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2021

Citation for published version (APA):
Yu, H. (2021). *Treatment of organic pollutants in high salinity wastewater: new catalysis systems*. Department of Water Resources Engineering, Lund Institute of Technology, Lund University.

Total number of authors:
1

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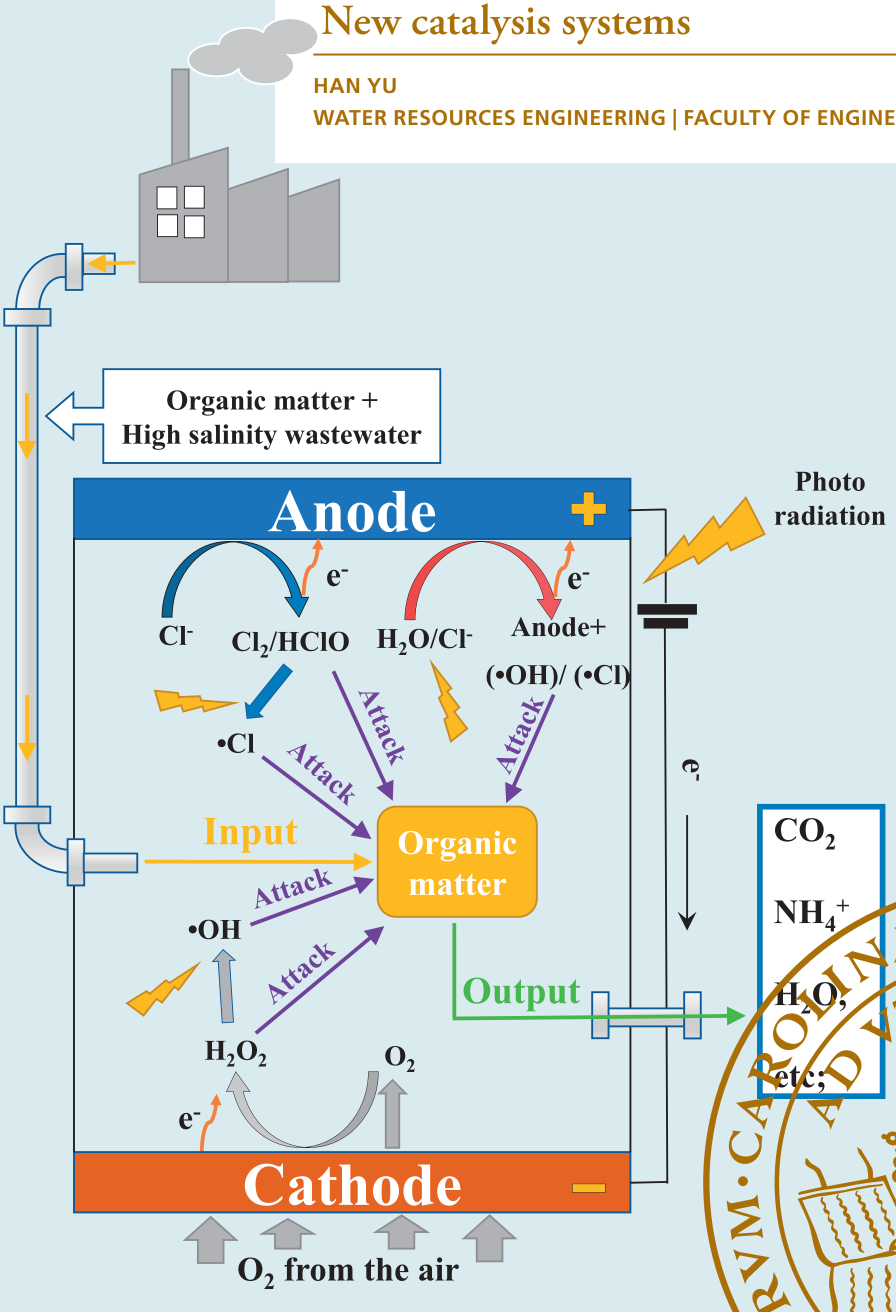
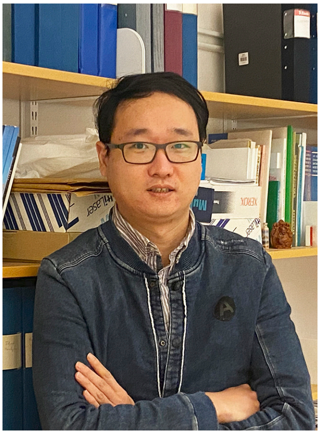
HAN YU
WATER RESOURCES ENGINEERING | FACULTY OF ENGINEERING | LUND UNIVERSITY





HAN YU is a doctoral scholar in the Division of Water Resources Engineering, Lund University. His research is mainly in the area of organic matter degradation and wastewater treatment by AOPs methods. Specifically, He is focusing on electrochemical and photo catalysis.

With the development of economy and industry, high salinity wastewater (HSW) from production processes has emerged as a new threat to environment and human beings in recent decades. The massive organic matters with a wide variety in HSW yield significant risk to environmental and human health. The efficient degradation of these organic matters before discharge is necessary. However, traditional methods have showed significant drawbacks for this purpose in various aspects.

Electrochemical catalysis (EC) and photo-electro catalysis (PEC) have shown their potential for organic matter degradation in HSW due to their high efficiency, environmental compatibility, saving of energy/material and automation, etc. Therefore, in this study, novel degradation systems were developed for the degradation of organic matters in HSW based on EC and PEC techniques. The performances of the new systems were investigated and improved. Effect factors, degradation mechanisms and kinetics were analyzed. The results showed a bright prospect of the new systems with remaining limitations. This leaves us significant value for the future study of these new systems. The final application of them can be expected after the further development.

Printed by Media-Tryck, Lund 2021 NORDIC SWAN ECOLABEL 3041 0903

LUND UNIVERSITY

Faculty of Engineering
Department of Building and Environmental Technology
Division of Water Resources Engineering

ISBN 978-91-7895-715-6
ISSN 1101-9824

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Han Yu

DOCTORAL DISSERTATION

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To be defended at the Faculty of Engineering. V-building, John Ericssons Väg 1,
Lund, room V:C on January 13th, 2021 at 10: 15 am

Faculty opponent
Professor Marc Cretin, Faculty of Sciences, University of Montpellier, France

Organization LUND UNIVERSITY	**Document name** **DOCTORAL THESIS**
Water Resources Engineering Box 118 SE-221 00 Lund, Sweden	**Date of issue:** 18th Dec, 2020
Author(s) Han Yu	Sponsoring organization

Title and subtitle

Treatment of organic pollutants in high salinity wastewater: new catalysis systems

Abstract

High salinity wastewater (HSW, NaCl mass fraction ≥ 1%) from industries and aquacultures contains massive organic matters with a wide variety. These organic matters have been considered as significant threaten to both human and environment. The removal and degradation of them before discharge emerge as necessity. However, the traditional treatment methods show significant drawbacks for this purpose. Therefore, new efficient treatment methods need to be developed. Electrochemical catalysis (EC) and photo-electro catalysis (PEC) have shown their potential for organic matter degradation in HSW due to their high efficiency, environmental compatibility, saving of energy/material and automation, etc. In EC and PEC methods, the working electrodes (anode or cathode) utilize the rich components in HSW to produce strong degradation agents, leading to high efficiency with no need of extra chemical agents. However, the issues of expensive electrode price, waste of electric energy and limited degradation performance still retain as bottlenecks for future application.

Therefore, in my thesis work, new EC and PEC systems were developed to address these issues. Low-cost and high-efficiency electrode materials were employed as anodes and cathodes. These systems were developed basing on the new concept of using duo working electrodes (EC-D and PEC-D), rather than the single working anode or cathode in traditional systems (EC-S and PEC-S). This allowed the synergistic degradation between anode and cathode, leading to the performance enhancement. The key results are as follows:

New EC-D system performed well and showed higher degradation and removal efficiency, with lower energy cost, compared to EC-S. This was due to the synergistic work between anode and cathode, where active chlorine and H_2O_2 produced on anode and cathode contributed to degradation work together. Several indicating factors such as pH value, pollutant content, current density and NaCl concentration yielded significant effect to the performance. Simple EC method showed shortage when dealing with complex and refractory organic matter, such as Norfloxacin (NOR). This should be attributed to the limited reaction activity of EC produced degradation agents (active chlorine and H_2O_2).

