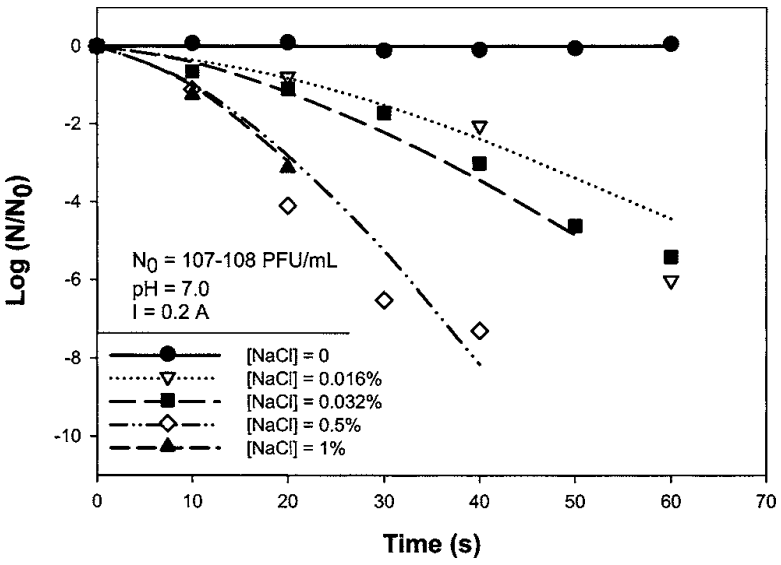

Figure2-6 Log reduction of bacteriophage MS2 versus time at different salt concentrations at a fixed current (0.2A)[124]

However, systems with high initial chloride concentrations can produce THMs and other halogenated disinfection as by products. This has deterred the use of chloride assisted ECO disinfection for high quality water production or other applications requiring a high demand for environmental protection.

2.4.2.4. Microbial disinfection performance

Electrochemical Oxidation (ECO) as a wastewater treatment technology has been well studied for chemical removal[83-84, 88, 99] and to some extent for microbial disinfection[92, 124-125]. The treatment performance is achieved mainly through the production of free chlorine from chloride oxidation or hydroxyl production through water hydrolysis[83, 100].

Cho *et al.* (2014)[125] investigated ECO treatment of domestic wastewater with chloride addition (1.86g/L). They built a pilot scale reaction system using multiple metal doped Titanium anode (Dimensional Stable Anode – DSA) and solar panel as the only power supplier. Under the operational current density of 2.09 mA/cm^2 (3.9V), this versatile system was able to achieve 95% removal in Chemical Oxygen Demand with an initial concentration of 200mg/L within 6 hours of

operation. 7.8×10^5 CFU/ 100mL of total coliform and 8×10^4 CFU/100mL of faecal coliform were successfully disinfected within 3 hours of operation with hydrogen production.

Lacasa *et al.* (2013)[126] conducted an ECO study using Boron doped diamond (BDD) anode for disinfection of synthetic ballast water with chloride concentration of 18.3 g/L. 6 log reduction of *E. coli* was achieved within 3 minutes under an operational current density of 25.5 mA/cm^2.

Schaefer et al. (2015)[127] tested ECO disinfection performance of pre-filtered aqueduct water (surface water) with a chloride concentration of 118mg/L. Under current density of 2.5 mA/cm^2, six log reduction was achieved for lab strain *E. coli* within 60 minutes through free chlorine production[127].

Another common pathway of ECO disinfection was achieved through the production of hydroxyl radical (·OH). Hydroxyl radical produced via water electrolysis in ECO system is a strong oxidant capable to decompose refectory organics that were not achieved using conventional oxidation processes (such as chlorination). Production of hydroxyl radical in water solution using ECO method does not rely on the presence of any additional chemicals. Rajab et al.[128] tested the disinfection performance of *Pseudomonas* in deionised water (electrochemical conductivity=0.08µs/cm) using BDD as an anode. Without the assistance of chloride, they had to run the system under a very high operational current density (167 mA/cm^2) to achieve sufficient hydroxyl radical production. 6 log reduction of *Pseudomonas* was achieved after 15 minutes of operation in this case.

Jeong et al. (2006)[129] investigated disinfection of *E. coli* in chloride free solution through ECO produced hydroxyl radical using BDD anode. They claimed that four log reduction of *E. coli* was achieved under the operational current of 50 mA/cm^2 while no obvious disinfection was observed (<1 log reduction) when the operating current was 33 mA/cm^2.

In general, current literature suggests effective ECO disinfection can be achieved under either high chloride concentration[88, 101, 124] or high operational current when hydroxyl radical production is required in low chloride matrices[85, 101, 128].

2.5. CONCLUSIONS AND KEY RESEARCH GAPS

The quality of stormwater harvested using current water sensitive urban design (WSUD) technologies does not satisfy the standard for general irrigation and recreational purposes because of the excessive microbial residual concentration. In response, a new technology should be applied for stormwater disinfection in order to treat stormwater at least satisfying the general irrigation standard (with *E. coli* concentration < 10 CFU). Electrochemical oxidation (ECO) has shown its promising disinfection performance in wastewater and surface treatment. Comparing to other disinfection technologies, ECO could be operated at low cost and with no chemical addition.

However, given the low level of EC in stormwater (in comparison to the wastewaters that have been tested), in order to maintain ECO as the low energy technology for stormwater disinfection, the available operational current is limited compared to previous applications. Therefore, it remains unknown that how ECO performs under low stormwater electric conductivity.

Presence of chloride ion is essential to the ECO treatment system using active type of anodes (such as DSA). It is the source for producing free chlorine which is credit for oxidation treatment performance. Chloride ion in stormwater is very low (mean value of 11.4 mg/L in Australia) compared to the level in previous application in wastewater, surface water treatment. The ECO disinfection performance of stormwater under low chloride condition remains unknown.

The longevity or performance reliability of ECO system used under stormwater operational condition remains uncertain. As it mentioned, stormwater has low electric conductivity, which means the system will be operated under higher voltage compared to wastewater and surface water applications.

Most of current ECO wastewater studies evaluated the disinfection performance on only few lab strain microorganisms (such as *E. coli* and other commonly used faecal coliform). However, wild indigenous microbe strains have the stronger resilience to the harsh environment compared to other lab strains microbes, which has lost the ability to protect them from external condition changes and chemical attack[130-131]. Therefore, previous understanding of the ECO disinfection performance on lab strain microbes is not valid for indigenous microbe species in stormwater. Testing using only limited

numbers of indicator microorganism does not reflect the true overall disinfection performance, especially for stormwater which usually contains substantial types of pathogen. It is unclear how ECO would perform on disinfection of stormwater pathogen such as *campylobacter* known as the major bacteria for food cause diarrhoea in Australia.

There are also commonly concerned other pollutants existing in both wastewater and stormwater, for example, nutrients, heavy metals and emerging chemicals such as pesticides. Section 2.4 and other studies[132-133] have shown these pollutants can be effectively treated using ECO or through the simultaneous Electrochemical Reduction (ECR) in wastewaters under optimised conditions. Due to their low concentrations in pre-treated stormwater and different optimisation target, the potential of ECO on reducing other pollutants as a side effect of stormwater disinfection is not of concern in this thesis.

2.6. RESEARCH QUESTIONS AND HYPOTHESES

The literature review found that significant research gap exists for applying electrochemical oxidation for stormwater disinfection. To evaluate the feasibility of using ECO for stormwater disinfection, a number of research question need to be addressed.

1. How ECO disinfection performs when synthetic stormwater is used and how it relates to different system configuration?
    - It is hypothesised that disinfection of stormwater can be achieved using ECO but the disinfection rate will be slower compared to the previous application with high chloride presence and high current density supply. In addition, the disinfection by-product level in treated stormwater will not be of concern as the low chloride concentration in stormwater.
    - It is hypothesised that the disinfection rate is governed by the operational current density when synthetic stormwater with fixed chemical composition is used.

2. What is/are the key mechanism(s) that drives the ECO disinfection performance of stormwater?
    - It is hypothesised that for the dimensional stable anode (DSA), the disinfection is achieved through free chlorine production using chloride ions in stormwater.
    - It is hypothesised that for boron doped diamond (BDD) anode, the disinfection is achieved through the production of hydroxyl radicals.
3. How durable the ECO system is when it is used under stormwater operational conditions?
    - It is hypothesised that the longevity of ECO system depends on the selection of anode type
    - It is hypothesised that permanent system performance deterioration will not occur; recoverable deterioration may happen when cation fouling formed on cathode due to the hardness of stormwater. And this could be recovered by applying regular acid washing method.
4. How ECO disinfection performs on multiple stormwater pathogens?
    - It is hypothesised that ECO could achieve good disinfection performance on Gram negative stormwater pathogens due to their low resistance to chemical attack
    - It is hypothesised that the disinfection effect on Gram positive and spore bacteria will be weaker compared to the performance on E. coli and other Gram negative bacteria.

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Chapter 3: Feasibility study of using electrochemical oxidation for stormwater disinfection

Declaration by the candidate:

In the case of Chapter 3, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Conception, design of the project, experimental work, analysis and interpretation of data, drafting the paper	75%

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	**Nature of Contribution**	**Extent of contribution (%) for student co-author only**
McCarthy, David	Experimental design and critical thesis revising	
Wang, Zhouyou	Experimental assistance, data analysis	2.5%
Zeng, Xiangkang	Experimental assistance, data analysis	2.5%
Zhang, Xiwang	Experimental design and critical thesis revising	
Deletic, Ana	Experimental design and critical thesis revising	

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the student's and co-authors' contributions to this work. In instances where I am not the responsible author, I have consulted with the responsible author to agree on the respective contributions of the authors.

Wenjun Feng

November 2017

Ana Deletic (Main Supervisor)

November 2017

Chapter 3 Stormwater disinfection using electrochemical oxidation: A feasibility investigation

INTRODUCTION

This chapter investigates the feasibility of Electrochemical Oxidation (ECO) for stormwater disinfection under laboratory condition using synthetic stormwater. The disinfection performance and the associated energy consumption are assessed under different operational voltages, electrode distances and the corresponding resulted operational currents. The reaction pathway is determined to evaluate the reliability of the disinfection performance. Disinfection by-products (DBPs) are tested in treated real stormwater that is collected from different stormwater catchment sites before treatment. The deterioration of tested anode type found during this study is also discussed.

In general, this chapter shows ECO has very promising performance on stormwater disinfection in terms of its treatment time and energy consumption. DBPs in treated stormwater samples are at least one order of magnitude lower than the threshold value suggested by the Australia Drinking Water Guidelines. It also shows the significance of longevity of anode type selected for the stormwater application, which will be further investigated in Chapter 4.

The work of this chapter has been written in a paper format and has been submitted to *Water Research* Journal.

Stormwater disinfection using electrochemical oxidation: A feasibility investigation

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ABSTRACT

Electrochemical Oxidation (ECO) has shown good potential for disinfection of wastewater discharges but has not been tested for stormwater. Due to far lower salinity and chloride levels present in stormwater than in wastewaters, the knowledge so far on the ECO disinfection performance cannot simply be used for stormwater applications. This paper presents the first study on the feasibility of ECO technology for disinfection of pre-treated stormwater. Disinfection performance of *E. coli* was tested using a Dimensional Stable Anode (DSA) in a series of batch experiments with synthetic stormwater of 'typical' chemical and microbial composition. The lab results showed that effective disinfection could be achieved with very low energy consumption; e.g. the current density of 1.74 mA/cm^2 achieved total disinfection in 1.3 minutes, using only 0.018 KWh per ton of stormwater treatment. Chlorination was found to be the key disinfection mechanism, despite the synthetic stormwater containing only 9 mg/L of chloride. Real stormwater collected from three stormwater treatment systems in Melbourne was then used to validate the findings for indigenous microbe species. Disinfection below the detection limit was achieved for stormwater from the two sites where chloride levels were 9 and 200 mg/l, respectively, but not for the third site where stormwater contained only 2mg/L chloride. Unfortunately, deterioration of the DSA anode was observed after only 8-10 h of its cumulative operation time, very likely due to high voltage that had to be applied to low saline stormwater to achieve the required current density. In conclusion, ECO was found to be a very

promising low energy disinfection technology for stormwater, but far more work is needed to optimise the technology for unique stormwater conditions.

INTRODUCTION

Stormwater harvesting, complying with the principles of Water Sensitive Urban Design (WSUD)[1] (also known as Low Impact Development, LID[2]), is an emerging practice in urban areas that are experiencing water scarcity[3-4]. Collected and treated stormwater using suitable WSUD technologies, such as stormwater biofilters (bio-retentions and raingardens) or wetlands, could be utilised for non-potable purposes[5] (e.g. irrigation and toilet flushing[6]), and in rare cases as a source for potable water supply[7]. Unfortunately, these green WSUD treatment systems are unable to remove pathogens from stormwater to the levels required for non-potable uses, requiring additional disinfection technologies. For example, a well-designed stormwater biofilter can generally provide around one log removal of the *E. coli* levels in stormwater[8-9], making it safe only for restricted irrigation[6]. This has become the major barrier to widespread adoption of WSUD stormwater harvesting technologies since due to its distributed nature and often low capacity, the systems need to be robust and of low running costs. There is, therefore, an urgent need for low cost, efficient and environmentally friendly technologies for disinfection of stormwater that is grounded in the proven WSUD principles[3].

ECO has been developed for wastewater treatment, primarily organics and inorganics from heavily polluted industrial streams[10-12], and to some extent wastewater disinfection[13-15]. Compared to other cutting-edge treatment technologies, such as chlorination, photo-catalytic oxidation, ozonation and UV irradiation, ECO can be operated without chemical addition and under lower capital and operational cost[12]. However, ECO has not been tested for stormwater treatment, and due to the differences between stormwater and wastewater, it is unclear how it will perform for this application; e.g. stormwater has significantly lower concentrations of chloride and very low Electrochemical Conductivity (EC), while its microbial concentrations are usually several orders of magnitude lower

than in wastewater[9, 16]. Stormwater is of intermittent nature[17] and with far larger variability in its quality[18-19] than industry or municipal wastewaters. This has caused considerable challenges for direct adoption of wastewater treatment technologies to stormwater applications[20].

Depending on the type of anode selection, the indirect ECO treatment performance relies either on the chlorine evolution from oxidising presented chloride ions or hydroxyl radical production through water hydrolysis[15, 21].Dimensional Stable Anode (DSA) – the anodes with titanium substrate coated with titanium group metals or metals oxides such as Iridium and Ruthenium – is one of the commonly used anodes due to their reasonable costs[10]; stormwater usually comes in high quantities over short time periods, therefore requiring very low treatment costs per unit volume. However, due to their low chlorine evolution potential, DSAs have been mainly utilised to treat wastewaters that contain high levels of chloride ions (160-10,000 mg/L)[16, 22,23]. In some cases, when wastewater contained low chloride concentration, additional sources of chloride had to be added to the water to achieve optimum treatment efficiency[24-26]. The operational concentration of chloride ranged from 160 to 10,000 mg/L depending on the targeted pollutants[25-28]. This poses a direct challenge to ECO's application to stormwater since chloride levels in stormwater are often very low; e.g. a mean concentration of chloride was found to be around 11 mg/L for a few urban catchments in Australia[6].

This paper presents the first feasibility study of ECO technology for stormwater disinfection by considering its performance, reliability, energy efficiency, anode durability, and disinfection by-product levels. One hypothesis was initially formed on the basis of aforementioned studies in wastewater treatment: Disinfection of harvested stormwater could be achieved by ECO technology, despite very low chloride levels usually present (usually <10 mg/L), possibly due to direct anodic oxidation or production of reactive oxygen species.

MATERIALS AND METHODS

The experimental set-up

A commercial Dimensional Stable Anode (DSA) using iridium and ruthenium oxides-titanium oxides (RuO_2+IrO_2), manufactured by Suzhou Fenggang Titanium Co., Ltd. in China, was used for this study, because of its low cost and good past performance for wastewater treatment[13, 16, 27]. The anodes were manufactured into rectangular plates with dimensions of 2.5cm by 5cm. Pure titanium mesh with the same dimensions was used as the cathode. Anode and cathode were mounted onto a glass beaker, at pre-determined distances, to create a single compartment electrolysis cell (see supplementary data SF1). The beaker was placed on a magnetic stirrer platform with a rotating speed of 800rpm during the experiment. A DC power supplier (EX-375L2, 0-60V/0-25A, TAKASAGO Ltd., Japan) applied the same voltage to three electrolysis cells (replicate) at the same time. System current of the electrolysis cell was measured continuously during the experiment.

Performance study using synthetic stormwater

Synthetic stormwater, that had characteristics as 'typical' stormwater treated by biofilters, was used to ensure that the same conditions were kept for a large number of tests (a similar approach was used in previous stormwater technology development studies[29-31]). The synthetic pre-treated stormwater chemistry is shown in Table S1 and briefly discussed below. The deionised water was mixed with natural sediment collected from a stormwater pond to achieve a total suspended solids concentration equivalent to a typical stormwater biofilter effluent's Event Mean Concentration (EMCs). After sampling this slurry to determine chemical properties of interest, laboratory-grade chemicals were added to top up and simulate chemical properties significant to electrochemical oxidation performance. These include typical biofiltrated stormwater EMCs of major cations ($Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}$), anions ($SO_4{}^{2-}, HCO_3{}^{-}, PO_4{}^{3-}$), total organic nitrogen, etc. chloride (9mg/L) was topped up to achieve the concentration of the lower 5th percentile in untreated urban stormwater based on Australian Stormwater Harvesting and Reuse Guidelines (*std.*=1.05)[6]. Disinfection performance validated for the lower 5th percentile chloride concentration ensured a conservative understanding of its feasibility in real application. The synthetic stormwater had electric conductivity of 105μs/cm and pH of 7.1, as is the case in field conditions[6].

In this initial study, *E. coli* K1 strain (ATCC 11775) was used as an indicator for bacteria water contamination. This strain is pathogenic to most poultry and was originally isolated from the colibacillosis[32]. It also has a stronger resilience to the harsh environment compared to other commonly used lab strains of *E. coli*. The initial *E. coli* concentration used in this study was estimated based on the 'worst case scenario' of *E. coli* levels in effluents from stormwater biofilters; since the 95th percentile *E. coli* concentration of raw stormwater is 183,382MPN/100mL[6, 33], and stormwater biofiltration systems could achieve on average of 1.2 log reduction[8, 19, 34], the *E. coli* concentration in synthetic biofiltrated stormwater was adjusted to 10,000 MPN/100mL following the culturing and preparation method used in our previous study.

400 ml of the prepared stormwater was placed in a beaker and the selected current density was applied. Three different operational voltages (4V, 7V and 14V) and three electrode distances (3 mm, 10 mm and 20 mm) were tested to assess the influence of system configuration on stormwater disinfection and energy consumption. A control with no voltage supply was also tested under the same conditions. Each configuration was replicated three times. It should be noted that the tested voltages were well above the anode's oxygen evolution voltage of 1.56V.

Six 10 ml stormwater samples were taken for each test; a sample before the test started and five during the test (the sampling times varied from experiment to experiment to ensure that the entire disinfection process was captured). These samples were then assayed for *E. coli* concentration using the Colilert^{TM} method (IDEXX-Laboratories). The detection range of aforementioned sampling method was from 10MPN/100mL to 24,196MPN/100mL.