PEC system significantly enhanced the performance of EC system. This was associated with the synergistic work between photo and electric power, by which the EC produced degradation agents transferred to stronger free radicals. PEC systems also avoid harmful residual chlorine result in EC systems by transferring them into free radicals.

In PEC system, anode and cathode both contributed significantly to degradation work, with anode as prior. Both direct adsorption-degradation and indirect degradation by agents contributed significantly, where indirect route performed more importantly. PEC-D showed high performance in real HSW treatment with low initial organic matter concentration, the biological harmless outflow can be achieved. It is suitable for the treatment of left refractory organic matters after the main degradation process.

In conclusion, both new EC and PEC showed bright prospects in organic matter removal and degradation in HSW. However, before large scale application, their performance of degradation and adaptability in various conditions should be further developed. The practical design of large-scale plant should be focused. In addition, not only organic matters, but also the treatment of other critical pollutions in HSW by EC and PEC should draw attention.

Key words: High salinity wastewater; Electrochemical catalysis; Photo-electro catalysis; Degradation;

Classification system and/or index terms (if any)		
Supplementary bibliographical information		**Language:** English
ISSN and key title: 1101-9824		**ISBN:** 978-91-7895-715-6 (print) 978-91-7895-716-3 (pdf)
Recipient's notes	**Number of pages** 188	Price
	Security classification	

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Cover photo by Han Yu

Faculty of Engineering, Department of Building and Environmental Technology,
Division of Water Resources Engineering

ISBN 978-91-7895-715-6 (print)
ISBN 978-91-7895-716-3 (pdf)
ISSN 1101-9824
Report number: 1086
Printed in Sweden by Media-Tryck, Lund University, Lund 2021

NORDIC SWAN ECOLABEL
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MADE IN SWEDEN

To my dear family and friends who share life with me; And research makes life different every day.

Abstract

High salinity wastewater (HSW, NaCl mass fraction ≥ 1%) from industries and aquacultures contains massive organic matters with a wide variety. These organic matters have been considered as significant threaten to both human and environment. The removal and degradation of them before discharge emerge as necessity. However, the traditional treatment methods show significant drawbacks for this purpose. Therefore, new efficient treatment methods need to be developed. Electrochemical catalysis (EC) and photo-electro catalysis (PEC) have shown their potential for organic matter degradation in HSW due to their high efficiency, environmental compatibility, saving of energy/material and automation, etc. In EC and PEC methods, the working electrodes (anode or cathode) utilize the rich components in HSW to produce strong degradation agents, leading to high efficiency with no need of extra chemical agents. However, the issues of expensive electrode price, waste of electric energy and limited degradation performance still retain as bottlenecks for future application.

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In conclusion, both new EC and PEC showed bright prospects in organic matter removal and degradation in HSW. However, before large scale application, their performance of degradation and adaptability in various conditions should be further developed. The practical design of large-scale plant should be focused. In addition, not only organic matters, but also the treatment of other critical pollutions in HSW by EC and PEC should draw attention.

Popular science summary

Water quality plays a key role for environmental and human health. In the last decades, with the help of modern water treatment and supply systems, life expectancy of human has increased significantly. However, with the development of economy and industry, massive high salinity wastewater (HSW) from production processes has emerged as new threats, which can pollute water bodies and therefore leads to risk for both human and environment. The high concentrations of organic matter in HSW can be directly toxic or indirectly negatively influential to environment and human's life quality. Organic matter often needs to be degraded before discharge.

Degradation is to decompose organic matters to inorganic CO_2, H_2O, NH_4^+, etc. Therefore, the risk by organic matters can be avoided. There are already several physical, chemical and biological degradation methods for this purpose. However, they are either highly energy and material costly or less efficient when dealing with HSW. Hence, the new electrochemical catalysis (EC) and photo-electro catalysis (PEC) have been developed to address these issues. Degradation requires chemical reactions occurring on the organic matters which decomposed their constructions. In chemical treatment, for instance, the added chemical oxidant agents are responsible for this work. In bio-treatment, on the other hand, organic matters are slowly digested by well-adopted microorganisms. EC and PEC utilize electric and photo power to transfer the ions and compounds in HSW to oxidant agents which can do the degradation work. Therefore, they show faster degradation than bio-treatment and cause less media consumption compared to chemical treatment.

In both EC and PEC, electrodes (anode or cathode) are the key catalyst to produce agents for degradation under electro and photo power. However, to achieve ideal performance, expensive noble metals and graphene with high catalysis activity are always needed as electrodes materials. Meanwhile, all effective reactions and degradation rely on the current circulating between anode and cathode. But in traditional EC and PEC systems, only single anode or cathode side is employed for degradation work, which ignores the possible synergistic work between the two electrodes and wastes the current passing the other side. Moreover, as new methods, the degradation performance should be further developed in both EC and PEC before future applications. This leaves us the space for further development and research.

This study aims to develop new EC and PEC systems with duo working electrodes (anode and cathode) and economic electrode materials for the organic matter degradation in HSW, with new systems named EC-D and PEC-D. The possible degradation routes for duo working electrodes were developed. Under EC, on anode, oxidation reaction occurred, resulting in the production of active chlorine. In cathode, a novel air-diffusion cathode was employed to diffuse O_2 into water and transfer it to H_2O_2 in reduction reaction. Both active chlorine and H_2O_2 can act as agents for degradation; They can be also transferred into stronger free radicals by photo radiation under PEC to enhance the performance. Methyl orange (MO) and Norfloxacin (NOR) and real HSW were selected as targeted pollutants. The electrode materials included economic SnO_2-Sb, carbon black and activated carbon with low price and high catalysis activity.

The result showed higher degradation efficiency of the new EC-D and PEC-D systems compared to single-working-electrode EC and PEC systems (EC-S and PEC-S), respectively, due to the synergistic work of anode and cathode in new systems. In EC-D, the degradation agents from both sides were produced as expected, which lifted the degradation efficiency and lowered the energy cost in the MO degradation in HSW. However, EC methods were unable to degrade refractory organic matters such as NOR. This was because neither active chlorine nor H_2O_2 contributed enough reaction activity. In degradation processes, the activity can be understood as a power for decomposing organic matters. Higher activity means faster reaction and more thorough destruction of the organic matters. The degradation efficiency was enhanced significantly by a PEC processes. With combined electrochemical and photo power, more active free radicals were produced from active chlorine and H_2O_2. The highest degradation performance was obtained in the PEC-D, since the free radicals were produced on both anode and cathode sides. The performances were in the order of PEC-D>PEC-S>single photo catalysis>EC. In general, this can be explained as the utilization of synergistic work between anode and cathode as well as between photo and electro in PEC-D. Therefore, the improvement was conducted in two dimensions and resulted in a significant lift of the performance.

By modelling, the anode and cathode were both proven to contribute significantly in degradation, with anode as prior. To further improve the performance, anode was formatted by a new urea precipitations method, resulting in larger surface area and higher photo and electro catalysis activity. These features created more reaction space on anode surface and faster reaction rate. Subsequently, high degradation performance was obtained.

Overall, the efficient and economic new EC and PEC systems were successfully developed and investigated in this work. They showed great potential for organic matter degradation in HSW. This is one step towards the future application of EC/PEC methods. However, the drawbacks such as the dependency to electric power and solar radiation, the limited electric and photo power utilization ratio as well as the difficult design of large-scale plants still retain as big challenges. This leaves us the space for future study.

Populär sammanfattning

Vattenkvaliteten har en nyckelroll för miljö och människors hälsa. Med hjälp av moderna system för vattenrening och försörjning under de senaste decennierna, har människans livslängd ökat betydligt. Med utveckling av ekonomi och industri ökar emellertid produktionen av avloppsvatten med hög salthalt (high saline water, HSW) från processer, något som visat sig kunna ge nya hot eftersom de kan förorena vattenförekomster och därför leder till risk för både människa och miljö. Höga koncentrationer av organiskt material i HSW kan vara direkt giftiga eller indirekt påverka miljön och människans livskvalitet negativt. Organiska ämnen behöver ofta brytas ned innan det renade vattnet släpps ut i miljön.

Nedbrytning innebär att organiska ämnen sönderdelas till oorganiskt CO2, H2O, NH4+, etc. På så sätt kan risker med organiska ämnen undvikas. Det finns flera fysikaliska, kemiska och biologiska nedbrytningsmetoder för detta ändamål. De förbrukar dock antingen mycket energi och material och är kostsamma eller mindre effektiva när det gäller HSW. Därför har den nya elektrokemiska katalysen (EC) och fotoelektrokatalysen (PEC) utvecklats för att ta itu med dessa problem. Nedbrytning kräver kemiska reaktioner så de organiska ämnena sönderdelas. Till exempel vid kemisk behandling är de tillsatta kemiska oxidationsmedlen ansvariga för detta arbete. Vid biologisk behandling, däremot, bryts organiska ämnen långsamt ned av mikroorganismer som anpassats till denna miljö. EC och PEC förbrukar el och ljus för att omvandla joner och föreningar i HSW till oxidationsmedel som kan bryta ned det organiska materialet. De är snabbare än biologisk behandling och kräver mindre kemikalier jämfört med kemisk behandling.

I både EC och PEC är elektroderna (anod eller katod) nyckelkatalysatorer för att producera ämnen som kan generera nedbrytning med hjälp av elektricitet och ljus. För att uppnå idealiska prestanda behöver elektroderna bestå av dyra ädelmetaller och grafen med hög katalysaktivitet. För att uppnå effektiva reaktioner och nedbrytning behöver elektrisk ström cirkulera mellan anod och katod. Men i traditionella EC- och PEC-system används endast en anod- eller katodsida till nedbrytning, vilket missar det möjliga synergistiska arbetet mellan de två elektroderna och slöser bort strömmen som passerar den andra sidan. Som nya metoder behöver nedbrytningsprestandan vidareutvecklas i både EC och PEC för framtida applikationer. Detta ger oss utrymme för vidare utveckling och forskning.

Denna studie syftar till att utveckla nya EC- och PEC-system med dubbla (D) arbetselektroder (anod och katod) och ekonomiska elektrodmaterial för nedbrytning av organiskt material i HSW. Systemen kallas därför EC-D och PEC-D. Vid anoden sker oxidationsreaktioner, vilket resulterar i produktion av aktivt klor. Vid katoden används en ny luftdiffusionskatod för att diffundera syrgas i vatten och reducera den kemiskt till väteperoxid. Både aktivt klor och väteperoxid kan bryta sönder organiskt material; de kan också överföra starkare fria radikaler genom fotostrålning för att förbättra prestandan. Metylorange (MO) och Norfloxacin (NOR) och ett naturligt salt avloppsvatten (HSW) valdes ut för att visa reningseffekten av EC-D och PEC-D. Till elektroder valdes prisvärt SnO2-Sb, kolsvart och aktivt kol av lågt pris och med hög katalysaktivitet.

Undersökningarna visade att nedbrytningseffektivitet för de nya EC-D- och PEC-D-systemen var högre jämfört med EC-respektive PEC-system med enkla arbetselektroder (EC-S respektive PEC-S, Singular, engelska)) på grund av det synergistiska arbetet med anod och katod i nya system. I EC-D produceras ämnena för nedbrytning från båda sidor som förväntat, vilket lyfte nedbrytningseffektiviteten och sänkte energikostnaden i MO-nedbrytningen i HSW. EC-metoder kunde emellertid inte bryta ned svårnedbrytbara organiska ämnen som NOR. Detta berodde på att varken aktivt klor eller H2O2 kunde åstadkomma tillräckligt med reaktionskraft för nedbrytning av organiska ämnen. Högre aktivitet innebär snabbare reaktion och mer omfattande nedbrytning av organiska ämnen. Effektiviteten förbättrades avsevärt av PEC-processer. Med kombinerad elektrokemisk och ljusinducerad radikalbildning producerades högre halt fria radikaler från aktivt klor och H2O2. Den högsta nedbrytningsprestandan erhölls i PEC-D, eftersom de fria radikalerna producerades på både anod- och katodsidan. Reaktionerna följde ordningen PEC-D>PEC-S>ren fotokatalys>EC. I allmänhet kan detta förklaras som användningen av synergistiskt arbete mellan anod och katod såväl som mellan ljus och el PEC-D. Därför genomfördes förbättringen i två dimensioner och resulterade i en betydande förbättring av prestanda.

Genom modellering visade sig både anoden och katoden kunna bidra avsevärt vid nedbrytning, där anoden bidrog mest. Prestandan ökade genom att anoden modifierades med en ny ureautfällningsmetod, vilket resulterade i större ytarea och högre foto- och elektrokatalysaktivitet. Dessa funktioner skapade mer reaktionsutrymme på anodytan och snabbare reaktionshastighet. Därefter erhölls hög nedbrytningsprestanda.

Sammantaget utvecklades och undersöktes de effektiva och ekonomiska nya EG- och PEC-systemen i detta arbete. De visade stor potential för nedbrytning av organiskt material i HSW. Detta är ett steg mot den framtida tillämpningen av EC / PEC-metoder. Nackdelarna, såsom beroendet av elkraft och ljustillförsel, det begränsade användningsförhållandet mellan el och ljus samt den detaljerade utformningen av storskaliga anläggningar är fortfarande stora utmaningar. Detta ger oss utrymme för framtida studier.

Acknowledgement

I would like to express my thanks to all the people who supervised me, helped me, worked with me and shared the beautiful 5 years with me. I appreciate the critical teaching and training, the nice work environment and great academic atmosphere provided by Lund University and TVRL.

I would like to show my deep gratitude to my supervisor, Prof. Linus Zhang. He is a great supervisor and a nice friend. Thanks to all the knowledges, methods and scientific thought he taught me as well as the generous helps both in my work and in daily life. These make me work happily, improve fast and feel like home. The most important thing I learned from him is the positive attitude and clear mind when facing issues, I really appreciate it.

Thanks to my co-supervisor Prof. Kenneth M Persson for providing me massive opportunities to join water-relative conferences and communicate with professional people in this area. I also received many valuable information about relative financial support and commercial models from him. I appreciate it.

Many thanks to Prof. Cintia Bertacchi Uvo and Prof. Magnus Persson to provide best work environment for us. Many thanks to my friends and colleagues for sharing these beautiful 5 years with me. Thank you for sharing my happiness, carrying my sadness and enduring my faults. I didn't list the names because I am afraid to omit someone, but you know my thanks refer to you.

I want to express my deep gratitude to Prof. Yu and Prof. Dong as well as all the other partners in Nankai University. I appreciate your great supervisor, guidance and assistance in my research work. Thanks to the significant environment and resources for experiment you provided.

I want to express my great appreciation to my parents! Thank you for the best childhood you give me and all your support in my life. You make me who I am and let me know who I want to be.

Finally, again, for all the people who supervised me, helped me, worked with me and shared the beautiful 5 years with me, thank you!