Disinfection mechanism study

This part of the study investigated the ECO processes which govern the disinfection. Firstly, the effectiveness of possible chlorination from a limited amount of chloride present in the stormwater was examined by comparing the ECO disinfection between the 'typical stormwater' using the above synthetic receipt with chloride of 9 mg/l and chloride-free synthetic stormwater. To prepare chloride-free stormwater, Sodium nitrate (that has minimum impact on electrochemical systems[15]) was used

as a substitute for Sodium chloride in the stormwater preparation, to achieve water of the same electrical conductivity as the original (105 µs/cm).

Although most previous studies showed poor direct production of hydroxyl radical from Titanium based metal oxides anodes due to their low oxygen evolution potential[13, 15, 28], it was speculated that hydroxyl radical production might be produced. Stormwater harvested using soil based biofilters usually have an excessive ferrous iron concentration (>0.3mg/L)[5], and it was hypothesised that hydroxyl radicals may be produced as an intermediary through the interaction between ferrous ion and hydrogen peroxide[35]. To verify the effectiveness of possible hydroxyl radical production, excessive amounts (0.03M) of tert-butanol (t-BuOH), a well-known hydroxyl radical scavenger[36], were added into the synthetic stormwater. Disinfection performance of this hydroxyl radical free solution was then compared with the performance of the original synthetic stormwater. An initial test of *E. coli* survival was done showing no biocidal effect from either added sodium nitrate or 0.03M of t-BuOH. The effectiveness of possible chlorination and possible hydroxyl radical production was tested under both low and high operational currents (0.75 mA/cm^2, 4.2 mA/cm^2). Three replicates were used, following the same sampling procedure as in the above performance study.

A fluorescent study of the intactness of *E. coli* cells was used to investigate the impact of ECO on stormwater microbes. Three types of images were taken by an optical Microscope[37]: (i) bright field image of *E. coli* for general inspection, (ii) fluorescent image of *E. coli* stained by Propidium Iodide (PI, 1µg/mL) to show all the *E. coli* cells present in water, (iii) fluorescent image of *E. coli* stained by 4, 6-diamidino-2-phenylindole (DAPI, 5µg/mL) to show the cells with permeable or broken membrane only. Due to the low concentration of cell numbers in the tested stormwater, a series of centrifugation (8000 rpm over 5 mins) was used to achieve a concentration of around 10^6 cells/mL in suspended solution. Samples were stained with a mixture of 1 µg/mL Propidium Iodide (PI, Sigma Aldrich,) and 5 µg/mL 4, 6-diamidino-2-phenylindole (DAPI, Sigma Aldrich) for 10 minutes. Stained samples were then washed three times using sterilized PBS solution to remove excess dye. Prepared

samples were examined using Nikon C-1 confocal microscope under 600 magnification and fluorescent light source.

Transmission Electron Microscope (TEM) was also used to examine the morphological and structural change of *E. coli* after ECO disinfection. Live and ECO disinfected *E. coli* samples (concentrated following the same method as describes in above fluorescent test) were firstly fixed with 2.5% of glutaraldehyde for 2 hours. Fixed cells were then dehydrated using acetone and resin embedded at 60°C for 48 hours. Embedded samples were then cut into 70 nm layers and examined using TEM (H7500, Hitachi).

Anode deterioration study

A drop in the anode performance was observed after 8-10 h of its cumulative usage time, so the experiments done after that time were not reported in this paper. However, after approximately 20 h of the active anode use, the experiments with the currents of 0.75mA/cm^2 and 1.75mA/cm^2 were repeated to assess the level of deterioration. Scanning Electron Microscope (SEM) images were done on samples (3 mm by 5 mm) of both unused and used (deteriorated) anodes. The anode samples were initially washed using 0.02M Hydrochloric Acid (HCl) and then by 97% ethanol within an ultrasonic bath (each washing lasted 15 minutes). The surface morphology and elements distribution were then obtained with FEI Magellan 400 FEGSEM (FEI, America) operated at 10 Kv. Distribution of doping metals (Ti, Ru and Ir) was examined using Energy Dispersive X-ray Detector (EDX) mapping[38].

Performance validation study using real stormwater

An attempt was made to validate the results obtained using synthetic stormwater by running a small subset of tests with actual stormwater. The tests also included monitoring of Disinfection By-Products (DBPs) in the treated stormwater.

Stormwater samples were collected at the Monash Carpark stormwater biofilter (well tested in the past, Hatt et al, 2009[39]), Troup's Creek stormwater constructed wetland, and Clifton Hill stormwater biofilter (all these WSUD systems are located within the Melbourne Metropolitan region). The selection of stormwater catchment sites aimed to capture variabilities in pre-treated stormwater

quality, so as to test the ECO for a wide range of possible field conditions. Monash Carpark biofilter receives stormwater runoff from concrete surfaces with a relatively small catchment size. Biofiltrated stormwater collected from this site is relatively less polluted compared to stormwater collected from the residential catchment and has similar chemical properties to the tested synthetic stormwater. Troups' Creek wetland is a typical end-of-the catchment stormwater treatment system located in the outer suburbs of Melbourne. It receives raw stormwater from residential, urban and non-developed (natural) surfaces. Clifton Hill biofilter is located in the inner Melbourne area, and mainly receives residential runoff.

One water sample was gathered at outflows of these systems during different rainfall events. ECO disinfection under 1.75 mA/cm^2 (that was found to be effective for synthetic stormwater) was then performed for 30 minutes using three replicates of these samples. The sampling method applied in this study followed the same procedure as described in the performance study. Both indigenous *E. coli* and total coliform were assayed using Colilert^{TM} method (IDEXX-Laboratories). Meanwhile, collected stormwater samples were sent to a NATA-certified (National Association of Testing Authorities, Australia) laboratory for testing of chloride, pH, Bicarbonate, Total Organic Carbon and Chlorination related disinfection by-products (DBPs). DBPs (THMs, HAAs and Hvols) were tested only in Troup's Creek water samples before and after ECO treatment since this source water contained the highest concentrations of chloride and organic matter (which possibly could lead to high levels of DBPs).

Data analysis

To assess the disinfection performance, *E. coli* concentration was plotted against the operational time for all the performed ECO tests. *E. coli* decay rate was calculated for each test using a simple linear regression model between *E.coli* concentration and elapsed time. The average linear decay rate, ***k*** was estimated for each configuration using the three replicates. In this study, the linear model showed better fitting to the observed data compared to conventional exponential models possibly due to special stormwater characteristics.

However, observed ECO disinfection kinetics of the synthetic stormwater during the tests under U=7 V, and I_d=0.75 mA/cm^2 was also qualitatively examined in relation to the wastewater ECO disinfection kinetic model proposed by Galvez et al[40] to illustrate the different ECO disinfection kinetics between wastewater and stormwater. This model assumes that there are two phases in the ECO disinfection of *E. coli* over time (Equation (1)): Phase 1 (the shoulder) where there is no or slow rate of disinfection due to time needed to achieve the cell damage and competition between microbe and organics for oxidants; and Phase 2 (tail or exponential decay) where the disinfection decay follows the simple first order kinetics.

$$N_i = \frac{(N_0 - N_{res}) \cdot e^{-k \cdot t} \cdot e^{-k \cdot sl}}{1 + (e^{k \cdot sl} - 1) \cdot e^{-k \cdot t}} \qquad (1)$$

where N_i is *E. coli* concentration at time i, N_0 is the initial *E. coli* concentration, N_{res} is the residual *E. coli* concentration, sl is the shoulder length, k is the specific exponential inactivation rate.

To compare the efficiency of the tested ECO configurations within the synthetic stormwater performance study, the time and energy needed to achieve a three log reduction (disinfection below the detection limit) of *E. coli* was used. For each configuration, $t_{3\text{-log}}$, defined as the time required achieving 3-log reduction (hour), was calculated using the average decay rate, *K*. Unit energy consumption, E_u, expressed in terms of KW·h electricity consumed to achieve 3-log reduction in one tonne of stormwater, was calculated as:

$$E_u = U \cdot I \cdot t_{3-log} \div 1000 \times 2500 \qquad (2)$$

where U is the applied voltage (V), I is the operational current (A), 1000 is the conversion from W to KW and 2500 is the volume conversion factor considering the volume increasing from 0.4L to 1000L.

To examine the key disinfection mechanisms, the ECO disinfection performance of four synthetic stormwater tests (with/without chloride and with/without hydroxyl radical scavenger) was plotted (together with the controls) for comparison.

Images taken by Optical Microscope, Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), and Energy Dispersive X-ray (EDX) detector were compared only qualitatively.

RESULTS AND DISCUSSION

Performance study using synthetic stormwater

The change of the *E. coli* levels over operational time for all tested configurations was plotted in Figure 1. A linear decay of disinfection was observed for most configurations; e.g. Figure 2-left shows an example of the observed decay kinetics for an applied current of 0.75 mA/cm^2. This was different from a traditional exponential decay kinetics reported in most wastewater ECO disinfection studies[25, 41-42]. The disinfection kinetics of synthetic stormwater did not follow the model proposed for wastewater by Galvez et al[40] (Equation (1)). A typical shoulder kinetic described in this model was not observed in the measured results. This may be due to the low level of organic matter (TOC=3mg/L) in pre-treated stormwater, where the oxidants produced from ECO could be more efficiently used for deactivation of microorganisms than in the case of wastewaters that have much higher organic content.

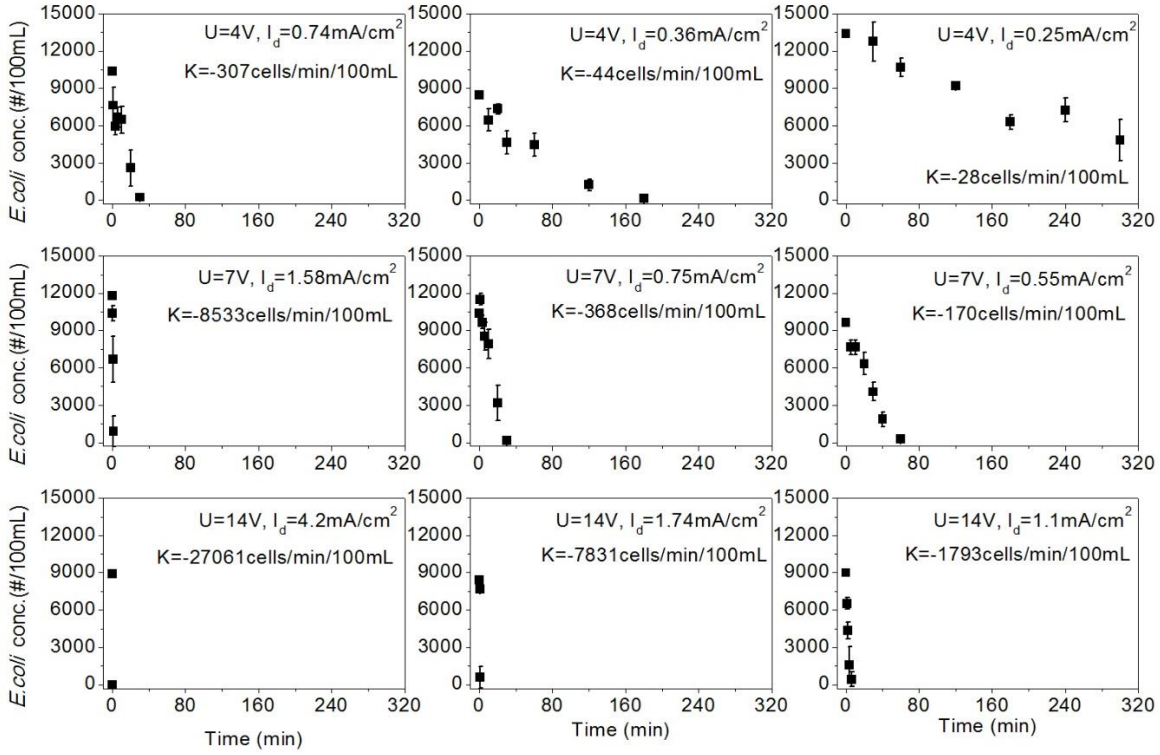
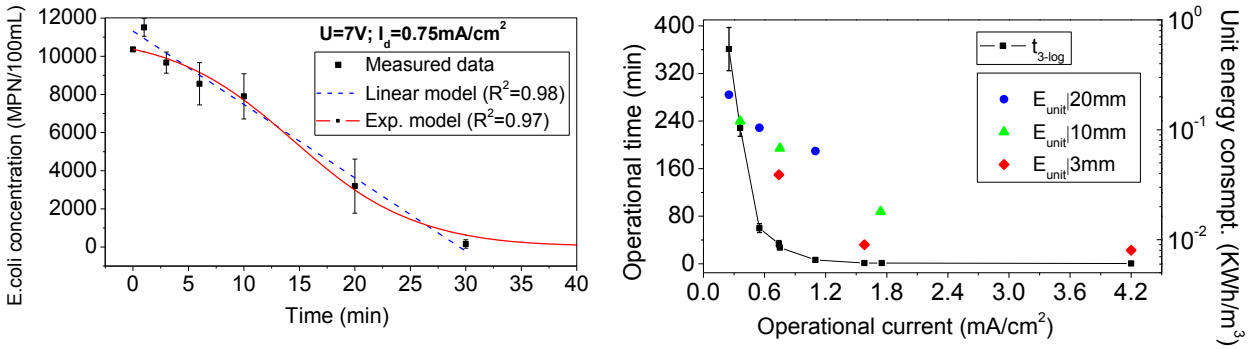


Figure 1: *E. coli* concentration (#/100mL) with operational time for all synthetic stormwater ECO performance tests (***K*** is the average decay rate of the three configuration replicates).



(a) (b)

Figure 2: Linear and Galvez's models of the measured disinfection decay for voltage of 7 V and current of 0.75 mA/cm^2 (a). Operational time ($t_{3\text{-log}}$) and unit energy (E_{unit}) needed to achieve a 3-log reduction of *E. coli* in synthetic stormwater as a function of the current density and electrode distance (b).

There was no difference ($p<0.01$) between the performance of 4V & 3mm and 7V & 10mm configurations (Figure 1). Since both configurations had the same current density, it is suggested that

concentration polarisation does not have a significant effect even when the electrode distance was the smallest (3mm). Due to the low Electricity conductivity of stormwater, minimum possible electrode distance is preferred in future practice to ensure energy efficiency. When the current was very low (0.25 mA/cm^2), the linear decay rate *K* was only 28 cells/100mL/min, almost the same as the decay rate of the control that had no current supplied. Under the highest testing current density of 4.2 mA/cm^2, total disinfection was achieved within the first 20 seconds, corresponding to a rapid decay rate of 27,061 per 100 mL/min.

A clear correlation was found between operational time to achieve 3-log reduction and the operational current (Figure 2-right). The unit energy consumed to achieve a 3-log reduction of disinfection decreased with an increase of the current (Figure 2-right). This is a surprising finding since the results from published wastewater ECO studies suggest a reverse trend; i.e. the consumed unit energy increases with an increase in the current[16]. This is discussed further in the section below.

The mechanism of ECO disinfection of stormwater

ECO did not perform any disinfection in the chloride free synthetic stormwater during both low and high currents (Figure 3 - top). In contrast, disinfection performance of the original synthetic stormwater (that contained Cl=9 mg/l) was good, replicating the decay observed in the above synthetic stormwater performance study. The results suggest that ECO in stormwater is driven by chloride ions, although the water contains chloride levels well below the previously tested concentrations of 160-10,000 mg/L in wastewater and surface water applications[24-27, 43-44].

The presence of hydroxyl radical scavenger (t-BuOH) did not influence the disinfection performance (Figure 3 - bottom). This is a confirmation of the findings presented in the literature on DSA applications to wastewater[21]. Therefore, it was shown that the high levels of ferrous iron in the stormwater did not play any role in the disinfection (opposite to our speculation).

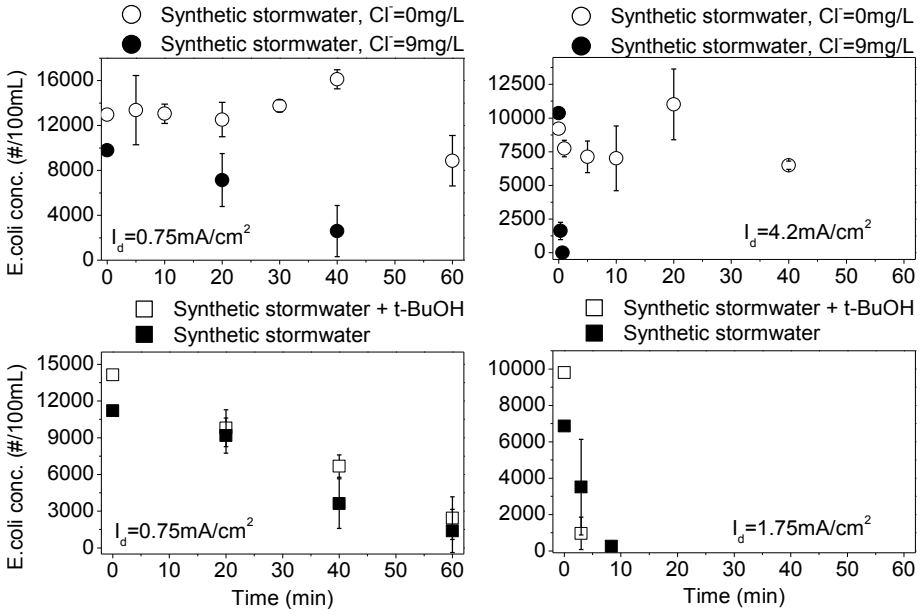


Figure 3: Impact of the presence and absence of the chloride on E. coli concentrations over time for low current (top left), and high current (top right); Impact of hydroxyl radical scavenger on E. coli concentrations over time under low current (bottom left) and high current (bottom right).

The above results suggest that for typical stormwater, chlorination is the key mechanism of *E. coli* disinfection; i.e. the ECO system can utilise very low concentrations of the present chloride for active chlorine production. However, we did not fully confirm this finding since we were not able to detect any active chlorine at the end of the control tests where no *E. coli* was added to stormwater; e.g. free chlorine was always below the detection limit of 0.02 mg/L at the end of control experiments with no spiked *E. coli* even under the highest testing current of 4.2 mA/cm^2 ($t_{3\text{-log}}$=0.33min). This was surprising since the calculation based on the chlorine contact time (CT) curve developed by White et al[45] would suggest that the required active chlorine concentration (as hypochlorous acid) to achieve 2 log inactivation of *E. coli* under the same condition (t_2-log=0.33 min, pH=7) should be at least 1.2 mg/L. We can only hypothesise why this is the case; it could be simply that White's CT curve cannot be applied to stormwater that has very low Cl concentrations.

It appears that there may be some differences between ECO disinfection mechanisms in stormwater in comparison to wastewater. It is hypothesised that in a wastewater environment, high

concentrations of chlorine are generated (due to high initial Cl concentrations). The disinfection reaction is limited by the interaction between the microorganism and free chlorine.[16]. This, therefore, slows an increase in the disinfection rate with an increase in current[16]. In contrast, the chlorine production is limited in stormwater (due to low Cl levels), so all the produced free chlorine will be rapidly taken up by microorganisms or organic compounds close to the anode (before it dissolves into the bulk solution). In this case, the reaction rate is limited by the chlorine production rate only. Increasing the current facilitates chlorine production to achieve a high reaction efficiency.

From Figure 4, that shows the TEM image of *E. coli* in untreated (a and b) and treated (c and d) synthetic stormwater, it is clear that the morphology of cell membranes changed significantly after ECO treatment. For example, the outer membrane became rough and wrinkled after the treatment, while cavities were formed inside some cells. This indicates that cytoplasmic membrane of these Gram negative bacteria was compromised[46]. According to previous studies, active chlorine can attack the phospholipid molecule existing in the bilayer system causing consequently increased membrane permeability[47]. The further attack leads to a fully damaged cytoplasmic membrane in which the exchange between intracellular and extracellular material will occur[15]. However, this was not directly seen from the TEM images. The cavities and fibrils formed on disinfected *E. coli* cells indicate the possible damage of DNA and intracellular material [48].

The fluorescent dying tests showed that, in untreated stormwater, there was almost no PI stained cell, although there were lots of DAPI stained *E. coli* (Figure 5-top). This means that almost all present *E. coli* in the untreated stormwater were intact. In the treated stormwater, the presence of both DAPI and PI stained cells was observed (with almost similar numbers), meaning that the majority of present *E. coli* were dead because of membrane damage. This confirmed the findings from the TEM images.

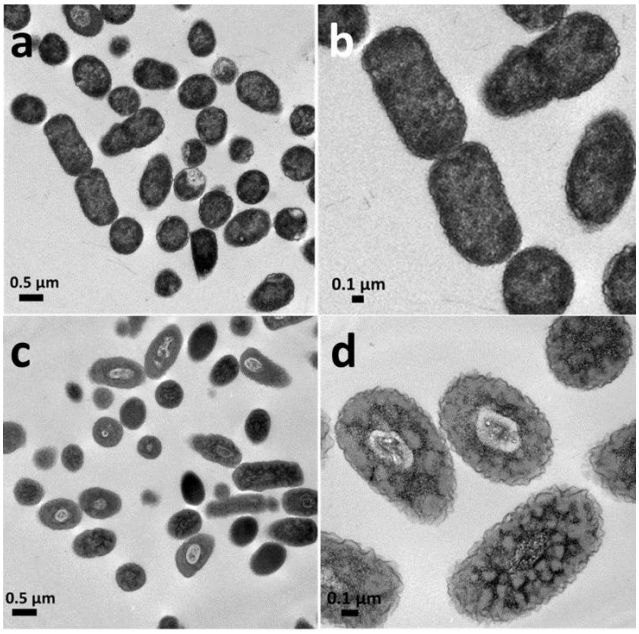


Figure 4: Transmission Electron Microscope image of *E. coli* in untreated synthetic stormwater (a and b) and in the same water after ECO treatment (c and d) (black sunken presenting on the cell surface represents a low electron density region).

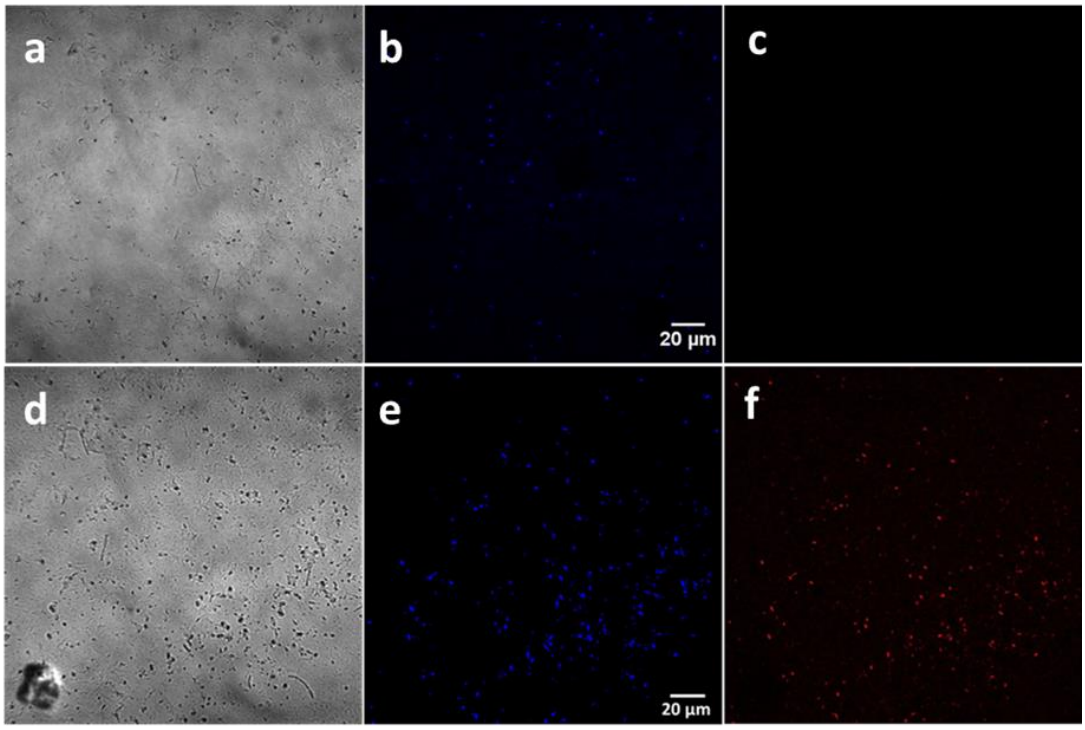


Figure 5: Optical microscope image of *E. coli* in synthetic stormwater: bright field of untreated *E. coli* (a), untreated *E. coli* stained with DAPI (b), untreated *E. coli* stained with PI (c), bright field of treated *E. coli* (d), treated *E. coli* stained with DAPI (e), and treated *E. coli* stained with PI (f).

Durability of the anode

During the first 8-10 h of cumulative operation (i.e. total usage time), no drop in the anode performance was observed. However, a rather sharp decrease of their performance was noticed with further usage; e.g. $t_{3\text{-log}}$ that was initially equal to 15 and 2 mins at the current densities of 0.75 mA/cm2 and 1.75 mA/cm^2 (respectively), increased to 40 and 11 mins (respectively), after approximately 20 hours of the anode use. It was also clear that the performance drop was more significant under lower current densities.

Scanning Electron Microscope (SEM) images of the new and used anodes explained this drop in performance (Figure 6). An image of a new anode showed a relatively even distribution of three functional doping elements - Titanium (Ti), Iridium (Ir), and Ruthenium (Ru) - across the surface (Figure 6a). The surface morphology of the anode changed significantly after approximately 20 h of operation, as indicated by non-uniform electron reflection from the sample surface (Figure 6b and Figure 6c); e.g. bigger cracks were formed on the surface. Element composition results from Energy Dispersive X-ray Detector (EDX) revealed a considerable reduction of the relative percentage of Iridium and Ruthenium on the sample surface. Also, some elements, which were not present on unused samples, were discovered on the used anode surface (such as Aluminium and Silicon).

Polarisation is one of the common reasons causing deterioration of DSA anodes, which is reflected by an increase in cell voltage during its operation[49]. However, the increased cell voltage was not observed in this study, suggesting that alternative mechanism may exist for the anode deterioration. Stormwater has very low concentration of chloride, which leads to an oxygen evolution dominated reaction across the anode surface. Fierro et al.[50], who performed an anode oxygen evolution study (using isotope oxygen in metal oxide coating of anode surface), detected the isotope oxygen from the oxygen gas produced from the anode surface; i.e. they suggested that oxygen gas was produced through a replacement of oxygen elements of the metal oxides by oxygen from water molecules. It is hypothesised that the dominant oxygen evolution process occurring on the anode in

stormwater will cause more rapid damage on the surface compared to ECO applications to wastewater, where oxygen evolution is negligible.

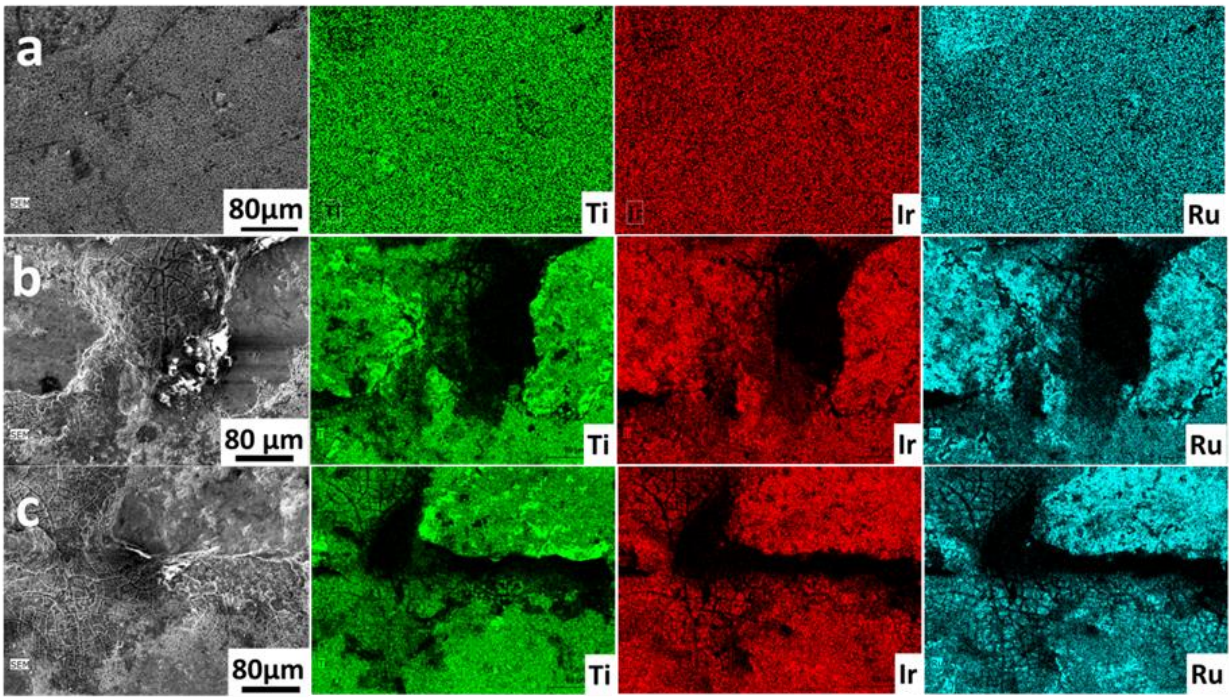


Figure 6: Scanning Electron Microscope (SEM) images and functional surface doping element distribution of an unused DSA anode sample (a) and two used (for approximately 20 h) DSA anode samples (b, c).

Preliminary validation using real stormwater

The collected stormwater samples from different sites had very different initial electricity conductivity, so to achieve the same current density of 1.75 mA/cm^2, different voltage had to be applied to each water sample (Table 1). Disinfection below the detection limit of both indigenous *E. coli* and Total Coliform was achieved after 5 mins for the Monash University Carpark biofilter sample, while approximately 15 mins were needed for the Troup's Creek wetland water. There was a small drop in performance with an increase in Cl^- levels; Troup's Creek wetland outflow had chloride concentration of 200 mg/L compared to the Monash biofilter of only 9 mg/L. This could be attributed to the higher total organic carbon (TOC) levels in Troup's Creek water in comparison to Monash samples, which could have caused competition with microorganism for the uptake of free chlorine. For example, high TOC levels were the reason that Cho et al. (2014)[24], who used DSA anode to treat

domestic wastewater with extra addition of 1860 mg/L chloride, achieved 3 log reduction of faecal *coliform* after a very long time (3 hours at the operational current density of 2.09mA/cm^2). ECO was not able to disinfect stormwater from the Clifton Hill biofilter, which contained only 2 mg/L of chloride. Clifton Hill sample had the lowest electric conductivity compared to other two samples. The chloride concentration was only 2 mg/L, which is significantly lower than the synthetic stormwater or samples from other two catchment sites. Other parameters in Clifton Hill sample that may have an impact on the treatment performance, such as pH, TOC, were comparable to other two catchments. In addition, the aforementioned disinfection mechanism study showed chloride plays a significant role in stormwater ECO disinfection. Therefore, it is hypothesised that the poor disinfection performance of Clifton Hill sample was limited by its low chloride concentration.

Table 1: Water properties and the *E. coli* concentrations with time of the ECO operation of stormwater samples collected from three sampling sites (the concentrations in brackets present standard deviation)

Water characteristics	Unit	**Monash car park biofilter**		**Troup's creek wetland**		**Clifton hill biofilter**	
Electricity conductivity	µs/cm	143.9		768		93.9	
Temperature	°C	13.9		12.6		16.6	
Chloride concentration	mg/L	9		200		2	
pH	-	6.6		7.6		7.1	
Bicarbonate	mg/L	63		100		30	
Total organic carbon	mg/L	3		16		7	
Test current	mA/cm^2	1.75		1.75		1.75	
Applied voltage	V	12.4		5.1		15.6	
Disinfection sampling (MPN/100mL)							
Operational time (minute)		***E. coli***	***Coliform***	***E. coli***	***Coliform***	***E. coli***	***Coliform***
0		182(38)[a]	3651(804)	75(14)	1062(71)	1079(164)	>DL[b]
5		<DL[c]	37(28)	49(7)	687(82)	903(168)	>DL
15		<DL	<DL	<DL	<DL	1002(223)	>DL
30		<DL	<DL	<DL	<DL	983(242)	>DL

[a]Mean concentrations are presented with standard deviation shown in parentheses
[b]Lower than the detection limit of 10MPN/100mL
[c]Higher than the detection limit of 24196MPN/100mL

As already outlined, Disinfection By-Products (Hvols, THMs, and HAAs) were only tested in the water originally collected from Troup's Creek, as, due to its high levels of chloride and organics, it presented the worst case scenario (out of the three sites). The tested result showed the negligible

concentration of Hvols. The concentration of THMs and HAAs were 0.015mg/L and 0.024mg/L, respectively. The Australian Drinking Water Guidelines suggest that the health concentration limits for these two compounds should be 0.25mg/L and 0.25mg/L, respectively[51]. Therefore, it was found that the DBPs in disinfected stormwater by ECO was of no concern.

CONCLUSIONS AND LIMITATIONS OF EVIDENCE

This study showed that Electrochemical Oxidation (ECO) disinfection could be used for stormwater applications. Chlorination was confirmed to the key disinfection mechanism and is similar to the main disinfection mechanism in wastewater. It was found that, although stormwater has a low level of chloride, it also usually contains low levels of organics and microorganism compared to most waste water cases, therefore ECO can operate efficiently even for low energy inputs; e.g. even in stormwater containing only 9 mg/L (the low 5th percentile chloride concentration in Australia stormwater) of the applied current of I=1.75 mA/cm^2 could very likely lead to the total disinfection of high (for stormwater) levels of *E. coli* after only 15 minutes. However, unsuccessful disinfection may occur under some extreme conditions; e.g. low chloride concentration. The threshold of these conditions should be further determined within the wider range of different physiochemical characteristics of stormwater. Untreated stormwater often has highly variable chemical properties, depending on catchment and rain characteristics[1, 52]; e.g. organic levels, total suspended solids and microorganism levels often vary considerably between catchments and different storm events[33]. This means that ECO operations need to be optimised for each catchment and that real-time control may be needed to maximise its effectiveness.

A comprehensive anode study should be performed to ensure that it maintains its effective treatment performance under the stormwater operational environment. For example, our study showed that low cost Dimensional Stable Anode (DSA) is not reliable for stormwater applications. Other types of anodes, such as Boron Doped Diamond (BDD) electrode with high oxygen evolution potential should be tested for stormwater.

One of the key weaknesses of this work is that although we have used both lab strain and stormwater indigenous *E. coli* as the indicator microorganism, it is not clear how ECO disinfection will perform for other pathogens. As the mechanism study showed that the damage to the cell cytoplasmic membrane is the key inactivation process, we could speculate that other Gram negative microbes could also be deactivated by ECO. However, it is not clear what ECO may do to Gram positive bacteria and protozoa that have thicker cell walls or protein shells[53] and can be more resistant to chlorine[54]. Future studies need to be conducted to verify the ECO effectiveness to real pathogens.

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SUPPORTING INFORMATION AVAILABLE

The schematic diagram of the set-up of stormwater ECO disinfection system is shown in Figure S1. Table S2 shows the physicochemical characteristics of synthetic stormwater matrices.

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Chapter 4: Anode material selection for stormwater ECO disinfection

Declaration by the candidate:

In the case of Chapter 4, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Conception, design of the project, experimental work, analysis and interpretation of data, drafting the paper	60%

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	**Nature of Contribution**	**Extent of contribution (%) for student co-author only**
Deletic, Ana	Experimental design and critical thesis revising	
Wang, Zhouyou	Experimental assistance, data analysis	7.5%
Zhang, Xiwang	Experimental design and critical thesis revising	
Gengenbach, Thomas	Experimental assistance, data analysis	
McCarthy, David	Experimental design and critical thesis revising	

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the student's and co-authors' contributions to this work. In instances where I am not the responsible author, I have consulted with the responsible author to agree on the respective contributions of the authors.

Wenjun Feng

November 2017

Ana Deletic (Main Supervisor)

November 2017

Chapter 4 Anode Material Selection for Stormwater Electrochemical Oxidation Disinfection

4.1. INTRODUCTION

This chapter aims to investigate the longevity of two selected anode type, Dimensional Stable Anode (DSA) and Boron Doped Diamond electrode (BDD) that have been tested for stormwater disinfection. The disinfection performance and reaction mechanism are studied under laboratory condition using synthetic stormwater. An *in-situ* accumulated operation test is conducted to assess their ongoing disinfection performance over accumulated usage. This chapter also provides an understanding of the deterioration mechanism that is observed on the tested DSA.

BDD showed comparable treatment performance, but promising durability over the accumulated operation time, compared to the tested DSA. Based on the study presents in this chapter, BDD is recommended as the anode type used for stormwater ECO disinfection.

This chapter is written in a journal paper format, it has been submitted to Environmental science & technology.

Electrochemical oxidation disinfects urban stormwater: major disinfection mechanisms and longevity tests

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ABSTRACT

Although electrochemical oxidation (ECO) has shown excellent potential for the disinfection of pre-treated wastewater, its application has not been tested on stormwater that runs off from urban surfaces. With the aim to improve the stormwater ECO design, this paper explores the major inactivation processes of stormwater ECO using both Boron Doped Diamond (BDD) and titanium Dimensional Stable Anodes (DSA). Both BDD and DSA generally showed comparable stormwater disinfection rates. The mechanism study suggested that BDD relied on both hydroxyl radical and the presence of chloride ions, while DSA disinfected stormwater mainly via the production of free-chlorine. A deterioration study, carried out at a catchment in Melbourne, showed a steady performance for BDD and revealed that DSA's performance degraded with time, likely linked to the high operational voltage required for stormwater's specific chemistry. Indeed, Scanning Electron Microscopes (SEM) and an Energy Dispersive X-ray Detector (EDX) tests confirmed elemental losses occurred on the DSA surface, together with an aluminium/silicon coating layer potentially

sourced from the stormwater's clayish sediments. Furthermore, disinfection by-products (DBPs) in electrochemical disinfected stormwater using either BDD or DSA were at least one order of magnitude lower than that of the Australia Drinking Water Guidelines. This study has further confirmed the feasibility of stormwater ECO, but the mechanism and long-term study demonstrated that careful anode selection is required as some anodes will deteriorate in stormwater matrices faster than others.