Papers

Appended papers

I. **Yu, H.**, Li, Y., Zhao, M., Dong, H., Yu, H.B., Zhan, S.H., Zhang, L., 2015. Energy-saving removal of methyl orange in high salinity wastewater by electrochemical oxidation via a novel Ti/SnO2-Sb anode-Air diffusion cathode system. Catalysis Today, v. 258, p. 156-161. http://dx.doi.org/10.1016/j.cattod.2015.04.030

II. **Yu, H.**, Zhao, M., Zhang, L., Dong, H., Yu, H.B., Chen, Z., 2017. Investigation and improvement of a novel double-working-electrode electrochemical system for organic matter treatment from high-salinity wastewater. Environmental Technology v. 38, I. 22, P. 2907-2915. http://dx.doi.org/10.1080/09593330.2017.1282543

III. **Yu, H.**, Zhang, X., Zhao, M., Zhang, L., Dong, H., Yu, H.B., 2019. Norfloxacin degradation by a green carbon black-Ti/SnO_2-Sb electrochemical system in saline water. Catalysis Today, v. 327, p. 308-314. https://doi.org/10.1016/j.cattod.2018.04.034

IV. **Yu, H.**, Dou, D.X., Zhang, X., Zhang, L., Dong, H., Yu, H.B., 2020. Degradation of Norfloxacin in saline water by synergistic effect of anode and cathode in a novel photo-electrochemical system. Journal of Cleaner Production, v. 242, article number: 118548. https://doi.org/10.1016/j.jclepro.2019.118548

V. **Yu, H.**, Zhang, Z., Zhang, L., Dong, H., Yu, H.B., 2021. Improved Norfloxacin degradation by urea precipitation Ti/SnO_2-Sb anode under photo-electro catalysis and kinetics investigation by BP-neural-network-physical modeling. Journal of Cleaner Production, v. 280, article number: 124412. https://doi.org/10.1016/j.jclepro.2020.124412

VI. **Yu, H.**, Dou, D.X., Zhao, J.Y., Pang, B., Zhang, L., Chi, Z.X., Yu, H.B., 2020. The exploration of Ti/SnO_2-Sb anode/air diffusion cathode/UV dual photoelectric catalytic coupling system for the biological harmless treatment of real antibiotic pharmaceutical wastewater. (Submitted to Chemical Engineering Journal, under review)

Author's contribution to appended papers

I. The author was responsible for experiment operation, data collection, data analysis, visualization and manuscript writing. The author and co-authors contributed together for conceptualization (ideas and novelty) and study plan. Co-authors also contributed significantly in study supervisor, paper review, paper adjustment and partly in experiment operation.

II. The author was the main contributor for experiment operation and data collection and analysis, visualization and manuscript writing. The author and co-authors contributed together for conceptualization (ideas and novelty) and study plan. Co-authors also contributed significantly in study supervisor, paper review, paper adjustment and partly in experiment operation.

III. The author was the main contributor for study plan, data analysis, visualization and manuscript writing. The author also contributed significantly for experiment operation and data collection. Co-authors contributed significantly for conceptualization together with the author. Co-authors also contributed significantly in experiment operation, data collection, supervisor, paper review and adjustment.

IV. The author was the main contributor for data analysis, visualization and manuscript writing. The author also contributed significantly for experiment operation and data collection. The author and co-authors worked together for conceptualization and study plant. Co-authors also contributed significantly in experiment operation, data collection, supervisor, paper review and adjustment.

V. The author was the main contributor for data analysis, visualization and manuscript writing. The author also contributed significantly for experiment operation and data collection. The author and co-authors worked together for conceptualization and study plant. Co-authors also contributed significantly in experiment operation, data collection, supervisor, paper review and adjustment.

VI. The author was the main contributor for conceptualization, experiment design and data analysis. The author also contributed significantly for experiment operation, data collection, visualization and manuscript writing. Co-authors contributed significantly in experiment operation, data collection, visualization, supervisor, manuscript writing, paper review and adjustment.

Abbreviations

HSW: High salinity wastewater
EC: Electrochemical catalysis
AOPs: Advanced oxidant processes
PEC: Photo-electro catalysis
PW: Pharmaceutical wastewater
DSAs: Dimensionally stable anodes
TSSA: Ti/SnO_2-Sb anode
ADC: Air diffusion cathode
EC-D: The new EC systems with duo working electrodes
PEC-D: The new PEC systems with duo working electrodes
MO: Methyl orange
NOR: Norfloxacin
CB-ADC: ADCs formatted by carbon black
AC-ADC: ADCs formatted by activated carbon
TS-CB: EC-D system with TSSA as anode and CB-ADC as cathode.
TS-AC: EC-D system with TSSA as anode and AC-ADC as cathode.
TS-SS: Single-working-electrode EC system with stainless steel mesh cathode
TS-Pt: Single-working-electrode EC system with Pt/C cathode.
SPC: Single photo catalysis
SEC: Single electrochemical catalysis
PEC-S/PEC-TS: PEC systems with a single working electrode
UTS: Urea precipitation prepared TSSA
PEC-UTS: PEC-D with UTS as anode

HER: Hydrogen evolution reaction

OER: Oxygen evolution reaction

ORR: Oxygen reduction reaction

CER: Chlorine evolution reaction

CRR: Chlorine reduction reaction

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1. Introduction

1.1 Background

High salinity wastewater (HSW) is characterized by high saline concentration (mainly NaCl) and massive organic matters. In the last decades, due to the development of technology and economy, the faster release of organic matters into the environment occurred with increasing HSW discharge from industries like dyeing, petroleum, leather, agro-food, pharmaceuticals, etc. and aquaculture (mariculture, etc.) (Boto, Almeida, & Mucha, 2016; Lefebvre, Vasudevan, Torrijos, Thanasekaran, & Moletta, 2005; Tahrani, Van Loco, Ben Mansour, & Reyns, 2016; Vitolo, Petarca, & Bresci, 1999; Yan, Du, Xu, & Liao, 2012). They may cause significant disturbance in the ecological systems, threatening all life's therein (Castillo-Carvajal, Sanz-Martin, & Barragan-Huerta, 2014; Vo et al., 2020). In particular, these organic matters may lead to biotoxicity, dyeing, risk of eutrophication, consumption of dissolved oxygen, etc. in the waterbody, which is relied by both human and other creatures. Therefore, the treatment (removal and degradation) of organic matters in HSW before discharge should draw global attention.

Several traditional methods including physical, chemical and biological processes have been widely studied for the organic matter degradation in wastewater (Lefebvre & Moletta, 2006). However, their limited degradation efficiencies (He et al., 2014) and other drawbacks have emerged during applications. By physical ways, effective remove of organic matters by destroying them, not just by phase transfer, are unable to be realized. Additionally, in chemical approaches, high energy consumption, high chemical reagent consumption and secondary pollution are usually found. Moreover, due to the refractory organic matters, biotoxicity and high saline concentration in HSW, the performance of the economic bio-treatments (activated sludge, etc.) stay low and unstable. Therefore, the development of new method for organic matter degradation in HSW is required.

Electrochemical catalysis (EC), a new member of advanced oxidant processes (AOPs), has emerged as a potential method for the degradation of organic matters in HSW. This is connected to its high efficiency, environmental compatibility, saving of energy/material and automation (Lyu et al., 2019; Oturan, Wu, Zhang, Sharma, & Oturan, 2013; Wu et al., 2012). Under EC, the assistance from outer chemical reagents is omitted. Instead, strong degradation agents (Cl_2/HClO/

•Cl/•OH, etc) can be in-situ produced from ions and compounds in water by catalyst and subsequently decompose organic matters. Therefore, the degradation route of EC can be enhanced by the rich ions and high conductivity, indicating its adaptability to the organic matter degradation in HSW.

The EC has been further improved by the assistance of photo catalysis recently (Hussain, Steter, Gul, & Motheo, 2017; Liu et al., 2013; X. Q. Wang et al., 2019). The new photo-electro catalysis (PEC) not only enhances the catalysis power by photo radiation, but also diversifies the degradation mechanism with synergistic effect between electro and photo catalysis. Potentials of organic matter degradation in HSW has been shown for both EC and PEC. However, the expensive raw materials and complicated craftmanship of catalyst for EC and PEC still retain as bottleneck. Moreover, the further improvement of degradation performance for both methods is also required before application.

This study aims to develop and evaluate new EC and PEC systems with economic raw catalyst materials, simple craftmanship, novel structures and high efficiency for organic matter degradation in HSW. Subsequently, new systems will yield high degradation performances and better environmental & economy sustainability.