KEYWORDS

Urban stormwater, stormwater harvesting, ECO, E. coli, bacteria, human health risks

INTRODUCTION

Safe access to drinking water is a major issue in many growing urban cities around the globe[1-2]. Stormwater harvesting (collection, treatment and use of runoffs from urban surfaces), simultaneously protects downstream receiving water bodies from pollution and provides an alternate water resource to feed our urban centres[3-5]. Harvesting urban stormwater can deliver fit-for-purpose water, close to where it is generated[6]. However, treatment of urban stormwater prior to use is necessary due to its high and variable concentrations of harmful pollutants, including pathogens[7].

Biofilters have demonstrated excellent ability to remove stormwater pollutants, including sediments[8-9], nutrients[9], heavy metals[10]. Recent work has also demonstrated their capacity to sequester around 90% of some faecal microorganisms[11-13]. However, due to the high initial concentration of faecal microorganisms in urban stormwater (e.g. *E. coli: an* average of 36,000 MPN/100 mL)[14], effluent concentrations from biofilters are still too high for uses other than restricted irrigation[14]. This has become the major barrier to widespread implementation of urban stormwater harvesting systems, especially for end-users that have close human contact and require higher quality water sources (such as toilet flushing, clothes washing, etc.). Therefore, low cost, energy-efficient,

low-maintenance and environmental friendly technologies are required to further disinfect biofilter effluent prior to harvesting.

Dimensional stable anodes (DSAs) are the most common electrode for wastewater ECO[15-16]. Titanium group metals or oxides are doped on the pure titanium substrate to form an anode with high conductivity and low chlorine evolution potential[16]. Due to these characteristics, their optimum effectiveness occurs in waters that contain high chloride levels[16-21] and when insufficient chloride concentrations exist most supplement their water to achieve high efficiency[16-17, 22-23]. While DSA anodes have been extensively investigated for degradation of chemicals in wastewater, there are only a few studies that have used them for wastewater and surface water disinfection. Cho et al., 2014[23] disinfected domestic wastewater using DSA by adding an extra 1.86 g/L of chloride, achieving a three log reduction of faecal coliforms in 3 hours (2.09 mA/cm2, 3.9 V). Fang et al., 2006[24] tested the disinfection performance of bacteriophages using synthetic wastewater containing chloride concentration of 6 g/L, achieving a three log reduction in 20 minutes (21.7 mA/cm). Schaefer et al. (2015) tested ECO disinfection performance of pre-filtered aqueduct water with a chloride concentration of 118mg/L. Under current density of 2.5 mA/cm^2, a six log reduction was achieved for lab strain *E. coli* within 60 minutes of operation[25].

There has been only one study that has used DSA to disinfect urban stormwater[26], where a 3 log reduction in *E. coli* was achieved in less than 2 minutes (1.75 mA/cm^2; 10 cm^2 anode surface area and 400 mL water matrix). It is important to note that this study[26] had chloride level of only 9 mg/L, which is orders of magnitude lower than that of the wastewater ECO studies described above and is, in fact, the 5th percentile concentration found in typical urban stormwaters[14]. However, Feng et al.[26] also reported an unexpected deterioration in disinfection performance of the DSA anode used, yet the mechanisms of this deterioration were not well described or quantified.

Boron Doped Diamond (BDD) electrodes have been gaining attention in recent years due to their high oxygen over-potential that results in a higher current efficiency[27-28] for oxidation and hydroxyl radicals are able to be produced during simultaneous water hydrolysis[29]. BDD has been

recognised as more capable of removing refractory chemicals, such as benzene homologs and derivates. Furthermore, BDD has been shown to be more durable compared to most of the DSAs under different operational conditions due to the chemical inertness of its diamond coating[27].

Due to the hydroxyl radical production, existing studies showed BDD can be operated with or without the presence of chloride ion. Lacasa's experiment (2013) showed when BDD was used for ECO disinfection, 6 log reduction of *E. coli* was achieved under 25.5 mA/cm^2 in synthetic ballast water with a chloride concentration of 18.3 g/L in 3 minutes. In addition, Rajab's experiment (2015) showed BDD is even capable to disinfect chloride free water. When deionised water was used (EC=0.08 μs/cm), 6 log reduction of *Pseudomonas* was achieved in 15 minutes under the operational current density of 167 mA/cm^2. However, BDD has not been tested for disinfection of stormwater. Its effectiveness required operational conditions (e.g. operational current), and inactivation mechanism still remains unknown for stormwater applications.

With the aim to improve ECO design for stormwater harvesting applications, this paper explores the major disinfection mechanisms for selected DSA and BDD electrodes, alongside their durability. Two hypotheses were made: (1) DSA's major disinfection mechanism is via chlorine production while BDD is via hydroxyl radical, and (2) DSA will deteriorate at a faster rate than BDD because of BDD's higher oxygen evolution potential and hence lower oxygen production.

MATERIALS AND METHODS

Disinfection performance study

This part of the study is aimed to understand the disinfection performance of selected anodes (DSA and BDD) under laboratory-scale when synthetic stormwater and commercially available electrodes were used.

BDD electrodes are coated on both sides of silicon substrate with boron doping concentration of 2500 ppm (Neocoat Ltd., Swaziland). Titanium substrate (Ti/RuO_2+IrO_2) DSA (Suzhou Fenggang Titanium Co., Ltd. in China) was also selected for this study, because of the high chlorine production

and reasonable cost of this type of anode for wastewater treatment[15, 20, 30]. All purchased anodes have a same working dimension of 2.5 cm by 4 cm. Pure titanium mesh with the same dimensions was selected as the cathodes.

Each pair of anode and cathode was fixed to an insulating slot with a distance of 3 mm. A 400 mL glass beaker was used as a single compartment electrolysis cell. The beaker was sitting on a magnetic stirrer platform with a rotating speed of 800 rpm during the experiment. Trial experiments confirmed that there was no significant impact on the tested microorganism at this rotating speed ($p<0.01$). A DC power supply (EX-375L2, 0-60V/0-25A, TAKASAGO Ltd., Japan) was used as the power source to the electrodes. The disinfection performance of both BDD and DSA were determined under two operational current densities (1.75 mA/cm^2 and 4.2 mA/cm^2), which have been verified to be effective for stormwater disinfection in our previous study[31], to ensure the study covers more possible mechanisms (e.g. direct anodic oxidation, production of chlorine, hydroxyl radicals and other reactive oxygen species).

Synthetic stormwater was used to ensure consistency between the large number of tests that were conducted (similar approaches have been used in other studies[9, 32-33]). The stormwater was made to ensure it had characteristics of 'typical' biofilter effluent. Deionised water was mixed with natural sediment collected from a stormwater pond to achieve a total suspended solids concentration that is equivalent to a typical stormwater biofilter effluent's event mean concentration (EMCs) based on previous studies[9, 32-33]. After sampling this slurry to determine chemical properties of interest, laboratory-grade chemicals were added to 'top-up' to levels similar to biofilter effluent. All chemicals employed in this experiment were of analytical grade and purchased from Merk Millipore (Australia). These include major cations ($Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}$), anions ($SO_4{}^{2-}, HCO_3{}^{-}, PO_4{}^{3-}$), total organic nitrogen, ammonia, nitrate, and total phosphorous. The full chemistry of the synthetic stormwater is shown in Table S1. Chloride (9 mg/L) was topped up to achieve the concentration of the lower 5th percentile in untreated urban stormwater based on Australian Guidelines for water Recycling – Stormwater Harvesting and Reuse[14]. Using the 5th percentile chloride concentration ensured a

conservative understanding of its feasibility in real applications. The synthetic stormwater had electric conductivity of 105 µS/cm and pH of 7.1, as is the case in typical field conditions[14].

In this study, *E. coli* K1 strain (ATCC 11775) was used as an indicator for bacterial behaviour. This strain is pathogenic to most birds and was originally isolated from the natural environment[34]. Wild strains have the stronger resilience to the harsh environment compared to other commonly used lab strains (such as K12), which has lost ability to protect them from external condition changes and chemical attack[35-36]. The initial *E. coli* concentration used in this study was estimated based on the 'worst case scenario' of *E. coli* levels in effluents from stormwater biofilters; since the 95th percentile *E. coli* concentration of raw stormwater is 183,382 MPN/100mL[14, 37], and stormwater biofiltration systems could achieve on average of 1.2 log reductions[11, 38-39], the *E. coli* concentration used here was 10,000 MPN/100mL.

Three replicate electrolysis cell tests were always conducted. Each electrolysis cell contained 400 mL of synthetic stormwater. Control with no voltage supply was also tested under the same stirring rate and operational time. One sample was taken for the prepared synthetic stormwater before reaction began and five kinetic samples were taken during the reaction for each replicate. 10 mL samples were then assayed for *E. coli* concentrations using the Colilert^{TM} method (IDEXX-Laboratories). The detection range was from 10 MPN/100mL to 24,196 MPN/100mL; no value exceeded detection limit, values below the detection limit were replaced with the lowest detection limit (10 MPN/L).

Disinfection mechanism study

To determine the significance of possible chlorination to the ECO disinfection performance, chloride-free synthetic stormwater was prepared using sodium nitrate as a substitute to maintain a similar electric conductivity. Sodium nitrate was selected in this case because of its minimum impact on ECO performance[16]. In contrast, to determine the significance of possible hydroxyl radical production to the disinfection performance, stormwater was prepared with the addition of *tert*-butanol (*t*-BuOH, 0.03 M) as a hydroxyl radical scavenger[40]. The disinfection performance obtained using

these altered stormwater matrices were compared with the performance obtained using the 'typical stormwater'. The testing configuration set-up, replication, *E. coli* sampling and assaying methods are same as the methods described in the performance study above.

***In-situ*, durability study**

In order to simulate the impact of the continuous ECO operation on both BDD and DSA under real operational conditions, a pilot system was established on Melbourne's Gardiner's Creek. This creek receives untreated stormwater runoff from an urbanised catchment; the fact that it receives untreated stormwater presents a worst-case scenario for these systems. Chloride levels in Gardiner's creek were roughly 20-40 mg/L based on our monitoring data, which is on the higher side of what is typically found in stormwater[14].

Three replicates of BDD and DSA (with matching cathodes) with identical setups were placed in the same single compartment electrolysis cell. The same voltage of 14 V was applied to all systems to simulate the operation in practical conditions. Water was pumped from Gardiner's Creek into the electrolysis cell at a flow rate of 2 L per minute. The field operational study was conducted over eight intensive experimental events, with a total accumulated operational time of 31 hours.

After each *in-situ* tests, both anodes and cathodes were washed using 10 % hydrochloric acid, the disinfection performance of both BDD and DSA after each event was examined in the laboratory using the same configuration and testing methods described above in the performance study section. During the in-situ durability study, considerable cathode fouling was observed, even with the hypochlorous acid wash. This was probably due to the high hardness and complexity of the stormwater. As such, for all events after eight hours of cumulative operation, all electrodes used in the BDD and DSA systems were ultra-sonicated (10% HCl, 15 minutes followed by acetone, 15 minutes). Although this new washing method was introduced part-way through the experiment, the same washing technique was always applied to both BDD and DSA systems, allowing a relative performance comparison between BDD and DSA under the same conditions.

Characterisation of anode deterioration

To investigate the morphology and elemental distribution change due to the ongoing operation, the used and unused BDD and DSA anodes were analysed using Scanning Electron Microscopes (SEM) and an Energy Dispersive X-ray Detector (EDX). Samples were initially prepared by cutting them into adequately small sizes (5 mm×5 mm) and were washed using 0.02 M HCl in and then 97% ethanol in an ultrasonic bath for 10 minutes each. The surface morphology of BDD and DSA anodes was obtained with SEM (FEI Magellan 400 FEGSEM, FEI, America) operated at 10 Kv. Elemental distribution on BDD and DSA surface before and after the field deterioration study was obtained using EDX mapping.

X-ray photoelectron spectroscopy (XPS) analysis was also performed using an AXIS Nova spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al Kα source at a power of 180 W (15 kV × 12 mA) and a hemispherical analyser operating in the fixed analyser transmission mode. The total pressure in the main vacuum chamber during analysis was typically around 10^{-8} mbar. Survey spectra were acquired at a pass energy of 160 eV. To obtain more detailed information about the chemical structure, oxidation states etc., high-resolution spectra were recorded from individual peaks at 40 eV pass energy (yielding a typical peak width for polymers of 1.0 eV). Each specimen was analysed at an emission angle of 0° as measured from the surface normal. Assuming typical values for the electron attenuation length of relevant photoelectrons the XPS analysis depth (from which 95 % of the detected signal originates) ranges between 5 and 10 nm for a flat surface. As the actual emission angle is ill-defined for rough surfaces (ranging from 0º to 90º), the sampling depth may range from 0 nm to approx. 10 nm. Data processing was performed using CasaXPS processing software version 2.3.15 (Casa Software Ltd., Teignmouth, UK). All elements present were identified from survey spectra. The atomic concentrations of the detected elements were calculated using integral peak intensities and the sensitivity factors supplied by the manufacturer. The accuracy associated with quantitative XPS is ca. 10% - 15%. Precision (ie. reproducibility) depends on the signal/noise ratio but is usually much better than 5%. The latter is relevant when comparing similar samples.

Data Analysis

To quantify the disinfection performance, the disinfection rate was calculated for BDD and DSA after each performance test. Calculated disinfection rates were then plotted against the operational time for assessment of any performance deterioration.

Images taken by Scanning Electron Microscope (SEM) were compared only qualitatively between anode before and after use. Element composition obtained using X-ray photoelectron spectroscopy (XPS) was compared quantitatively between anode before and after use.

RESULTS AND DISCUSSION

Disinfection performance

The initial disinfection performance of BDD and DSA in standard synthetic stormwater is shown in Figure 1 (a, b). BDD and DSA achieved disinfection (below the detection limit) within 15 and 2 minutes under operational current densities of 1.75 mA/cm^2 and 4.2 mA/cm^2, respectively. The disinfection performances of these two types of anodes were comparable under these initial conditions.

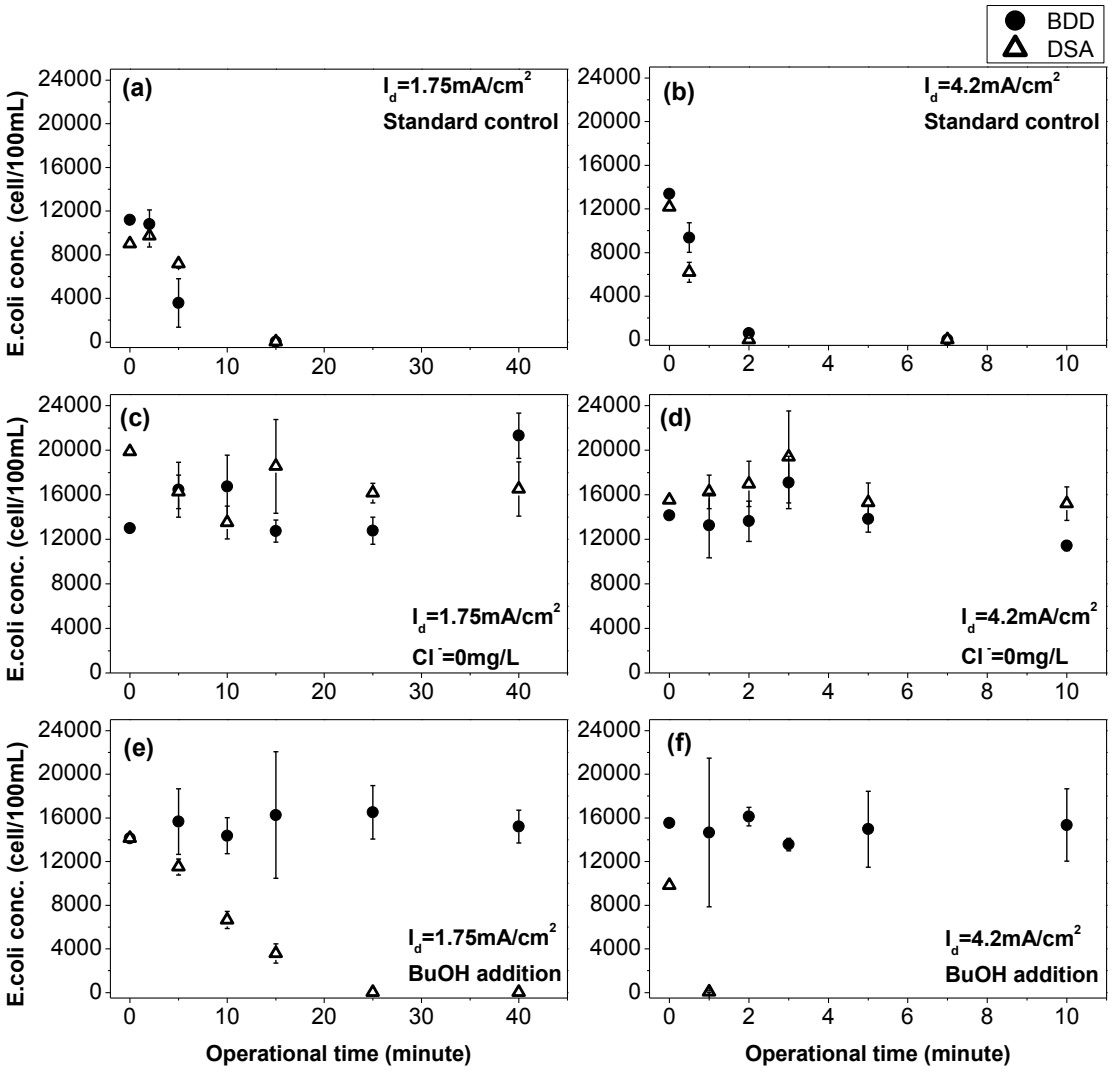


Figure 1: BDD and DSA disinfection performance with respect to different testing conditions. (a): I_d=1.75 mA/cm^2, synthetic stormwater (control), (b): I_d=4.2 mA/cm^2, synthetic stormwater (control), (c): I_d=1.75 mA/cm^2, chloride free synthetic stormwater, (d): I_d=4.2 mA/cm^2, chloride free synthetic stormwater, (e): I_d=1.75 mA/cm^2, synthetic stormwater with hydroxyl radical scavenger addition, (f): I_d=4.2mA/cm^2, synthetic stormwater with hydroxyl radical scavenger addition.

Disinfection mechanisms

For DSA, the presence of a hydroxyl radical scavenger (*t*-BuOH) did not influence the disinfection performance (Figure 1e, 1f). This may suggest that the production of effective hydroxyl radicals was not the key disinfection mechanism, which agrees with the low oxygen evolution potential of this type of anode[41]. When chloride ions were excluded from the synthetic stormwater, however, the system was unable to disinfect *E. coli* (Figure 1c, d), suggesting that chlorination was a

key disinfection pathway for DSA, agreeing with current studies on surface water and wastewater applications, where chloride concentrations were often orders of magnitude higher than that used in our stormwater study[16-18, 21, 23, 42] (e.g. 118 mg/L up to 10 g/L[16-18, 21, 23, 4216-18, 21, 23, 4216-18, 21, 23, 4216-18, 21, 23, 4216-18, 21, 23, 4216-18, 21, 23, 4216-18, 21, 23, 4216-18, 21, 23, 4216-18, 21, 23, 4216-18, 21, 23, 4216-18, 21, 23, 42] compared to just 9 mg/L in the synthetic stormwater). The similar effectiveness that was obtained for both low-chloride stormwater and high-chloride wastewater could be linked to the relatively lower microbial and organic compound concentrations in stormwater. Importantly, no free chlorine was ever detected at the end of our disinfection tests, even under the highest testing current of 4.2 mA/cm^2 (detection limit=0.02 mg/L). The reason might be that the produced free chlorine was quickly consumed in the system.

In contract with DSA, the disinfection performance of BDD used for stormwater relied on both chloride presence and hydroxyl radical production (Figures 1c, 1d, 1e and 1f). Because of the low electric conductivity of stormwater and our efforts to keep this as a low-energy technology, the highest operational current density used here was 4.2 mA/cm^2. This was significantly lower than the current densities applied in most previous BDD disinfection studies[41, 43-44], and hence this study was likely to have low hydroxyl radical generation. Because of the poor chlorine evolution ability of BDD electrodes[15, 22], the chlorine production from the anode surface was also limited. It was hypothesised that the observed disinfection performance in BDD system was due to a synergy that occurs between chloride presence and hydroxyl radical production. Indeed, higher oxidative state chlorine free radicals (CFRs) could be formed through the reaction between hydroxyl radical and chloride ions[45-49]. Yu et al.[49] described the formation of different CFRs including hydrochloric radical anion ($ClOH^{\cdot -}$), chlorine radical ($Cl^{\cdot}$) and dichloride radical anion ($Cl_2^{\cdot -}$) through a series of subsequent reactions (Equations 1-3). Furthermore, De Moura et al.[45] also showed the production of chlorine monoxide radicals through the reaction between hydroxyl radicals and chloride (Equation 4).

$$OH\bullet + Cl^- \rightarrow ClOH\bullet^- \ (k = 4.3 \times 10^9 M^{-1} S^{-1}) \qquad (1)$$

$$ClOH\bullet^- + H^+ \rightarrow Cl\bullet + H_2O \ (k = 3.2 \times 10^{10} M^{-1} S^{-1}) \quad (2)$$

$$Cl\bullet + Cl^- \rightarrow Cl_2\bullet^- \ (k = 7.8 \times 10^{9} M^{-1} S^{-1}) \quad (3)$$

$$OH\bullet + Cl^- \rightarrow OCl\bullet \quad (4)$$

However, further studies should be conducted to confirm the suggested mechanisms.

***In-situ*, durability study**

Figure 2 shows the disinfection performance of the two anodes over the *in-situ* accumulated time of usage (N.B. y-axis is a disinfection rate). Over 31 hours of usage, BDD showed no obvious performance deterioration. The slight decrease in performance that occurred near the 8th hour was possibly due to the carbonate fouling observed on the cathodes. After applying the new washing method, the performance of BDD recovered and remained relatively stable. This was expected since BDD is well known for its high oxidation ability[18, 50], high current efficiency[16] and its proven durability under multiple operational conditions[15-16, 29, 41].

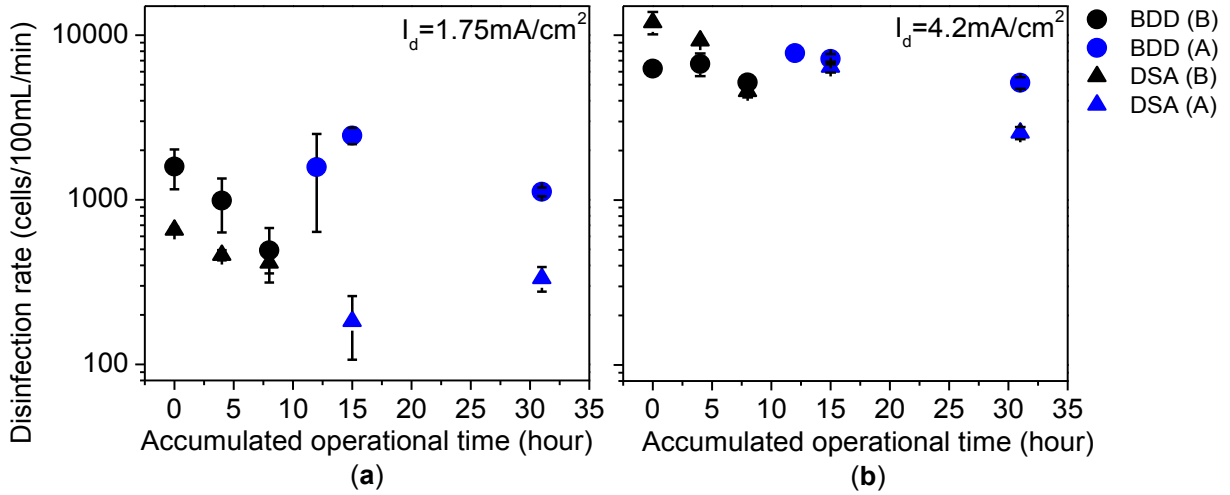


Figure 2: Disinfection rate change of BDD (B: before changing the washing method; A: after changing the washing method) and DSA (B: before changing the washing method; A: after changing the washing method) over accumulated operational time. (a): testing current density I_d=1.75mA/cm^2, (b): testing current density I_d=4.2m/Acm^2

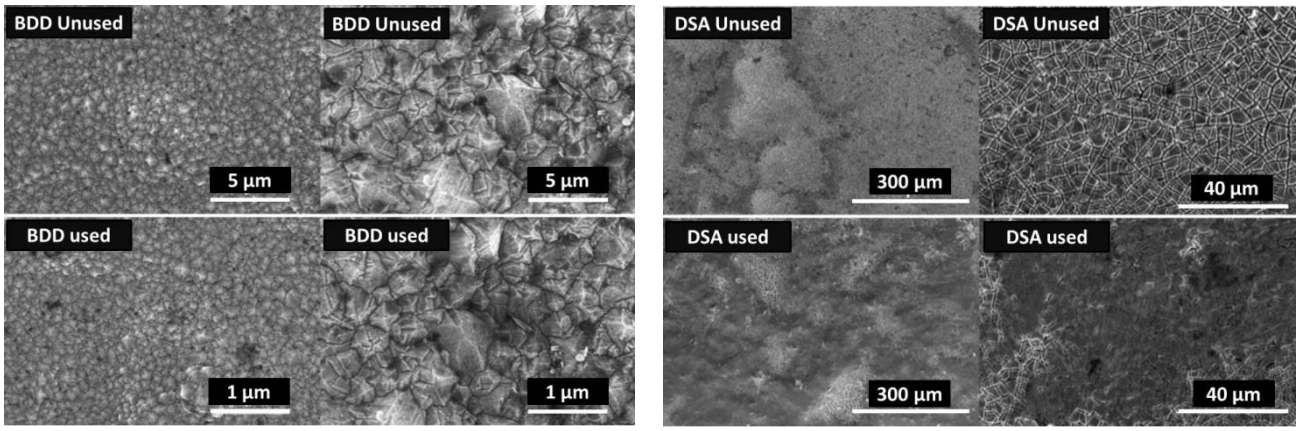
In contrast, the washing methods did not improve the disinfection performance of DSA after the 8th hour, and its performance deteriorated almost constantly with time. In fact, the deterioration

mechanism of DSA has been studied previously[15-16, 51]. Metal oxide coating membrane was getting passivated through the increasing of its resistance. This is usually caused by long-term operation and will be accelerated by the high operational current, polarity reversal, etc. Consequently, the increase of the coating resistance increases the cell voltage, and hence the energy efficiency reduces. Interestingly, in our experiment, obvious cell voltage increase was not observed. The performance deterioration still occurred even when the testing operational current was fixed at its initial value. This suggested a possible different deterioration mechanism of DSA used in our study compared to the previous studies[15].

DSAs have been developed for water treatment mainly relying on its chlorine production. In previous studies, DSA were commonly studied for wastewater treatment, which has high electric conductivity and high chloride levels[16]. In those cases, effective chlorination could be achieved under a small operational voltage (normally around 2-4 V)[23, 45]. However, comparing to most wastewaters, stormwater has much lower electric conductivity (often around 100 µS/cm) and chloride concentration (C_{50}=11 mg/L)[14]. As such, in stormwater, the applied voltage needs to be significantly increased to achieve an adequate operational current which can utilise chloride ions for effective chlorination. Furthermore, because of the increased applied voltage and low chloride ions, dramatic oxygen evolution is capable at the anode surface. Although it appears that sufficient chlorine was able to be produced through this process, the DSA, in this case, was working under an oxygen evolution dominated environment. Based on Fierro et al.'s findings[52], it is hypothesised that the rapid and dramatic oxygen exchange occurring between the water/coating interface under stormwater operational conditions will cause damage to the metal oxide structure, thereby reducing its effectiveness under long-term stormwater operational conditions.

Characterisation of anode deterioration

As shown in Figure 3(a), there was no visualised difference between the initial and the used BDD. Its unanimous electron reflection and well-defined diamond crystals were well maintained. In contrast, after 31 hours of accumulated usage, the surface of DSA showed significant morphology change (Figure 3b). Nonuniform electron and dark reflection became more obvious on the deteriorated samples, this indicated change of the surface composition and decrease of the conductivity in some regions. The images also showed the unused DSA's uniform and well defined sharp edge cracks distributed; a characteristic of most DSAs, formed during the cooling process after thermal deposition of oxide coating[53] and can increase effective catalyst surface area[54]. However, on the deteriorated sample, these characteristics have "weathered" indicated by the fuzzy and dark surface, suggesting either pealing of the surface coating or surface fouling by weak conductive materials. This potentially confirmed the results observed in the accumulative usage study.



(a) (b)

Figure 3: SEM images of BDD (a) and DSA (b) before and after 31 hours operation.

To further investigate the "weathering" effect, EDX was applied. The commercially-acquired titanium substrate DSA was coated with two main functional metal oxides (RuO_2, and IrO_2), as detectable by EDX (Figures 4 and 5). Interestingly, the signal intensities of Al and Si increased significantly on the deteriorated samples (Figure 4) and both Al and Si had high intensities in regions where the doping elements' relative concentrations reduced (Figure 5). Importantly, the even distribution of aluminium and silicon showed on the unused anodes in Figure 5 simply implies an

even distribution of these elements which could be background noise. Collectively, these results suggest fouling of Al and Si onto the catalyst surface, potentially sourced from the aluminosilicate found in the clayey sediments of urban stormwater (indeed, sediments exist in both the synthetic waters and Gardiner's Creek waters). The attachment of this substance to the anodes seems to be quite robust, withstanding ultra-sonication in hydrochloric acid and acetone exposure. It is hypothesised that the attachment of the aluminosilicate was enhanced when severe oxygen evolution causes damage to the original metal oxides lattice. In that case, "weathered" metal oxides containing defect may act as a good substrate for the fouling.

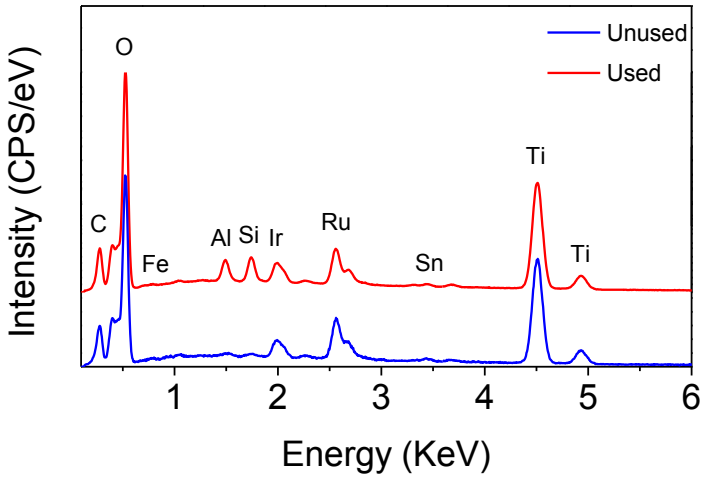


Figure 4: Energy Dispersive X-ray (EDX) mapping spectrum of the deteriorated (red) and unused (blue) DSA surfaces.

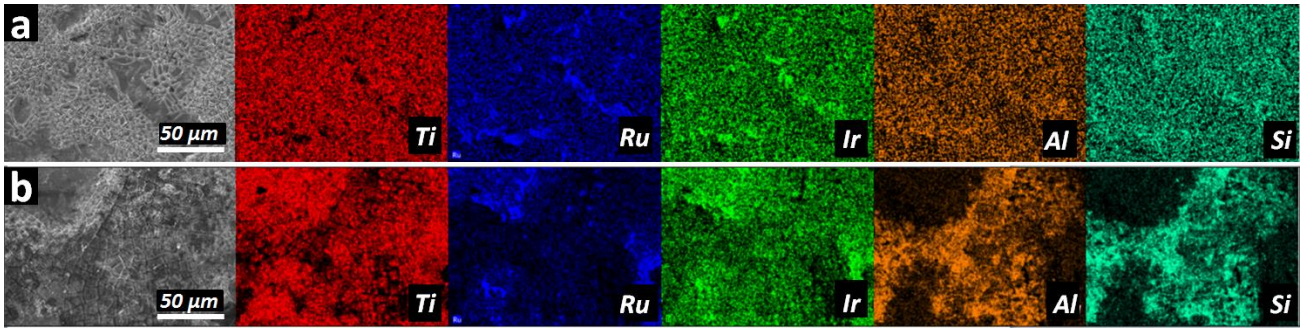


Figure 5: Energy Dispersive X-ray (EDX) mapping image of the used (a) and unused (b) DSA surfaces.

The EDX results were confirmed by XPS (Table 1), demonstrating higher relative levels of Al, Si and O on the used electrode and reduced relative levels of Ti, Ru and Ir. The binding energy values measured for the Al 2p and Si 2p peaks (ca. 75 eV and about 103.5 eV respectively) clearly indicate that those two elements are present as alumina and silica (or aluminosilicate), confirming the EDX findings.

Table 1: Elemental composition (atomic concentrations %) of unused and deteriorated DSA, as determined by XPS. Mean values (+/- deviation) are based on measurements at two different locations on each electrode.

Element	DSA unused		DSA used	
	% of atom number		% of atom number	
	Mean	*Dev*.	Mean	*Dev*.
O	51.95	0.34	55.56	0.28
Ti	21.65	0.04	16.06	1.14
Ru	1.26	0.05	0.94	0.02
C	21.61	0.45	18.77	0
Sn	0.61	0.01	0.52	0.02
N	1.51	0.07	1.29	0.02
Ir	0.44	0.01	0.31	0.01
Fe	0.41	0.06	1.11	0.04
Cl	0.21	0.04	0.21	0.01
Si	0.34	0.04	3.42	0.65
Al	0	0	1.81	0.27

CONCLUSIONS

This paper confirmed that ECO is a promising disinfection technique for stormwater applications. The lab mechanism and *in-situ* durability studies demonstrated that careful anode selection is required. By comparison, BDD and DSA had different disinfection mechanisms. A

synergy between chloride ions and hydroxyl radical production was required for the effective disinfection performance using BDD. This is possibly explained by the low operational current supplied where partial hydroxyl radical production is insufficient for effective disinfection. In contrast, disinfection using DSA solely relied on the presence of chloride ions, because of its high chlorine production capability. DSA showed gradual deterioration over the accumulated usage where BDD performed consistently over 31 hours of accumulated usage. The deterioration of DSA was believed to be caused by the rapid oxygen exchange on the anode surface under stormwater operational conditions. Under this condition, the high operational voltage and low chloride ions resulted in severe oxygen evolution, which caused damage to the catalyst surface. Using EDX and XPS, fouling was observed on the deteriorated DSA surface, originating from the aluminosilicate that exists in stormwater. This fouling was hypothesised to be enhanced by the surfaced weathering caused by server oxygen evolution under stormwater operational conditions.

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Chapter 5: Performance validation of ECO stormwater disinfection using BDD Anode

Declaration by the candidate:

In the case of Chapter 5, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Conception, design of the project, experimental work, analysis and interpretation of data, drafting the paper	65%

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of Contribution	Extent of contribution (%) for student co-author only
McCarthy, David	Experimental design and critical thesis revising	
Henry, Rebekah	Experimental assistance, data analysis	
Zhang, Xiwang	Experimental design and critical thesis revising	
Deletic, Ana	Experimental design and critical thesis revising	

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the student's and co-authors' contributions to this work. In instances where I am not the responsible author, I have consulted with the responsible author to agree on the respective contributions of the authors.

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November 2017

Ana Deletic (Main Supervisor)

November 2017

Chapter 5 Performance validation of ECO stormwater disinfection using BDD Anode

5.1. INTRODUCTION

This chapter presents a validation study to access the reliability of applying ECO technology, that has been tested and optimised using laboratory studies discussed in Chapters 3 and 4, for field conditions. ECO disinfection performance of indigenous *E. coli* and the consequent disinfection by-product (DBPs) were tested from real stormwater collected from different catchment sites across Melbourne. The ECO disinfection performance on other microbe species (*Enterococci*, *Campylobacter* and *C. perfringens*) was also tested through the spiking tests.

The results showed total disinfection of indigenous *E. coli* was achievable for all collected stormwater samples after only 30 mins. Higher initial stormwater chloride concentration resulted an increased disinfection rate. DBPs (total halogenated methanes and haloacetic acids) tested from treated stormwater were below the Australian Drinking Water Guideline value for health. Stormwater samples with higher pH value yielded more DBPs. Besides *E. coli*, total disinfection was also achieved for all the other microorganisms.

The work done for this chapter is presented in paper format. This paper will be submitted in Environmental science & technology in a near future.

Electrochemical Oxidation for stormwater disinfection: How does real stormwater chemistry impact on pathogen removal and disinfection by-products level?

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ABSTRACT

Preliminary laboratory work has shown that Electrochemical Oxidation (ECO) is a promising technology for disinfection of harvested stormwater. This paper focuses on understanding how stormwater chemistry (that can vary substantially between sites) may impact the disinfection performance of ECO. We collected stormwater samples from 4 different urban catchments and tested the ECO performance of stormwater pathogens using a Boron doped diamond (BDD) anode. The applied current density was 4.2 mA/cm^2. Results showed that total disinfection of indigenous *E. coli* was achievable for all the tested stormwater within 30 minutes. Total disinfection was also achieved for *Enterococci*, *Campylobacter* and *C. perfringens* after 30 minutes. Most importantly, higher initial stormwater chloride concentration resulted an increased disinfection rate. Disinfection by-products (DBPs) in the

treated stormwater were well below the Australian Drinking Water Guideline values. It was noted that stormwater samples with higher pH value yielded more DBPs.