1.2 Objectives

1. Initial development of a new EC system for organic matter degradation in HSW with double working electrode (Methyl orange as pollutant). (Paper I)
2. Improvement of the new EC system by formatting new metal-oxide-carbon electrode catalyst ((Methyl orange as pollutant). Investigation of critical factors and mechanisms for degradation performance (Paper II).
3. Initial application and evaluation of the new EC system for refractory antibiotics removal and degradation in HSW. (Paper III).
4. Development of new PEC system based on the EC system. Investigation of critical factors and mechanisms of the PEC system for antibiotics degradation in HSW. Development of the new model for the simulation and analysis of PEC degradation performance. (Paper IV).
5. Further improvement of the PEC system by new urea precipitation electrode catalyst. Further development of a new simple modelling for the simulation and analysis. Further investigation of critical factors and degradation mechanisms. Discussion on prospect of PEC system and study plan for future work. (Paper V).
6. Evaluate the effectiveness and performance of PEC-D method in real HSW treatment (Paper VI).

2. Theoretical background

Characterized by high concentration and various categories, organic matters in HSW lead serious threatens to both human and ecology, which require efficient removal and degradation before discharge. However, the traditional physical, chemical and biology treatment methods yield unsatisfactory results. EC and PEC techniques, as new member of AOPs, have shown their potential to address this issue. Despite the bright prospects of EC/PEC, the drawbacks of them need solutions and the degradation performance requires enhancement. Therefore, development and improvement of EC/PEC systems show their significant value.

2.1 Organic matters in HSW

Various industries and aquacultures, with their complex production processes, intensify and diversify the organic matters in HSW.

In food industry, massive protein, oil, fat, pigment as well as cleaning and disinfection agents are commonly included in saline wastewater. This is attributed to the production, cleaning, disinfection, refrigeration procedures in food industry (Krzeminska, Neczaj, & Borowski, 2015; Vaiano, Iervolino, Rizzo, & Sannino, 2017). In addition, when marine organisms are involved, seawater from dehydration is one significant source of organic matter and salinity.

Pharmaceutical wastewater (PW) contains complex organic components (Comoglu, Iscen, & Ilhan, 2016) mainly derived from chemical synthesis, fermentation, etc. These components include various chemical agents, stubborn organic matters and residual drugs, where fluorine, cyanide, phenol, and residual drugs, etc. are considered as highly toxic.

Dyeing process produces wastewater with rich residual dyestuff (Raman & Kanmani, 2016), various organic salts and organic acids, thereinto, dyestuff is as primary. In petroleum industry, the HSW is mainly corresponding to the refined processing, where petroleum is transformed to different products. oil, phenols, various fatty and aromatic petroleum hydrocarbons contributed to the organic composition indicating high toxicity and low degradability (B. Wang, Shui, Ren, & He, 2017).

Except industry, aquaculture also generates notable amount of HSW (Boto et al., 2016). These HSW contain excreta, nutrient ingredient (fodder, etc.), medications (antibiotics. etc.) as main organic matters.

Hazards of HSW to human and ecology are considered as manifold, they are distributed as below:

1. Toxicity: Toxic organic matters enter the body of aquatic organisms, threatening their life. Possible toxicity carriers like natural water, tap water, food, creatures and materials deliver toxic organics into human body during drinking, eating, touching, etc. Residual drugs enter bodies of human and other creatures, causing medication resistance of pathogenic microorganism.
2. Consumption of oxygen: Organic matters consume dissolved in water bodies, affecting the living of aquatic organisms, damaging ecological environment.
3. Coloured organic matters shield solar radiation after discharged into water body, impacting normal growth and activities of aquatic organisms.
4. Organic matters containing nitrogen and phosphorus enter water body, causing eutrophication and the following over-reproduction of algae and other plankton.
5. Due to these risks caused by the organic matters in HSW, efficient, stable, environmentally friendly and low−cost methods for the degradation work are needed before HSW discharge.

2.2 Traditional treatment methods

Recently, a number of traditional physical, chemical and biology methods have been attempted in HSW treatment, including flocculent precipitation, membrane treatment, aerobic treatment and anaerobic treatment, etc.

2.2.1 Flocculent precipitation

As a common physical method for water purification, flocculent precipitation separates suspended particles from water by flocculants such as polymeric ferric sulfate (PFS). After the polymerization driven by flocculants, the particles precipitate from water under gravity. This method has been involved in various removal work of organic matters from wastewater. In 2006, researchers reported 72% COD removal in landfill leachate by flocculent precipitation coupled with ozone oxidation (Ntampou, Zouboulis, & Samaras, 2006). In 2016, insoluble organic matter was treated in distiller's grain sewage with chitosan as flocculant, leading to in 84% COD removal ratio (Ferral-Perez, Bustillos, Mendez, Rodriguez-Santillan, & Chairez, 2016). In the HSW treatment, flocculent precipitation also yields considerable results. In 2003, 90% COD was removed in the wastewater from cuttlefish food processing industry, where poly-dimethyl ammonium chloride was as flocculent (Ellouze, Amar, & Salah, 2003). In 2014, another reported showed an effective degradation of organic matters in dyeing wastewater, rather than simple removal, when combined flocculent-precipitation-Fenton-oxidation applied (Rodrigues, Boaventura, & Madeira, 2014).

Overall, as a simple method, flocculent precipitation suggests a considerable removal efficiency for organic matters. Meanwhile, salinity leads to no significant effect to this physical method in HSW. However, the unavailability to soluble organic matters, the limited ability of degradation and the need of outer chemical reagents not only lower the treatment efficiency but also increase running cost and environmental burden.

2.2.2 Membrane treatment

Membrane treatment filters out bacteria, virus, suspended organic matters, etc. from water. As early as 2002, ultrafiltration membrane has been utilized to treat organic wastewater from seafood industry, with successful removal of suspended and colloidal organic matters (Afonso & Borquez, 2002). Another similar report showed a considerable removal of soluble solid particle from mariculture wastewater (Chiam & Sarbatly, 2011). Recently, in 2016, an advanced composite membrane technology was applied in petroleum industry wastewater treatment, resulting in 99% removal of COD and 94% removal of soluble solid particle, indicating high treatment efficiency of organic matters from HSW (Riley, Oliveira, Regnery, & Cath, 2016).

A high removal performance of organic matters can be achieved in membrane treatment, requiring no extra chemical reagents. However, the consumption, regeneration and replacement of membranes retain as severe issues. In addition, this physical method removes rather than degrades the organic matters. Therefore, efforts and budgets are still needed in further disposal.

2.2.3 Aerobic treatment

Aerobic treatment degrades organic matters in water by the metabolism effect on aerobic microorganisms, thereinto, the most common method is activated sludge process. Though, the salinity inhibits the normal growth and degradation work of microorganisms in aerobic treatment, it’s still possible to be used in organic matter treatment in HSW. Generally, microorganisms from salt-intolerant (best grow environment: 0-0.2% NaCl) to halophilic (best grow environment: 2.5-5.0% NaCl) can be cultured in water (Zhuang, Han, Bai, Zhuang, & Shim, 2010). However, despite the theoretical possibility, the tolerance to salinity is reported to be limited, with 5% of NaCl as highest (Dincer & Kargi, 2001). Meanwhile, salt tolerance of aerobic treatment can rapidly decrease when the high salt concentration in wastewater dropped. This leads to unstable efficiency. The toxicity of organic matters in HSW is another bottleneck of the application of aerobic treatment in HSW treatment.

2.2.4 Anaerobic treatment

Anaerobic treatment degrades organic matters to small molecular like CO and CH_4 by anaerobe. Rather than the simple removal, this method degrades organic matters in the water. Various researchers have reported successful application of anaerobic techniques in HSW. For instance, more than 70% COD removal by up-flow Anaerobic Sludge Blanket (UASB) can be obtained (Boardman, Tisinger, & Gallagher, 1995; Mosquera-Corral, Sanchez, Campos, Mendez, & Lema, 2001). In 2013, an anaerobic sequential batch reactor removed 99% COD and 96% VSS in returned sludge in mariculture (Luo, Li, Tan, Du, & Liang, 2013). However, the drawbacks have been also determined for anaerobic treatment. The UASB system was found only efficient in low organic matter loading (Lefebvre, Vasudevan, Torrijos, Thanasekaran, & Moletta, 2006). Meanwhile, with NaCl concentration> 2%, the treatment performance was significantly inhibited (Xiao & Roberts, 2010).