1. INTRODUCTION

Stormwater, that is runoff from urban surfaces, is one of the major sources of pathogens in urban estuaries and coastal areas[1-3]. Stormwater is also a valuable source of freshwater in drought challenged cities. Stormwater treatment for environmental protection and harvesting for human use is often practiced as a part of Water Sensitive Urban Design (WSUD)[4-5] or Low Impact Design (LID)[6]. WSUD stormwater systems can reduce the level of pathogens in stormwater; e.g. stormwater biofilters (also known as raingardens or bioretentions) could provide around 1 log reduction of key microorganisms [7-8]. Unfortunately, even the best performing WSUD systems can only deliver water of acceptable quality for irrigation-based end-uses, and additional disinfection is needed for any other end-uses[9]. Lack of effective, low-cost, and low-maintenance disinfection systems has limited adoption of stormwater harvesting[10]. One such disinfection technology that has not been widely tested for stormwater applications is Electrochemical Oxidation (ECO)

ECO has been well studied for chemical removal[11-14] and to some extent for microbial disinfection[15-17] of different wastewaters. Cho et al. (2014)[16] investigated ECO for treatment of domestic wastewater that contained between 0.8-7.8 $\times 10^5$ CFU/100 mL of total coliform (and added chloride to 1.86 g/L), using multiple metals doped Titanium anode (Dimensional Stable Anode – DSA). Under the current density of 2.09 mA/cm^2 (3.9 V), they managed to totally disinfect the wastewater within 3 hours. Lacasa et al. (2013)[18] used Boron Doped Diamond (BDD) anode and the current density of 25.5 mA/cm^2 for disinfection of synthetic ballast water with a chloride concentration of 18.3 g/L, achieving 6 log reduction of *E. coli* within 3 minutes. They were also successful in disinfecting the same water even without chloride presence. Rajab et al.[19] tested the disinfection performance of *Pseudomonas* in deionised water (that had an

electric conductivity of 0.08 µS/cm) using a BDD anode. Without the assistance of chloride and under a very high operational current density (167 mA /cm^2), they achieved 6 log reduction of *Pseudomonas* after only 15 minutes, claiming that this was due to high hydroxyl radical production. In conclusion, effective ECO disinfection could be achieved by either free chlorine (when high chloride concentration is present)[13, 17, 20] and/or by hydroxyl radicals (when high operational current is used)[19-21].

Stormwater has very different chemistry compared to the above wastewaters. Firstly, it has very low chloride level; e.g. Event Mean Concentration (EMC) of 11 mg/L with a standard deviation of 1.05 mg/L has been recorded in an Australian study[9]. This could limit free chlorine production through chloride oxidation. Stormwater has also very low electric conductivity normally from below 100 to a few hundred µS/cm[22-25], which may mean that very high operational voltage must be used (generally greater than 10V, depending on the system configuration and stormwater EC). However, these are only speculations since there are very limited studies on disinfection performance of ECO for stormwater[26].

Our team conducted some of the first studies on ECO stormwater disinfection using both commercial DSA (Ti/RuO_2+IrO_2) and BDD anode. Both anodes showed comparable promising disinfection performance, but unfortunately, the selected Ti/RuO_2+IrO_2 anode deteriorated very quickly (stopped functioning after 20 h of operations). To date, the ECO disinfection has only been tested using lab strain *E. coli* and mainly synthetic stormwater, while its performance for real stormwater still remains unclear (especially under different stormwater chemistry). This is a problem, since *E. coli* may be a poor indicator microorganism, because of its low resistance in disinfection[26-27] and low correlation to pathogens found in natural water systems[28-29].

This paper presents the results of the first study that examined the impact of stormwater chemistry on indigenous *E. coli* disinfection and disinfection by-products (DBPs). It also

validates ECO disinfection performance on the following stormwater pathogens: *Enterococci*, *Campylobacter* and *C. perfringens*. Three initial hypotheses were tested: (i) Disinfection performance is dominated by chloride concentration; (ii) DBPs in treated stormwater is positively correlated to the chloride, total organic carbon (TOC) and ammonia concentration in stormwater; (iii) ECO disinfection is effective in removal of the three tested stormwater pathogens. The first and the last hypotheses were confirmed, while only pH was found to be significant to DBPs levels in stormwater.

2. MATERIALS AND METHODS

2.1. Stormwater sample collection and experimental set-up

The stormwater used in the study was collected from the following four sites located in Melbourne, Australia: (1) outflow from the Clifton Hill stormwater bioretention system, (2) outflow from Banyan stormwater bioretention system, (3) Gardiner's creek stormwater drain, and (4) outflow from Troup's creek stormwater constructed wetland.

Clifton Hill biofilter, located in the north-east of the Melbourne inner area (37.790056S, 145.006501E), receives stormwater generated from a residential catchment with a total area of 7.3 ha and 39% imperviousness and provides treatment to the collected stormwater. The Banyan site is located in south-east Melbourne (35.593488S, 142.848549E). It provides treatment of stormwater from a residential catchment with a total area of 239 ha and 49% imperviousness. Gardiner's Creek receives both treated and untreated stormwater from a large urbanised catchment; it is a stormwater drainage channel located close to Melbourne's Central Business District (37.850383S, 145.050253E). The area of this catchment is 19,010 ha among which 47% of it is impervious. Troup's creek stormwater constructed wetland is located south-east of Melbourne (37.996427S, 145.290939E). It receives stormwater from a moderate size mixed land use urban catchment with a total area of 1,020 ha and 46% imperviousness.

Stormwater is further treated and harvested from the wetland's outflow pipe for irrigation and toilet flushing end-uses.

Stormwater samples were collected from the above four sites during three rainfall events on 1st May 2016, 10th May 2016 and 15th June 2016, respectively. The samples were brought back to the laboratory and were stored at 4 °C for no more than 24 hours. Sub-samples from each catchment were sent to a NATA-certified (National Association of Testing Authorities, Australia) laboratory for testing of chloride concentration, pH value, bicarbonate concentration, ammonia and total organic carbon concentration. Three replicates of each sample were then used to test ECO disinfection performance as outlined below.

Boron Doped Diamond (BDD) electrode, produced by Neocoat Ltd. (Swaziland), was selected for the study. The anode that was coated on both sides of silicon substrate with boron doping concentration of 2500 ppm had working dimensions of 2.5 cm by 4 cm. Pure titanium mesh with the same dimensions was selected as the cathode.

Three 400 ml beakers were used as reaction cells for the ECO disinfection experiment (one for each replicate). The anode and cathode were fixed into each beaker with 3mm distance apart. Each beaker was placed on a magnetic stirrer platform with a rotating speed of 800 rpm during the experiment. A DC power supplier (EX-375L2, 0-60V/0-25A, TAKASAGO Ltd., Japan) applied the same currents to three electrolysis cells (replication) at the same time (see supplementary information SF1).

2.2. Disinfection study of indigenous *E. coli*

The aim of this study was to assess the impact of stormwater chemistry on the level of disinfection of indigenous *E. coli* by the ECO. Each of the three replicated reaction cells contained 400 ml of the collected stormwater. The current density of 4.2 mA/cm^2 was applied to the 3 replicates of each stormwater sample since in our previous study we have found that this current is effective for stormwater disinfection[30]. The current was applied over pre-

determined times (i.e. operational time) without knowing the initial concentration of *E. coli*. The following approach was taken to make sure that we run experiments for enough time to complete the disinfection but not to waste resources; in the first run, a 30-minute operational time was applied for all different stormwater samples as an initial trial, and the results were used to adjust the operational time in the next run, and so on.

One 10 mL water sample was taken just before the current was applied, and 4 samples were taken during the set operational time (time between these samples varied since the operational time varied between the runs). The last sample was taken 24 hours after the ECO was finished to check if any *E. coli* regrowth occurred. The 10 mL samples were then assayed for *E.coli* concentration using the Colilert^{TM} method (IDEXX-Laboratories)[31]. Samples assayed using this method have the detection range from 10 MPN/100mL to 24,196 MPN/100mL. The level of trihalomethanes (THMs), often used for monitoring of chlorination related reaction[32], was also tested in all samples.

Historical data showed that stormwater collected from Troup's wetland has the highest chloride and organics concentration, and therefore very likely should have the highest Disinfection by-products yield. Therefore, due to budgetary constraints, production of Haloacetic Acids (HAAs) was only tested in the first experiment run for water collected from Troup's wetland; we selected to monitor both THMs and HAAs because they are the two main DBPs most likely to occur and to be of concern to health as indicated in the Australia Drinking Water Guidelines[32]. For each experiment run, treated and untreated stormwater sub-samples were sent to a NATA-certified (National Association of Testing Authorities, Australia) laboratory for testing of THMs and HAAs.

To assess the impact of chlorine production on disinfection rate, during the last experiment run of each stormwater sample, kinetic sampling was also taken for chlorine

concentration using N,N Diethyl-1,4 Phenylenediamine Sulphate (DPD) method (DR5000, HACH).

2.4. Disinfection study of stormwater pathogens

The aim of this study was to assess ECO disinfection performance on a number of microorganisms that may be present in stormwater. According to literature, the biocidal effect of free chlorine is achieved through the attack of phospholipid molecule bilayer existing in the bilayer system causing consequently increased membrane permeability. Further attack will lead to a fully damaged cytoplasmic membrane in which exchange between intracellular and extracellular material will occur[33]. *E. coli* as a gram negative bacterium without the protection of outer cell wall is directly exposed to the chlorine attack and is more sensitive to chlorination disinfection. Therefore, evaluating the ECO disinfection effect on other microorganisms such as gram positive and spore bacteria is required. For this study, besides *E. coli,* three additional microorganisms were tested for ECO disinfection performance: *Campylobacter*, *Enterococcus* and *C. perfringens. Campylobacter* is a gram negative stormwater and can be a significant human health risk (causing diarrhoea and fever)[34]. In Melbourne, it is the leading cause of gastroenteritis illnesses. *Enterococcus* is usually monitored as an indicator organism in water system to show the degree of faecal bacteria contamination. In addition, it is usually used as a typical example of Gram positive bacteria for disinfection efficiency study. Comparing to gram negative bacteria, enterococci have a polysaccharide cell wall as an outer layer resulting in a relatively stronger resistance to chlorination. *C. perfringens* is a Gram positive spore bacterium[35], and can also be pathogenic. It is sometimes used as a surrogate of protozoa[8] since they exhibit remarkable resistance to the change of habitat including high temperature, drought and chemical exposure, etc[36-37] attributed to their protein spore coating and robust structure[38].

Stormwater samples collected from all the four sites during the last rainfall event (collected on 15th of June, 2016) were first treated using gamma irradiation to inactivate any

background microorganisms. Four lab strain microbe species: *E. coli*, *Campylobacter*, *Enterococcus* and *C. perfringens* were dosed into the sterilised stormwater samples, targeting concentration of 15000 MPN/100mL, 10000 MPN/L, 3000 MPN/100mL and 1000 MPN/100mL, respectively. These target concentrations were selected to mimic levels of the micro-organisms in stormwater post WSUD treatment; they were calculated by applying the reported bioretention removal rates[8, 39-40] to the 95th percentile concentrations of these microbes found in stormwater[9]. However, for both *Campylobacter* and *C. perfringens*, the target concentrations were set to be higher than the pre-treated 95th percentile concentration because of their concentration fluctuation in culturing process and practical issues during assaying process.

The experimental set-up was the same as in the *E. coli* indigenous study (see above). Firstly, a trial experiment was carried to determine the operational time required to achieve the total disinfection of the spiked *E. coli* only, in each of the collected stormwater samples. This pre-determined time was then applied as the operational time to the stormwater spiked with all the microbes.

One water sample was also taken as a disinfection control prior to the addition of the 4 microbes. A positive spike control for each stormwater matrix was then collected to quantify microbe concertation prior to ECO disinfection test. Control and ECO treated samples were then divided into 4 sub-samples for assaying of *E. coli*, *Campylobacter*, *Enterococcus* and *C.perfringens*. The assays applied have been widely used in past studies[41]; (i) *E. coli* was assayed using the previously described Colilert method[31]; (ii) *Enterococcus* was assayed using the Enterolert^{TM} method (IDEXX-Laboratories)[42]; (iii) *Campylobacter* was assayed using the modified 11 tube (1×1mL, 2×0.1mL, 4×0.05mL, 4×0.01mL) MPN method described by Henry et al., (2015)[41], and (iv) *C. perfringens* was assayed by ALS Environmental Services (Scorsby, Victoria) using the Australian Standard AS/NZS 4276.17.1:2000.

2.5. Data analysis

To quantify the stormwater ECO disinfection performance T_{90} - the time required to achieve the first one log reduction - was calculated for all ECO tests (T_{90} was used instead of the first order decay coefficient *k* because quantification of *k* assumes a log-linear decay, yet it is well known that microbial interactions often do not follow this pattern[43]). Mean values of indigenous *E. coli* concentration (of the three replicates) were plotted against the operational time. Adjacent points on this plot were linearly connected to form a linear-step exponential curve. T_{90} was then interpolated on this curve by finding the time which corresponded to the 10% of its initial concentration.

Due to the weak normality ($p>0.05$) and limited numbers of the sample set, non-parametric Spearman's rank test[44] was used to analyse the influence of stormwater chemistry (pH, Cl_2^-, HCO_3^-, NH_3 and total organic carbon) on disinfection performance (assessed T_{90}) and levels of DBPs in treated stormwater.

To assess the disinfection performance of spiked microorganisms, their log removal performance after treatment were simply compared.

3. RESULTS AND DISCUSSION

3.1. Overall Disinfection performance

The overall disinfection performance of indigenous *E. coli* for all stormwater samples in 3 runs are presented in Table 1. Total disinfection was not always achieved since the pre-determined operational time was not long enough in some experiments. No *E. coli* regrowth was observed in treated stormwater samples after 24 hours.

The disinfection rates of indigenous *E. coli* observed in these experiments were lower than the disinfection rates of lab strain *E.coli* in the synthetic stormwater[45]. This was expected due to a number of reasons. The chemical composition of real stormwater is more complex

compared to the lab made synthetic stormwater, which may have had a negative impact on the overall ECO performance. In a similar way, other microorganisms in real stormwater could have been competing for the oxidant consumption against indigenous *E. coli*, while lab strain E. coli was the only microbial spices present in the synthetic stormwater study. Finally, indigenous *E. coli* strain usually has a more robust resistance to environmental condition changes compared to the lab strain *E. coli*[46-47].

Table 1. Disinfection performance, water chemistry and disinfection by-product levels of stormwater samples in three experimental runs

Catchment for stormwater collection		First Run				Second run				Third run			
		Clifton Hill	Banyan	Gardiner's creek	Troup's wetland	Clifton Hill	Banyan	Gardiner's creek	Troup's wetland	Clifton Hill	Banyan	Gardiner's creek	Troup's wetland
Initial *E.coli* conc. (cells/100mL)		238(9%)[a]	4543(10%)	4564(20%)	382(19%)	7002(19%)	3617(42%)	11012(8%)	6787(12%)	6375(18%)	3187(16%)	7521(16%)	9001(24%)
Total operational time[b] (min)		30	30	30	30	40	12	32	4	30	12	40	8
Residual *E.coli* conc. (cells/100mL)	After operation	10(58%)	0(0%)	0(0%)	0(0%)	0(0%)	17(28%)	63(24%)	42(9%)	0(0%)	0(0%)	0(0%)	0(0%)
	After 1 day	3(141%)	0(0%)	0(0%)	0(0%)	0(0%)	0(0%)	20(71%)	0(0%)	0(0%)	0(0%)	0(0%)	0(0%)
Calculated T_{90} (min)		12.8	4.5	9.3	<X[c]	17.7	8.7	14.4	3.9	9.4	5.6	9.5	4.5
Stormwater chemistry	pH	6.7	7.0	7.4	7.5	6.9	6.9	7.5	7.3	7.2	6.9	7.9	7.6
	TOC (mg/L)	3.8	4.1	4.1	4.6	4.5	3.2	4.4	5.0	2.3	6.2	5.1	6.7
	Cl^- (mg/L)	6	35	37	110	6	6	17	63	7	34	36	120
	NH_3 (as *N*, mg/L)	<0.1	0.2	<0.1	0.2	<0.1	0.1	<0.1	0.1	<0.1	0.2	<.1	0.1
	HCO_3^- (mg/L)	29	40	46	71	41	25	41	48	51	53	72	80
Disinfection by-products	THMs[d] (mg/L)	<0.001[f] 0.003	<0.001 0.015	<0.001 0.017	<0.001 0.034	<0.001 0.004	<0.001 0.002	<0.001 0.007	<0.001 0.002	<0.001 0.004	<0.001 0.003	<0.001 0.015	<0.001 0.011
	HAAs[e] (mg/L)	N.A.[g]	N.A.	N.A.	<0.005 0.024	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.

[a] *E. coli* mean concentration of triplicates are presented with the coefficient of variance in percentage shown in parentheses

[b] Estimated before each batch of test based on previous studies, the actual total disinfection could occur before or after this time

[c] X is the time of the first, disinfection below the detection limit was achieved before the first sampling point, T90 was unable to be calculated

[d] Trihalomethanes was tested before and after treatment shown in top and bottom row respectively

[e] Haloacetic acids

[f] Values below the detection limit of the DBP test

[g] Test was not performed due to cost and practical reasons

3.2. Effect of Stormwater Chemistry on Disinfection Performance

Chloride concentration had a significant influence on the treatment performance ($p=0.017$) in all three experimental runs. T_{90} was found to be negatively correlated to the chloride concentration ($r_s=-0.697$, see Figure 1). This was not surprising since our previous study with synthetic stormwater has shown the stormwater electrochemical disinfection is limited by free chlorine production[1]. This is because the low stormwater electric conductivity restricts the available operational current as a consequence of maintaining stormwater ECO as a low energy technology. Hydroxyl radical production is insufficient for effective disinfection under this condition. The disinfection performance was achieved through synergy between both hydroxyl radical production and chlorination.

Disinfection performance of each stormwater sample in the third run and their simultaneous chlorine production was shown in Figure 2. Total disinfection of stormwater was achieved within 20 minutes even when chloride concentration was as low as 6 mg/L (in Clifton hill, Figure 2). This is an interesting finding, considering that the past wastewater ECO treatment studies were done using water samples that contained chloride concentrations between 160 and 10,000 mg/L[2-5]. Although stormwater produces far less chlorine compared to wastewater, it also contains less organic substance and lower microbial concentration, which leads to an efficient disinfection rate.

The high free chlorine production rate occurred in Troup's wetland sample was attributed to its high initial chloride concentration (120 mg/L). The first log reduction, in this case, was achieved after only 4.5 minutes (T_{90}=4.5min), as shown in Figure 2. Wetland as an alternative stormwater treatment measure very likely increased the stormwater chloride concentration because of decomposition of bio-debris through the detention process[6-7]. In comparison, raw stormwater or stormwater treated using biofilter have had much lower chloride concentrations; i.e. Gardener's Cr stormwater had 36 mg/L and outflow from Banyan biofilter had 34 mg/L of chlorine.