2.2.5 Summary for traditional methods

Traditional methods showed their effectiveness in organic matter removal/degradation in HSW. However, these methods lead to massive cost of energy and materials, instability, low efficiency and secondary pollution, etc. To address these issues, new treatment methods with higher efficiency, lower energy and resource cost and better environment sustainability are needed to be developed.

2.3 EC/PEC treatment

EC and PEC are regarded as new potential methods to degrade organic matters from water in recent years. This is due to their high efficiency, energy and material saving, environmental compatibility and automation, etc, as mentioned above. Rather than adding chemical reagents in water, these new techniques aim to transfer components in water to strong degradation agents (Cl_2/HClO/•Cl/•OH, etc.). Under electro/photo catalysis, redox reactions occur on the surface of electrodes (anode and cathode), the agents can be therefore formatted. Subsequently, the agents can decompose organic matter (*R*) into inorganic CO_2, H_2O, NH_4^+ (Eq. 1), etc, as shown in Fig. 1.

According to degradation mechanism, EC can be distributed to direct and indirect routes (Costa & Olivi, 2009; Jia, Zhang, Zhang, & Zhou, 2008).

$$Agents + R \rightarrow intermediate \rightarrow CO_2 + H_2O + NH_4^+ \quad (1)$$

In direct route (Fig. 1 (a)), organic matters diffuse to anode surface driven by concentration gradient. They are then degraded by attached agents on the surface, where •OH is the most common agent for use and study (Eq. 2). This is due to its high reaction activity and non-preference in the degradation processes, leading to high performance for multifarious organic matters in water. The dimensionally stable anodes (DSAs) perform as catalyst for •OH production, which are the core part of EC system. DSAs are commonly formatted by noble metals and their oxide like Pt, RuO, IrO and boron-doped diamond (BBD), efficient degradation of organic matters has been determined by these anode materials for direct route (Ganzenko, Huguenot, van Hullebusch, Esposito, & Oturan, 2014).

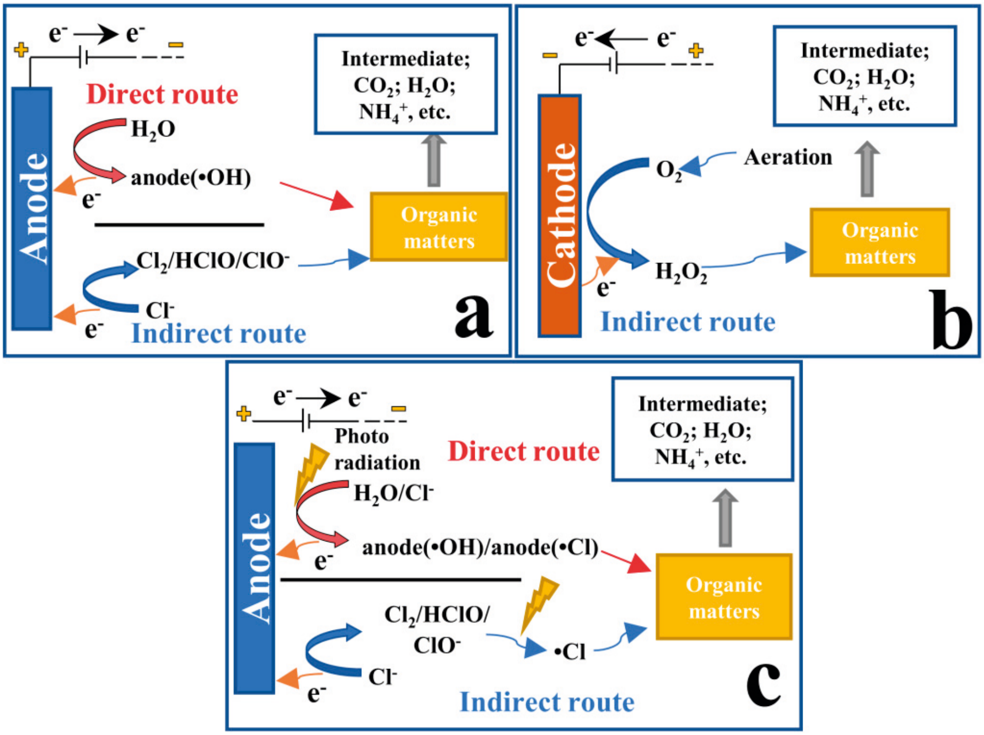

Fig. 1. Schematic diagrams of (a) direct and indirect degradation routes on anode under EC; (b) indirect degradation route on cathode under EC; (c) direct and indirect degradation routes on anode under PEC.

The indirect route (Fig. 1 (a) and (b)) is distributed into anode indirect route (AIR) and cathode indirect route (CIR), according to the variety of working electrode. In

AIR, the produced degradation agents diffuse from DSAs surface to the entire waterbody. They oxide and decompose the organic matters via electron transformation. Active chlorine (Cl_2/HClO/ClO^-), the most typical agent in AIR, was formatted from Cl^- via chlorine evolution reaction (CER) during EC (Eq. 3-5). AIR has been widely attempted in HSW treatment. In 2005, Ti/RuO_2–TiO_2, a DSAs, has successfully removal microcystin by produced active chlorine (Shi, Qu, Wang, & Ge, 2005). In 2009, 100% of removal ratio for glyphosate was obtained when initial Cl^- concentration reaches 2662 mg L^{-1}, with RuO/IrO_2 as working anode (Neto & De Andrade, 2009). In 2011, refractory organic matters in reverse osmosis water were completely removed by AIR with Ti/IrO_2-RuO_2 as working anode, the adaptability of AIR to wide range of pH value was also found (M. H. Zhou, Liu, Jiao, Wang, & Tan, 2011). In CIR, the degradation work is usually corresponding to the H_2O_2 transferred from O_2 via oxygen reduction reaction (ORR) under EC. The O_2 derives from cathode aeration or cathode air diffusion from environment. 2,4-dichlorophenol has been efficiently degraded by generated H_2O_2 under EC on Pd-graphene air diffusion cathode (H. Wang & Wang, 2009). H_2O_2 can be further transferred to stronger agent like •OH under further stimulations. In 2015, a report showed further transformation to •OH from H_2O_2 after reaction with O_3. The obtained •OH degraded 1,4-dioxane completely (Huijiao Wang et al., 2015). However, the adding of O_3 leads to the cost of resource. Electro-Fenton method, another member of CIR, solves this issue, which transfers H_2O_2 to •OH by Fe^{2+} as catalyst. In 2010, electro-Fenton has been studied for the degradation of dyeing wastewater with active cathode, showing 70% COD removal (C.-T. Wang, Chou, Chung, & Kuo, 2010). In 2015, new graphene was used to upgrade the cathode material, resulting in higher generation rate of H_2O_2 and faster degradation (Thi Xuan Huong et al., 2015).

$$H_2O \xrightarrow{electric\ field} \bullet\, OH + e^- + H^+ \tag{2}$$

$$2Cl^- - 2e^- \rightarrow Cl_2 \tag{3}$$

$$Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O \tag{4}$$

$$H^+ + ClO^- \rightarrow HClO \tag{5}$$

Similarly, the PEC also owns direct and indirect degradation routes (Fig. 1 (c)). Meanwhile, it has shown even more potential than the individual EC upon organic matter treatment. The EC and photo catalysis (PC) can both yield electron transformation and emission, leading to the following degradation with organic matters. Therefore, the enhancement of performance with coupled PEC becomes possible. In particular, the high conductivity of the saline wastewater inspires the application of photo-electro catalysis technology. Pollutant degradation mechanisms in the photo-electro catalysis system include indirect oxidation in electrolyte and direct adsorption-oxidation on electrode surface. In the indirect route, the active chlorine (Cl_2/HClO/ClO^-) is generated rapidly in high salinity wastewater under electrochemical catalysis, which can be further transferred to stronger oxidant agents (•Cl, •O^-, •OH, etc.) by the photo-excited holes (hv) (Eq. 6-8) (Ye, Zhang, Zhang, & Zhou, 2016). On the other hand, electric field force enhances photo-driven free radical generation (Eq. 9) by accelerating the separation of photo-excited electrons from hv (Ayoubi-Feiz, Mashhadizadeh, & Sheydaei, 2019; Re et al., 2018). In direct process, the free radicals formatted on the electrode surface decompose the organic matters adsorbed (Eq. 10 and 11) under photo-electro catalysis. Besides, various free radicals can transfer to each other (Eq. 12).

$$ClO^- + hv \rightarrow \bullet Cl + \bullet O^- \tag{6}$$

$$HClO + hv \rightarrow \bullet OH + \bullet Cl \tag{7}$$

$$Cl_2 + hv \rightarrow 2 \bullet Cl \tag{8}$$

$$H_2O + hv \xrightarrow{electric\ field} \bullet OH + e^- + H^+ \tag{9}$$

$$MO + H_2O + hv \xrightarrow{electric\ field} \mathrm{MO}(\bullet OH) \tag{10}$$

$$\mathrm{MO}(\bullet OH) + R \rightarrow MO + CO_2 + H_2O \tag{11}$$

$$\mathrm{MO}(\bullet OH) + Cl^- \rightarrow \mathrm{MO}(\bullet Cl) + OH^- \tag{12}$$

Overall, various EC and PEC own potential for organic matter treatment in HSW. However, the severe issues of these techniques should not be ignored. In EC direct degradation, as its adsorption-degradation of organic matter on anode surface, the performance is limited significantly by the surface area and diffusion speed. In AIR, this issue is solved by the diffusion of the degradation agents to the entire water body. However, the degradation performance is still limited when dealing with refractory organic matters. The CIR is considered as cleaner process as it produces H_2O_2, rather than active chlorine. However, the activity of simple H_2O_2 is limited, which needs further transformation to •OH by electro-Fenton. However, the efficiency of electro-Fenton is also relied on the Fe^{2+} concentration and pH value. PEC showed higher efficiency for degradation than EC. But EC and PEC techniques own a common issue of expensive raw materials for anode and cathode, including noble metals (Pt, Au, Ag, Ir, etc.), noble metal oxide (RuO_2, IrO_2, etc.) and new carbon materials like reduced graphene. Besides, in common EC and PEC systems, only one side of electric system (anode or cathode) works as degradation contributor. Few of them considers the synergistic work of both side to enhance the performance, which is a significant waste of electric quantity and energy.

Therefore, for the organic matter treatment, development of novel EC and PEC systems with low cost raw materials and new structures are required. In these systems, the issues in traditional EC and PEC systems should be addressed.

2.4 Development of new EC and PEC systems in this study

Both EC and PEC have shown the potential for the organic matter degradation in HSW. However, before the application, their issues should be addressed and their degradation efficiency should be further improved. Therefore, the development of new EC and PEC systems emerges as necessity.

For this purpose, the theory of new systems should be firstly established. After investigation, the current EC and PEC systems are found only focusing on one side of the electrodes (anode or cathode), ignoring the synergistic work of both electrodes. This leaves us the space to further develop the EC and PEC by utilizing both anode and cathode as working electrodes.

In the EC process, oxidation reaction occurred on anode resultes in active chlorine (Cl_2/HClO/ClO^-). On cathode side, the dominated hydrogen evolution reaction (HER) generates insoluble H_2, with zero contribution to degradation. However, when cathode surface contacts with enough O_2, the HER can be replaced significantly by OER, resulting in the reduction from O_2 to the degradation agent H_2O_2. The degradation efficiency is expected to be lifted if combined production of active chlorine and H_2O_2 on anode and cathode, respectively, can be obtained.

In the PEC systems, EC produced active chlorine on anode surface can be further transferred to stronger oxidant agents (•Cl, $•O^-$, •OH, etc.) by the photo-excited holes (hv), as mentioned in Section 2.3. Meanwhile, the direct production of •OH and its reaction with organic matters should not be ignored. On cathode side, we also found a possible decomposition from EC produced H_2O_2 into •OH under photo radiation (Eq. 13). Therefore, the further generation of free radicals by photo catalysis after EC on both electrodes can be expected.

$$H_2O_2 + hv \rightarrow 2 \bullet OH \tag{13}$$

To establish double-working electrode system for both EC and PEC, the electrode materials should be studied and selected.

On anode side, the requirement of materials includes high efficiency of active chlorine production, high photo reaction activity and low cost. Among all DSAs, a new Ti/SnO_2-Sb anode (TSSA) has drawn attention for the electrochemical degradation of organic matters in wastewater. This is due to its high electrochemical activity (Mu et al., 2019), cost efficiency (Mora-Gomez, Ortega, Mestre, Perez-Herranz, & Garcia-Gabaldon, 2019) and large gap between required chlorine and oxygen evolution potentials (Y. Wang, Shen, Zhang, Zhang, & Yu, 2016). As a semi-conductive material, TSSA can be also expected as high-photo-sensitive, therefore, it was a suitable option for anode in this study.

On cathode, to transfer O_2 into H_2O_2 with no energy-cost O_2 supply from aeration, an air diffusion material is needed. In this case, we selected a novel air diffusion cathode (ADC) with separated catalysis layer (CL) and diffusion layer (DL). Formatted by low-cost carbon materials, this cathode has shown an efficient adsorption of O_2 from environment into waterbody a previous work (Dong, Yu, Wang, Zhou, & Feng, 2012). The schematic diagram of the new EC and PEC systems with duo working electrodes (EC-D and PEC-D) is as shown in Fig. 2.

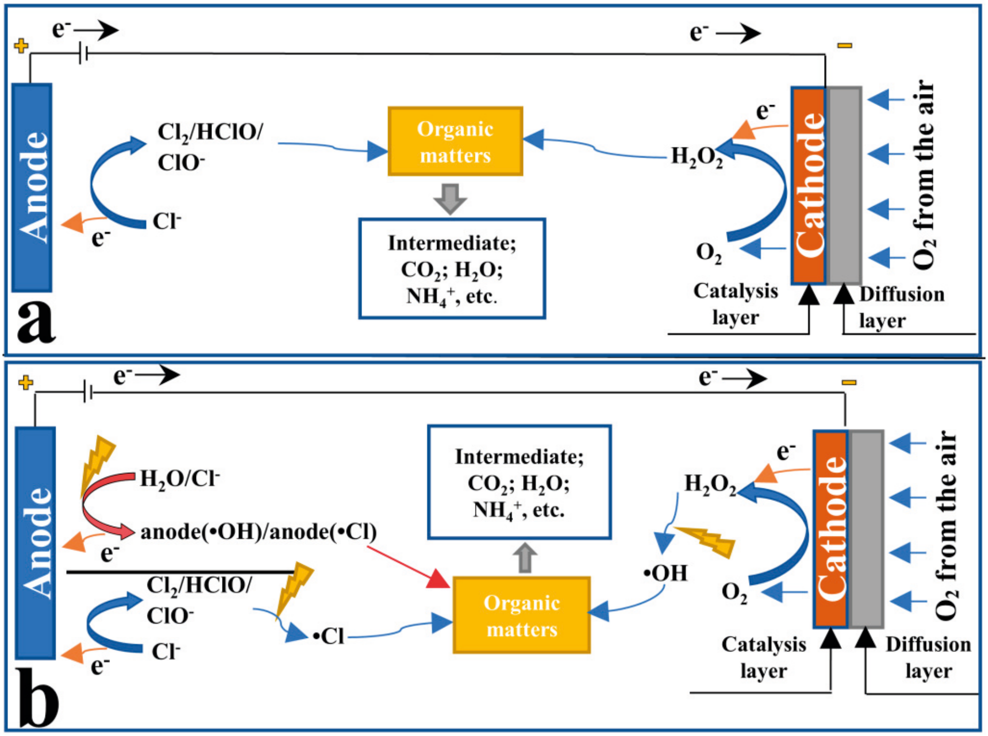

Fig. 2. The schematic diagrams of new EC (a) and PEC (b) systems with duo working anode and cathode.