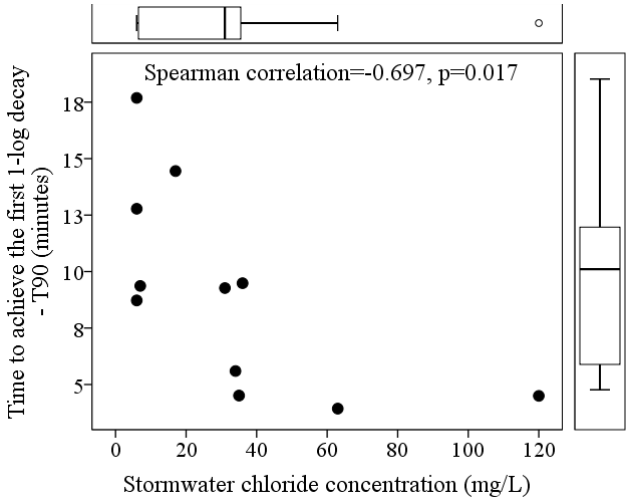

Figure 1: Correlation between T_{90} and stormwater chloride concentration (Spearman correlation)

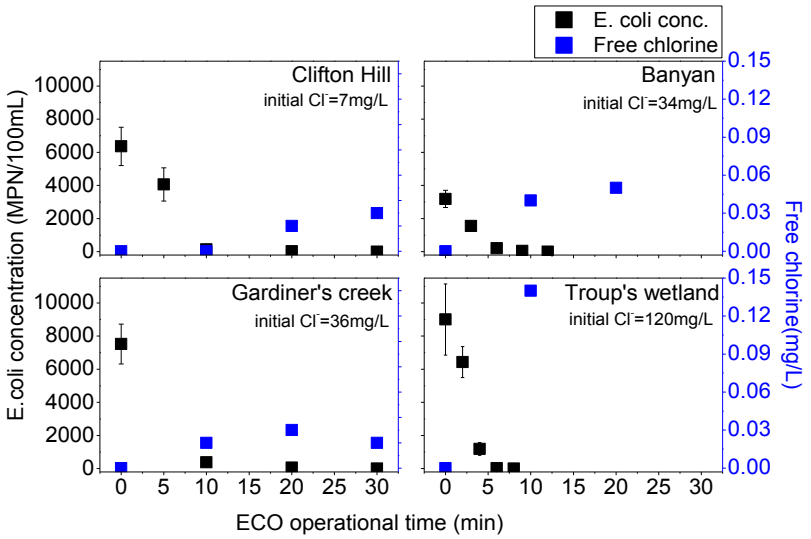

Figure 2. E. coli disinfection performance and free chlorine concentration vs. operational time: results for indigenous *E. coli* disinfection run 3 (for brevity, mean *E. coli* concentration of three replicates over operational time was plotted for the third experiment run only).

pH was found to have no statistical influence on ECO disinfection for all stormwater samples collected in the three experimental runs ($p<0.05$). This is surprising, as many of literature highlighted its significance in ECO disinfection systems. Hypochlorous acid is formed (Equation 1) when free chlorine (Cl_2) is produced in water due to electrical current. This weak acid further dissociates into hypochlorite (Equation 2). The fraction of hypochlorous acid and hypochlorite presented in solution significantly depends on the pH[8]. The percentage of hypochlorous acid increases when solution pH

decreases. As hypochlorous acid has more biocidal impact comparing to hypochlorite, chlorine related ECO disinfection is usually low pH favoured[9-11].

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \quad (1)$$

$$HOCl \rightleftharpoons H^+ + OCl^- \quad (2)$$

The weak pH dependency observed in this study could possibly be explained by the small pH range of the collected stormwater. Urban runoff is often neutral (pH_{mean}=6.9, std.dev.=0.6 and pH_{median}=7, Duncan, 1999[12]), which reduces the concern of pH impacting disinfection ECO performance.

Both total organic carbon (TOC) and bicarbonate concentration had no significance ($p>0.05$) to the resulted disinfection performance. This was also not expected, since literature states that they could compete for the chlorine or hydroxyl radical consumption with micro-orgasm and organic compounds[3, 10, 13-14]. This is possibly explained by their relatively low levels in stormwater, compared to wastewater. However, further studies which include stormwater collected from more urban catchments are needed for confirmation of this hypothesis.

3.3. Disinfection by-Products in the treated stormwater

The concentration of DBPs in the stormwater samples before and after ECO disinfection were shown in Table 1. No DBPs were detected in any collected stormwater sample before treatment. Trihalomethanes (THMs) was detected in all post-treatment samples, with the highest concentration of 0.034 mg/L being recorded in the treated Troup's creek water (the first sampling run). THMs in this study were found to be higher than the concentration tested using synthetic stormwater in our previous study[1]. This was possibly due to the complexity of natural organic matters (NOM) present in real stormwater. However, all measured DBP levels were well below the Australian Drinking Water Standard of 0.25 mg/L[15], meaning that DBPs are of no concern. It was interesting to see that in all treated stormwater samples chloroform, as a sub-division of THMs, dominates THMs. The levels of HAAs after the treatment were well below the Australian Drinking Water Guidelines of 0.24

mg/L[15] even for the first experimental run of Troup's creek water that contained the highest levels of chloride (HAAs was 0.024 mg/L and therefore 10 times below the limit).

It was hypothesised that the DBPs production in a chlorine evolution ECO system is mainly dominated by the chloride, organic compounds, and ammonia present in stormwater. Spearman's rank test however showed that none of these parameters was strongly correlated (r_s<0.4) or statistically significant (p>0.05) to the levels of DBPs in the treated stormwater. Previous studies have shown that the chlorination related DBPs were formed through multiple reaction pathways involving chlorine, natural organic matters (NOM), bromide and nitrogen compounds such as ammonia or amino acids[16-19]. Considering the results presented in the previous section, only chloroform was the main DBPs detected in treatment stormwater. This revealed low the relevance of bromide or nitrogen (either inorganic or organic) to the concern of DBPs in stormwater treated using ECO technology. The 95th percentile concentration of total nitrogen (TN) in raw stormwater generated from a typical Australian urban catchment is 7.46mg/L[20]. After biofiltration, this value could be further reduced. In addition, the ammonia concentration in collected stormwater fluctuated around the detection limit of 0.01mg/L. It is then hypothesised that the low level of brominated and nitrogen initiated disinfection by-products is explained by the low concentration of bromide and nitrogen in stormwater compared to the industrial application cases. Stormwater chloride concentration was not found to be significant (r_s=0.343, p>0.05) to the final yield of disinfection by-products. Our previous study showed the necessary operational time to achieve the total disinfection will decrease with a higher order than the increase of chloride concentration[1]. Because the time available for DBPs generation depends on the point when total disinfection was achieved. It is hypothesised that the reduced required operational time eventually compensated the impact of higher disinfection by-products production rate under the higher chlorine level.

Spearman's rank test showed a significant positive correlation between stormwater pH value and DBPs (mainly chloroform) yield (r_s=0.606, p=0.048) as shown in Figure 3. This was confirmed by other studies. Suh et al. conducted a chloroform formation mechanism study using sodium citrate

as the organic compound under the chlorination of hypochlorous acid[19]. Chloroform formation was found to be significantly higher at a higher pH solution value. Graham et al.[21] verified the formation of THMs is higher pH favoured reaction under chlorination using algae and algae-derived compound as the organic source. A study of the effect of pH ($6 \leq pH \leq 8$) on DBPs formation was also conducted by Hansen using water collected from swimming pool[22]. Through the results, they claimed that the effect of pH on DBPs varies depends on specific DBPs groups among which THMs formation showed to be increased when pH increasing. A similar pH dependency was also verified in other studies in drinking water chlorination[23-24]. Hua et al. claimed that such dependency is due to the increased formation of THMs from base-catalysed hydrolysis reaction of unknown halogenated by-products under alkaline pH condition[25].

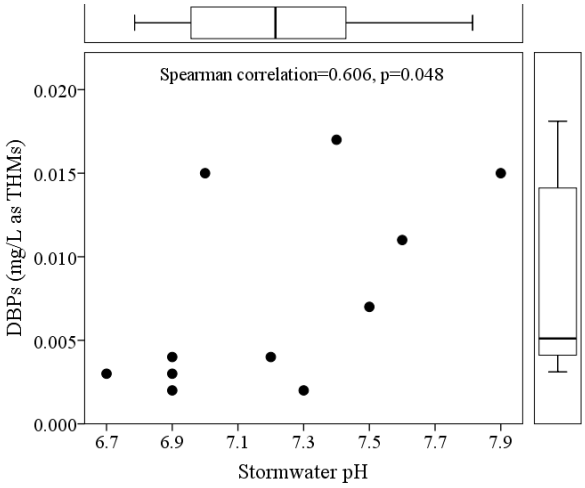

Figure 3: Correlation between DBPs (as THMs) and stormwater pH (Spearman correlation)

3.4. Disinfection Performance Validation of Selected Pathogen Indicators and Microorganisms

Table 2 provided the treatment performance of all 4 spiking microorganisms in 4 stormwater matrix. All organisms, for all four stormwater sites, were inactivated to below their respective detection limits within the pre-determined operational time. The results, to some extent, confirmed the ECO biocidal efficiency to Gram positive bacteria in stormwater.

Table 2. Validation performance for the selected microorganisms

Unit		*E. coli* MPN/100mL		*Enterococci* MPN/100mL		*Campylobacter* MPN/L		*C. perfringens* (spores) MPN/100mL	
95th percentile concentration in stormwater[a]		184382		34465		7.02		546	
Target concentration[b]		15000		3000		10000		1000	
	Opt. time (min)	Int. conc.	Resid. conc.	Int. conc.	Resid. conc.	Int. conc.	Resid. conc.	Int. conc.	Resid. conc.
Clifton Hill	30	20597(9%)	0(0%)	5147(15%)	0(0%)	395(141%)	0(0%)	43(66%)	0(0%)
Banyan	20	19725(5%)	0(0%)	5460(8)	0(0%)	2565(76)	0(0%)	467(10%)	0(0%)
Gardiners creek	20	18193(5%)	0(0%)	5403(14%)	0(0%)	2939(2%)	0(0%)	143(12%)	0(0%)
Troup's wetland	8	20526(4%)	0(0%)	8090(9%)	0(0%)	3717(31%)	0(0%)	267(7%)	0(0%)

[a]The 95th percentile concentration based on lognormal summary statistics of untreated urban stormwater
[b]The target concentration was established when assuming a practical stormwater biofilter pretreatment. *Campylobacter* and *C. perfringens* target concentrations were increased due to their low detection limit

Many researches have shown the weakness of using just chlorination as an inactivation measure[26-27]. However, hydroxyl radical and its initiated chlorine radicals have confirmed to be effective to the *E. coli* disinfection observed in our previous study under the same system configuration and operational condition but synthetic stormwater instead. Hydroxyl radical and chlorine radicals have stronger oxidative capacity compared to free chlorine[28-29]. Although there is no direct measurement of these two oxidant species in this study, it is still hypothesised the promising inactivation performance of *C. perfringens* was mainly due to the hydroxyl radical production of the BDD electrode.

It is noticeable that the actual initial concentration of both *Campylobacter* and *C. perfringens* were below the targeted dosing concentration. The target concentration of these two species was increased several orders higher than their estimated concentration after biofiltration pre-treatment due to the practical issues existing in their culturing and assaying process. The actual initial concentrations of these two species are still on the conservative side.

The operational time of stormwater collected from each catchment sites were determined by the time required for total disinfection of *E. coli* was achieved, respectively. *E. coli* as a Gram negative bacterium is recognised has a low tolerance to the chlorination disinfection compared to Gram positive and spore bacteria. However, it is the most abundant species existing in the natural water system with its concentration usually several orders higher than gram positive or spore bacteria.

Therefore, it was hypothesised previously that for general stormwater ECO disinfection among different microbe species, *E. coli* will take the longest time to achieve full disinfection. The results presented confirmed the hypothesis, as all the other species achieved total disinfection within the predetermined operational time. Therefore for future practice, residual *E. coli* concentration could be possibly used as a monitoring indicator for stormwater disinfection using ECO system.

4. CONCLUSION

This paper has confirmed the ECO disinfection performance of selected gram negative (*E. coli* and *Campylobacter*), gram positive (*Enterococci*) and spore-forming (*C. perfringens*) bacteria in stormwater. The promising disinfection performance is possibly due to the synergy effect between chlorine and hydroxyl radical production. Effective disinfection of indigenous *E. coli* was achieved in all collected stormwater samples even when chloride concentration was 6mg/L. However, ECO disinfection rate of real stormwater samples was found to be slower compared to our previous study that was done using synthetic stormwater. This is explained by the chemical complex and consumption of ECO produced oxidants in real stormwater. Only stormwater initial chloride concentration was found to be significant to the treatment performance. All treated stormwater samples showed disinfection by-products (DBPs) well below the Australian Drinking Water Guidelines. It was found that DBPs level in treated stormwater is positively correlated to the initial pH value of stormwater.

However, the above conclusion is constrained by the limited stormwater samples and microbe species tested in this study. The ECO disinfection performance needs to be validated across a wide range of various stormwater properties (e.g. chloride concentration). This helps to determine the boundary conditions of stormwater required for effective ECO disinfection performance (e.g. minimum chloride concentration). In addition, disinfection performance of four selected microbe species cannot truly reflect results of entire microbe community in stormwater. A more comprehensive microbe community needs to be taken into account in future studies.

Although total organic carbon concentration was not found to significantly impact disinfection performance, this should be confirmed using a larger suite of stormwater sites and samples. Due to the possible oxidant competing for organic compounds in ECO system it is still recommended for future implementation that stormwater biofilter is a good pre-treatment measure compared to other Water Sensitive Urban Design technologies (e.g. stormwater treatment constructed wetland) contributed to its low organics output.

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Chapter 6: Implications for Design and Implementation of Electrochemical Oxidation for Stormwater Disinfection

Chapter 6 Implications for Design and Implementation of Electrochemical Oxidation for Stormwater Disinfection

6.1. INTRODUCTION

This chapter provides recommendations for the design of electrochemical oxidation systems for stormwater disinfection. System design, operational conditions and the microorganism indicators monitored are discussed.

6.2. IMPLICATION OF DESIGN ELEMENTS AND OPERATIONAL CONDITIONS ON SYSTEM PERFORMANCE

Through a serious of laboratory and field experiments, the key reaction pathway of ECO disinfection under stormwater operational condition has been determined in this study. We found that when DSA anode is used, the presence of chloride ion is significant to the observed disinfection performance (see Chapter 3 and 4). Hence, it is hypothesised that chlorination is the key disinfection mechanism. This is in accordance with past studies[1-4]. In fact DSAs especially titanium anodes are well known for their high chlorine evolution capability compared to other types of anodes such as graphite or BDD anodes. However, it is noteworthy that the chloride concentration in synthetic stormwater used in disinfection mechanism study is only 9 mg/L, which is at least one order of magnitude lower than the operational chloride concentration reported in past studies[1-4]. The effective disinfection under such low chloride concentration has not been achieved in wastewater or surface water applications possibly because of their high organics and microbial concentration, which requires higher free chlorine demand and the consequent chloride ion concentration.

We found for BDD anode, effective disinfection of stormwater relies on both presence of chloride ions and hydroxyl radical production (Chapter 4). While most studies claim the effectiveness of hydroxyl radical production in disinfection[2, 4], partial hydroxyl radical production was not able to produce satisfactory disinfection in this study. This can be explained by the low operational current

applied because the stormwater had a low electric conductivity and to keep in line with the desire to develop a low-energy system. This finding, to some extent, complements the BDD disinfection mechanism reported in past studies[2, 5-6].

The disinfection mechanism study (Chapter 3 and 4) confirmed the significance of chloride presence for all tested anode types. This has a profound impact on the design of ECO system for stormwater harvesting: the chloride level of stormwater from the harvesting site needs to be carefully assessed. The event mean concentration (EMC) of chloride ion should be at least 9 mg/L as confirmed in our study. However, further study in the further is needed to define the lowest boundary of required chloride ion level for effective stormwater disinfection.

In addition to the mechanism governing the ECO reaction, several other factors, such as system durability, energy consumption and the concentration of disinfection by-products, need to be considered for the successful implementation of the disinfection system.

The present understanding of the practicality of using ECO for stormwater disinfection is limited by the results obtained under the controlled lab condition. Before ECO could be applied for large scale stormwater disinfection, two main gaps are remaining before it can be implemented in real practice.

The first gap exists in the actual disinfection rate of the scaled-up system on the field. Comparing to the present lab situation, the disinfection rate will obviously be changed in the scaled-up system due to the different system configuration such as the treating volume/anode surface ration and the new mixing method that facilitates the reaction mass transfer. Besides the system configuration change, determination of the disinfection rate is also catchment and rainfall event specific. Hence, the practical disinfection rate should be re-evaluated under a comprehensive understanding of the new system configuration, site condition and rainfall event. To compensate for the uncertainty causing from specific site and rainfall situation, some significant stormwater physiochemical characteristics (such as chloride, TOC and electric conductivity) that dominate the reaction rate should be monitored during the treatment process. Therefore, development of a real-

time parameter monitoring system and a reliable routine that calculates required energy input to achieve the designed disinfection rate is required for the scaled-up system. It is noteworthy that under the present lab condition, stormwater was disinfected using batch reactor (beaker). However, this is not practical for the real application due to the large quantity of stormwater. A continuous-flow reactor with practical size should be designed for such system. While the size of the continuous-flow reactor is determined by the disinfection rate. Therefore from the practical and economic perspectives, whether the scaled-up system could accomplish both reasonable energy efficiency and engineering cost still remains unknown.

The second gap between satisfactory lab performance and real application exists due to lack of reliable and accurate expression of the actual disinfection rate using monitored significant stormwater physiochemical characteristics. As mentioned previously, such expression is needed not only for the determination of required energy input and operational time (or flow rate, in the case of the continuous-flow reactor) but also for the understanding of the degree of reliability of such technology used for stormwater disinfection. However, the present lab study only provides a qualitative understanding of how stormwater physiochemical characteristics influence the disinfection rate. A detailed disinfection performance model using basic monitoring parameters should be developed and the reliability of this model should be validated before implementation of such technology for stormwater disinfection. Therefore, this thesis only provides preliminary implications for future design.

In addition, the ECO system requires regular maintenance to ensure the stable ongoing disinfection performance. As reported in Chapter 5, significant cathode fouling was observed after stormwater ECO disinfection. Although, biofilm formation was not observed on experimental components during this study. It is very likely due to the short time of operation and cleaning after each experiment. Formation of biofilm is very likely to occur after a long time of operation during real practice. Hence, a regular system washing regime should be developed based on calcium and magnesium levels of each catchment as well as the biofilming process.

6.2.1. The Importance of Anode Material

DSA as a widely used anode for wastewater disinfection was initially selected for study due to its reported high performance and good durability. However, the observed rapid performance deterioration indicates that DSA is not suitable for effectuating disinfection governed by oxygen production. For stormwater disinfection, the high voltage applied to DSA results in substantial oxygen production as chlorination is limited by the low concentration of chloride ion present in stormwater. Scanning Electron Microscope (SEM) results showed morphological change and loss of doping element on the deteriorated anode surface. Meanwhile, aluminium and silicon fouling were found in regions of low doping element concentration.

On the other hand, BDD electrode showed continuous stable performance in the cumulative operation study. BDD is a non-active electrode; unlike active anodes, it is not oxidised during the reaction. As such, severe oxygen evolution has minimum impact on BDD performance. , BDD can be recommended for stormwater disinfection until a more durable and oxygen-evolving resistant DSA anode is developed

6.2.2. The Significance of Operational Current

In addition to anode type and stormwater chemistry, the operational current dictates ECO disinfection performance. This study showed that treatment performance increases with increasing applied operational current. This is in accordance with previous studies. Interestingly, the results also found that when applied current increases, the corresponding unit energy consumption E_{unit} decreases. This suggests that operational current can be optimised for both required operational time and energy consumption. For instance, increasing the current could reduce the operational time and more importantly reduce the energy consumption. However, due to the low electrical conductivity of stormwater, the maximum current density tested in this study was limited to only 4.2 mA/cm^2. Therefore, it is not certain whether the aforementioned observation remains valid for current densities outside the tested range.

As a result of the low current density applied in this study, BDD anode was not able to produce sufficient hydroxyl radical for effective disinfection performance. Previous studies[2, 7-8] that demonstrated effective disinfection due to hydroxyl radical production, used an operational current greater than 30 mA/cm^2. Applying similar high current densities is not practical in stormwater systems due to the low electrical conductivity of pre-treated stormwater and need for low-energy systems.

6.2.3. The Influence of Stormwater Physicochemical Characteristics

The thesis examined the influence of stormwater physicochemical characteristics on ECO disinfection performance. Disinfection was not observed for either DSA or BDD anode in the absence of external chloride addition in the present lab scale process-based study. This suggests that stormwater ECO disinfection relies on chlorination production through oxidation of chloride ions present in the stormwater matrix. Results from Chapter 5 also showed that the required disinfection operational time was negatively correlated to the chloride concentration in collected real stormwater samples. This study demonstrated that increasing the concentration of the chloride ion may increase the chlorine production and hence the treatment performance. It is, therefore, possible that in catchments discharging stormwater of very low chloride concentrations, ECO may not be viable for stormwater disinfection. An assessment of catchment properties/land-use, including chloride concentrations present in generated stormwater is thus of importance when considering the implementation of the ECO technology.

Interestingly, no significant correlation was found between the amount of disinfection by-products (DBPs) produced (after treatment) and influent stormwater chloride concentration. Because of the lower amount of time required to achieve complete disinfection, overall levels of DBPs remain relatively the same in stormwater with high chloride concentration as with normal stormwater. Addition of chloride in adequate amounts to pre-treated stormwater may represent a possible solution to augment the efficiency of ECO. Although, adding chloride will inevitably bring additional cations (in form of salt) to stormwater leading to a high bioavailability of heavy metals to aquatic organisms

by competing for the available metal binding sites[9] (e.g. organic ligands and clay). However, this concern should be negligible as all heavy metals in pre-treated stormwater are well below the threshold values stated in Australian guidelines for environmental protection.

Past work showed that ECO disinfection is typically favourable under low pH [10-12]. pH was not found to have an effect on ECO disinfection efficiency in the present study. Mean pH of the stormwater studied was 6.35 (*SD*=0.54)[13]. Nevertheless, pH had a significant impact on the DBPs level following treatment. DBPs increased with an increase in stormwater pH. Although DBPs tested in this study were at least one order of magnitude lower than the health value suggested by the Australia Drinking Water Guidelines[14]. However, in this study, the highest pH value detected in all stormwater samples were only 7.9. Considering the variable characteristics of stormwater and catchment conditions, pH may still be a matter of concern for catchments associated with surface runoffs of elevated pH. Future study is needed to define the pH boundary for satisfactory DBPs level in treated stormwater.

Total organic carbon (TOC) may have a negative impact on the treatment performance because of the competition for chlorine. Given this, it is highly desirable that pre-treated stormwater used for the disinfection process be low in TOC. Interestingly, during pre-treated stormwater collection for the present study, it was found that effluent from the biofiltration system had lower TOC concentrations than that from the wetland system. Biofiltration systems may, thus, represent an effective pre-treatment option before stormwater disinfection using ECO.

6.2.4. *E. coli* as a Pathogen Indicator

E. coli required the longest time for disinfection among all tested microorganisms. Despite the weakness of this Gram negative bacterium, it is the most abundant species existing in the natural water system with concentrations usually several orders higher than gram positive or spore bacteria. Therefore, it is recommended that for future monitoring, residual *E. coli* concentration could possibly be used as a monitoring indicator for stormwater disinfection using ECO system.

6.3. KEY RECOMMENDATIONS FOR DESIGNING ECO SYSTEM FOR STORMWATER HARVESTING

The objectives for the development of an effective stormwater ECO system are to optimise overall disinfection performance, reduce the energy consumption, minimise disinfection DBPs level and ensure reasonable system longevity. These can be achieved through optimisation of the different design and operational parameters. Moreover, the stormwater physicochemical characteristics have a strong influence on the performance of the ECO system. Both design optimisations and ongoing site monitoring will ensure proper system functioning. Based on the results of the presented study, the following recommendations can be made in regards to optimum design and operational parameters:

- Boron doped diamond (BDD) electrode is the recommended anode for stormwater ECO disinfection at present until a more durable commercial low cost anode is developed;
- The electrode distance should be 3 mm as tested in this study or if it is not achievable in practice due to system design or installation constraints, the distance should be as minimum as possible. to achieve optimal energy efficiency;
- Prior to recommending the use of an ECO system, the following stormwater characteristics should be monitored:
    - Chloride levels to determine if they are 9 mg/l or above. In case they are below this value, consideration should be made whether the external addition of chloride is required (if yes, how feasible will it be to ensure a continuous supply).
    - If pH values are above 8, disinfection by-products (DBPs) should be monitored to assure that they are below the recommended levels for safe water use.
- *E. coli* could be used as an indicator microorganism for disinfection performance of other stormwater pathogens.
- Whenever it is possible, solar panels should be used to power the system.

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Chapter 7: Conclusion and Future Work

Chapter 7 Conclusion and Future Work

7.1. INTRODUCTION

This chapter starts with an assessment of the strengths and weaknesses of the research presented in this thesis. Key findings pertaining to the use of electrochemical oxidation for stormwater disinfection are presented together with recommendations for practical implementation. Lastly, recommendations for further research are provided.

7.2. STRENGTHS AND WEAKNESSES OF THE EVIDENCE

This study proposed electrochemical oxidation (ECO) as the next generation stormwater disinfection technology. Electrochemical oxidation as a technology widely used in wastewater treatment has not been tested for stormwater. Due to the inherent difference between stormwater and wastewater characteristics (including salinity, chloride levels), previous knowledge could not be simply transferred for ECO stormwater disinfection. This research study tested for the first time the applicability of ECO for stormwater disinfection. The key strengths and weaknesses of the methods used and therefore the obtained results are discussed below.

7.2.1. Stormwater ECO Disinfection Performance

A synthetic stormwater mix was used instead of real stormwater in the laboratory studies to ensure consistency and minimise design variables to assess the impact of anode type and operational conditions on treatment performance. So the fact that we used relatively stable and similar stormwater characteristics in the majority of our processed-based studies could be regarded as the strength since the results were not 'clouded' by constantly changing water characteristics (naturals stormwater is notoriously variable in its chemistry).

However, it is recognised that the physicochemical characteristics of the synthetic mix may not be completely reflective of real pre-treated stormwater. This is why the results of the laboratory

studies were validated with real stormwater. A few ways in which performance differed across the two different mixes include: (1) real stormwater took longer to achieve complete disinfection (due to a higher concentration of DOC); (2) the levels of disinfection by-products were higher during disinfection of real stormwater (due to the presence of humic acid).

It should be noted that only a limited number of natural stormwater samples were tested in this study. This could be regarded as a limitation and further research should look into testing a wider range of real (pre-treated) stormwater samples to inform on the influence of the different stormwater physicochemical characteristics on treatment performance.

Dimensional stable anode (iridium and ruthenium doped titanium electrode) as electrode material was initially selected for study based on its proven efficiency in wastewater treatment. However, the present study found a rapid deterioration in performance after only 8 hours of operation. This led to the study of the boron doped diamond anode which showed good performance longevity. However, due to its high cost, it is less likely to be implemented in practice. Within the timeframe of this doctoral study, the (subsequent) development of a more affordable anode material was not possible. Much work remains for the implementation of an effective and sustainable ECO system for stormwater disinfection.

Boron Doped Diamond (BDD) anode showed good and durable disinfection performance for stormwater ECO disinfection in the present study. However, performance was only tested under specific, predetermined operational conditions, including chloride concentration and operational current (4.2 mA/cm^2). Given that the minimum level of chloride required (in pre-treated stormwater) for effective disinfection likely depends on the operational current, effective disinfection of stormwater may be possible under very low or absence of chloride when BDD anode is used as an electrode and under a more appropriate operational current. This is the subject of future research.

Unit energy consumption (KW•h/ton) with the definition of electric energy required to achieve a 3-log reduction of one ton of stormwater was calculated by linearly multiplying the energy consumption of 400ml testing volume by a volume conversion factor (Chapter 3). In addition,

effective mixing of water during treatment enhances mass transfer between microbes and the oxidants generation on anode surface. This is essential to the observed treatment performance. However, the energy consumption required by effective mixing is not considered in this study.

7.2.2. Microorganism Indicators Used in this Study

Lab strain *E. coli* was used to spike the synthetic stormwater in order to assess the disinfection performance and energy consumption under more controlled conditions. An attempt to validate the laboratory results was, nevertheless, made by comparing disinfection performance with real stormwater (discussed in Chapter x). As such, in the validation study, *E. coli* together with other stormwater indicators and pathogens (*Enterococci*, *Campylobacter*, and *C. perfringens*) were tested. So the strength of the presented study is that we found that at least for these microbes, *E. coli* is a good surrogate indicator.

However, there are several other types of stormwater pathogens that need to be assessed for the implementation of a real system. Given that all selected microorganism indicators and pathogens were spiked at levels representing their 95th percentile concentration in pre-treated stormwater to make up the synthetic stormwater and *E. coli* took the longest time to achieve full disinfection, this suggests that *E. coli* could be possibly used as a monitoring indicator for stormwater disinfection using ECO. Yet, this is true for only the tested indicators. It should be noted that the number of microbe species tested in this study is very limited. A kinetic sampling of microbe species except *E. coli* was not available due to limited resources. Moreover, the concentration of *E. coli* relative to the other microbe species varies to a great extent in natural stormwater. In general, this study provides an understanding of the disinfection performance of a limited range of stormwater pathogens; future research should aim to provide a more comprehensive analysis of the behaviour of all relevant stormwater pathogens (or their indicators).

7.3. KEY FINDINGS

The Experimental studies (Chapter 3) show that ECO can achieve efficient disinfection performance within a practical timeframe without chemical addition. Titanium electrode (DSA) achieved 3 log reduction of *E. coli* under very low energy consumption. For example, when the operational current density was 1.75 mA/cm^2, disinfection below the detection limit was achieved within 1.3 minutes, the corresponding unit energy consumption was 0.007 KWh per ton of stormwater treatment. Energy consumption is promisingly low, which signifies that solar panels can be used to power the system.

Chlorination was found to be the key disinfection mechanism for tested DSA despite the synthetic stormwater containing only 9 mg/L of chloride. However, the tested type of DSA (RuO_2, IrO_2 doped titanium anode), discussed in Chapters 3 and 4, was not suitable for operation under stormwater condition. Due to the low electric conductivity of stormwater (as 100 µS/cm used in the synthetic stormwater), high operational voltage (as 14V used in this study) resulted in severe oxygen production on the selected DSA surface causing rapid performance deterioration. This research study revealed a DSA deterioration mechanism is different from the deterioration processes found in the previous wastewater ECO studies. Selection of an appropriate anode type for an ECO system operating under low salinity, low chloride level and high voltage have not been previously studied.

The laboratory experiment (Chapter 4) showed that BDD anode achieved comparable disinfection performance to the DSA anode under the same operational condition. However, the disinfection process was achieved through different pathway compared to the hydroxyl radical production process reported in past wastewater ECO studies; a synergy between hydroxyl radical and free chlorine production was found to be responsible for the disinfection of stormwater. Therefore, the presence of chloride ion in stormwater is essential for the effective disinfection using BDD. In addition, BDD also showed promising stable performance in the accumulated *in-situ* test over 31 hours of operation (Chapter 4).

Chapter 5 has confirmed the ECO disinfection performance (using BDD) of selected gram negative (*E. coli* and *Campylobacter*), gram positive (*Enterococci*) and spore-forming (*C. perfringens*) bacteria in stormwater. Effective disinfection (below the detection limit) of indigenous *E. coli* was achieved in all collected stormwater samples even when chloride concentration was 6mg/L. Below this threshold, disinfection performance is severely negatively impacted upon. This thus defines a new lower boundary of chloride concentration that is adequate for chlorination disinfection.

However, ECO disinfection rate of real stormwater samples was found to be slower compared to the findings of the laboratory tests on synthetic stormwater (reported in Chapter 3 and 4). Among all tested stormwater physicochemical characteristics (pH, TOC, bicarbonate, chloride, ammonia and bicarbonate), only stormwater initial chloride concentration was found to be significant to the treatment performance. All treated stormwater samples showed disinfection by-products DBPs (THMs-total halogenated methanes and HAAs-haloacetic acids), which are much lower than the health threshold value suggested by the Australian Drinking Water Guidelines. It was found that DBPs level in treated stormwater is positively correlated to the initial pH value of stormwater.

In general, ECO has a great potential to be used as a new Water Sensitive Urban Design (WSUD) technology for stormwater disinfection under the suggested implementation in Chapter 6. Comparing to existing WSUD technologies such as stormwater biofilters, the effective treatment performance is not influenced by the weather condition (antecedent dry or wet event). It could provide higher and variable removal performance based on fit for purpose uses. Although it might require relatively higher capital cost and ongoing maintenance, it gives us an opportunity to reliably treat stormwater to a higher standard.

7.4. RECOMMENDATIONS FOR FUTURE WORK

This study has provided a preliminary understanding on the use of electrochemical oxidation as disinfection technology for stormwater disinfection. However, there are still a number of knowledge gaps remaining.

In this study, it is hypothesised that a synergetic disinfection effect occurs between hydroxyl radical and free chlorine based on the observed significance of chloride presence and hydroxyl radical production. However, this is a hypothesis only, the synergy effect has not been proved during lab experiment. Future studies should analyse the mechanism responsible for BDD disinfection of stormwater in more details.

This study showed that BDD anode is a good option for stormwater ECO disinfection. However, due to the very high price of this material, it is not practical to use BDD anode in real practice. Therefore, a more comprehensive anode selection study should be performed in the future to select an affordable and durable anode that could achieve effective disinfection of stormwater.

This research mainly tested stormwater disinfection under using a synthetic stormwater recipe with simple physicochemical properties while in the validation study, limited real stormwater samples were tested. Hence, the understanding of the reliability of such system under variable stormwater properties is very limited. It is suggested that the ECO disinfection mechanisms should be tested under challenging operational conditions to define the boundary conditions for effective disinfection (e.g. low chloride concentration).

Although this study presents an accumulated performance assessment, its operational time is limited to a bit more than 30 hours. It is suggested that the durability of the ECO system be assessed over a longer time period. In addition, significant cathode fouling was observed due to the hardness of the water. Accordingly, suitable system maintenance regimes should be developed. Unlike wastewater treatment systems which operate under a relatively stable time period and frequency, stormwater inflows usually are more intermittent. The reliability of ECO system under such operational regime requires further study.

7.5. REFERENCES

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APPENDIX

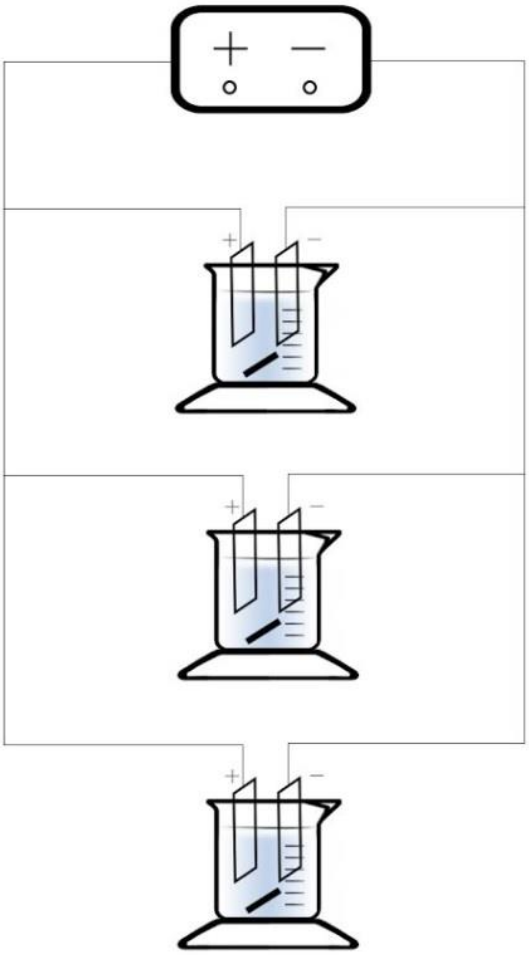

Figure S1. Schematic diagram of the experimental set-up with three replicated electrolysis cells

Table S1. Physicochemical characteristics of synthetic stormwater matrices. DI water with stormwater slurry; DI water with stormwater slurry and topped up chemicals (final synthetic stormwater matrix)

Characteristics	Unit	DI water + stormwater slurry	Final synthetic stormwater
Ammonia (N)	mg/L	0.040	0.047
Bicarbonate	mg/L	<0.1	42
Chloride	mg/L	0.797	9.0
Electricity Conductivity	µs/cm	18.1	105.0
Nitrate & Nitrite (N)	mg/L	0.005	0.302
Organic Nitrogen - dissolved (N)	mg/L	0.009	0.580
Organic Nitrogen - particulate (N)	mg/L	0.079	0.200
pH	-	6.9	7.1
Phosphate - ortho (P)	mg/L	0.00028	0.063
Phosphate - total (P)	mg/L	0.02427	0.093
Sulphate	mg/L	0.13	7
Total Nitrogen (N)	mg/L	0.13	0.90
Total Suspended Solids	mg/L	3.525	3.501
Aluminium	mg/L	0.512	0.468
Antinomy	mg/L	<0.001	<0.001
Arsenic	mg/L	<0.001	<0.001
Barium	mg/L	0.003	0.003
Beryllium	mg/L	<0.001	<0.001
Boron	mg/L	<0.02	<0.02
Cadmium	mg/L	<0.0002	<0.00002
Chromium	mg/L	0.00087	0.0011
Cobalt	mg/L	<0.001	<0.001
Copper	mg/L	0.008	0.019
Iron	mg/L	0.45	0.35
Lead	mg/L	0.003	0.003
Manganese	mg/L	0.002	0.002
Mercury	mg/L	<0.0001	<0.0001
Molybdenum	mg/L	<0.001	<0.001
Nickel	mg/L	<0.001	0.001
Selenium	mg/L	<0.001	<0.001
Silver	mg/L	<0.001	<0.001
Strontium	mg/L	0.002	0.002
Thallium	mg/L	<0.001	<0.001
Tin	mg/L	<0.001	<0.001
Titanium	mg/L	<0.001	0.025
Vanadium	mg/L	<0.001	<0.001
Zinc	mg/L	0.074	0.039
Calcium	mg/L	0.10573	8.9
Magnesium	mg/L	0.052	2.4
Potassium	mg/L	0.04333	2.8
Sodium	mg/L	0.03293	7.6