This study aims to develop, evaluate and improve new EC and PEC systems for organic matter degradation in HSW. TSSA and ADC are expected to work simultaneously as degradation contributors. The degradation efficiency was evaluated, the mechanisms and kinetics were determined, the modelling were explored. The catalyst materials and system structures were investigated and developed.

3. Method and material

3.1 Selection of target pollutant

Massive organic matters in various categories have been detected in HSW and lead to severe risk for human and environment. For study purpose, typical organic matters should be selected as representatives for the evaluation of degradation performance. In this case, we selected two typical organic matters widely existed in HSW. Meanwhile, to further evaluate the potential of EC/PEC systems for real application, a real high salinity antibiotic pharmaceutical wastewater (PW) was employed. They are discussed as follow.

Methyl orange: As their stability and toxicity, azo dyes in saline dyeing wastewater have shown threaten to environmental and resistance to traditional bio-treatment (Chen, Liu, Yu, Yin, & Li, 2008; Gong & Cai, 2007). Accordingly, the treatment of them has drawn global attention for research with various treatment methods attempted. Among these methods, AOPs, including UV/H_2O_2, Photo degradation, Fenton, etc. have shown high performance and bright prospect (Chen et al., 2008). The removal and degradation performance of the new systems designed in this study induced our interest. Therefore, methyl orange (MO), as a typical azo dye, was selected as a target organic pollutant in HSW for degradation test in this study.

Norfloxacin: Norfloxacin (NOR) is one of popular antibiotics widely used both for human cure and animal breed, owing to its strong effect against bio-infection (Chen et al., 2018; Li et al., 2018a; Li et al., 2018b;Wang et al., 2018b; Zhou et al., 2018). Inevitably, the residual antibiotics are found in the corresponding saline wastewater such as production wastewater and effluent of marine aquaculture (Boto et al., 2016; Shi et al., 2018; Tahrani et al., 2016). Unfortunately, the enrichment of the antibiotics in the ecosystem will cause serious issues (Cheng et al., 2018; Dong et al., 2018), including killing effective nature microorganisms, developing antibiotics resistance for bacteria, etc (Jiang et al., 2018; Mora-Gomez et al., 2019). Therefore, the wastewater with antibiotics must be properly treated before they are discharged to the natural environment. Same as the case of MO, bio-treatment has insufficient degradation capacity for refractory antibiotics (such as Norfloxacin) (Tao et al., 2018; Tegze et al., 2018), due to the stable molecular structure and huge biotoxicity. Moreover, the high saline concentration in HSW challenges the adaptability of biotreatment (Liu et al., 2018a; Maeng et al., 2018; Wang et al., 2018a). Overall, as its wide existence, stability and toxicity, it's meaningful to study the NOR degradation performance of the new EC and PEC systems.

PW: To further investigate the new systems in the real applications, a real antibiotic PW was used in this study. It was obtained from an antibiotic pharmaceutical factory which mainly produces cefotiam (CTM, $C_{18}H_{23}N_9O_4S_3$) and 7-phenylacetamide-3-chlorormethyl-3-cepham-4-carboxylic acid p-m-ethoxybenzyl ester (GCLE, $C_{24}H_{23}O_5N_2SCl$). In the process of CTM and GCLE synthesis and wastewater production, antibiotic pharmaceutical wastewater comes from various links in the synthesis process, which leads to the complex composition of antibiotic pharmaceutical wastewater. This PW is suitable for the evaluation of the adaptability and degradation performance of EC/PEC systems in real HSW with complex contents.

3.2 Experiment processes

3.2.1 Experiment design

The design of study follows to principle of controlled factor experiment. In one series of experiment, the value/condition of one parameter changed with others fixed. To avoid unexpected bias, degradation efficiency with no catalysis applied performed as background. Before application, the formatted anode and cathode materials were firstly tested for their physical, electro-chemical and photo characteristics. This is for the determination of their components, structures and activities. The target organic pollutants with certain electrolyzes were used as simulated wastewater. Samples were collected at certain times during the running of experiment. Subsequently, the degradation performances in various conditions was determined by pollutant concentration, COD and TOC tests. The measurements of assumed degradation agents were also conducted. In this work, the studied parameters including different systems (EC/PEC with single or duo working electrodes), different anode and cathode materials, critical effect factors as pH, current density, pollutant concentration, electrolyze, etc.

After the experiment, the degradation performances, mechanisms and behaviours were further explored by mathematics approaches, including statistics, first-order and second-order physical models and neural networks. The results were discussed comprehensively with characteristics tests for materials and detection of degradation agents. As a result, the final conclusions and explanations were figured out.

3.2.2 Reaction system in experiment

In this work, the reaction systems were established to remove and degrade organic matters in simulated HSW, with EC and PEC systems involved. The EC system for electrochemical degradation showed basic structure and concept (Fig. 3). Necessary re-design was conducted in synergistic photo-electro catalysis.

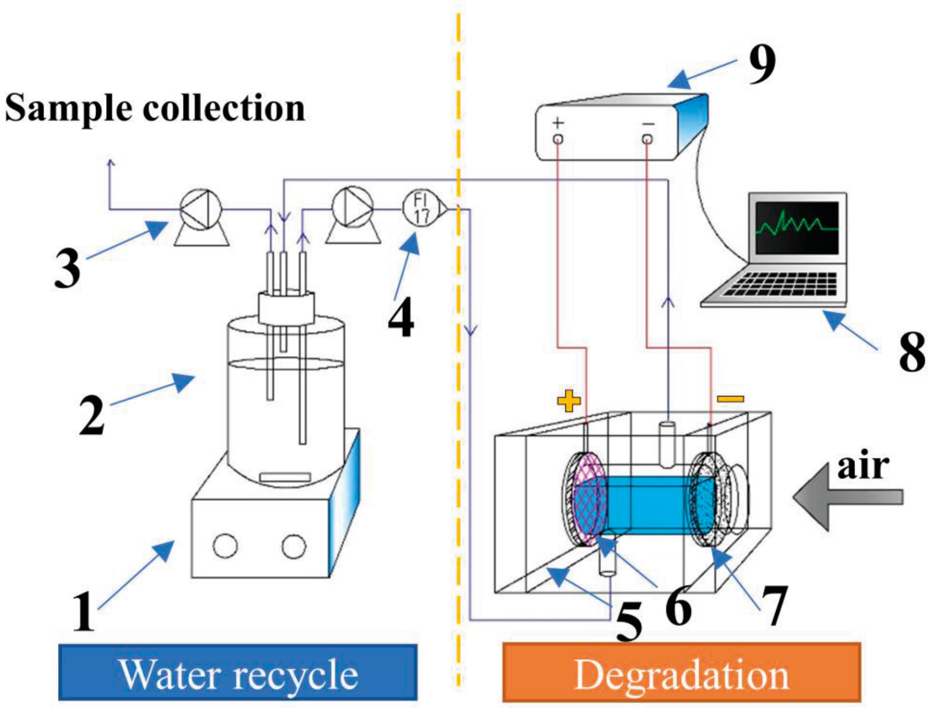

Fig. 3. Schematic diagram of the EC reaction system in this study. (1. Magnetic stirrer; 2. Wastewater (electrolyte); 3. peristaltic pump; 4. Fluid flowmeter; 5. EC reactor; 6. TSSA anode; 7. Air diffusion cathode; 8. Personal computer; Constant power source.)

The reaction system was distributed into two parts according to their functions: (1) water recycling and sampling part, including eristaltic pump, brown bottle, magnetic stirrer, liquid flow meter and soft hose, etc. This part worked for liquid flowing in and out of reactor with designed rate, as well as sampling. (2) degradation and recording part, formatted by anode, cathode, reactor module, constant power source and computer, responsible for organic matter degradation and monitoring.

In dynamic experiment, before start, the HSW in bottle was pumped into reactor until it was fulfilled. The power source was settled to a designed current density and linked to anode and cathode, with a certain flowrate settled on eristaltic pump. The experiment was started by switching on power source and peristaltic pump. The catalysis and degradation began with HSW circulation between reactor and storage bottle. In static test, the HSW flowing was cancelled, with only degradation and recording part left, as shown on the right side in Fig. 3.

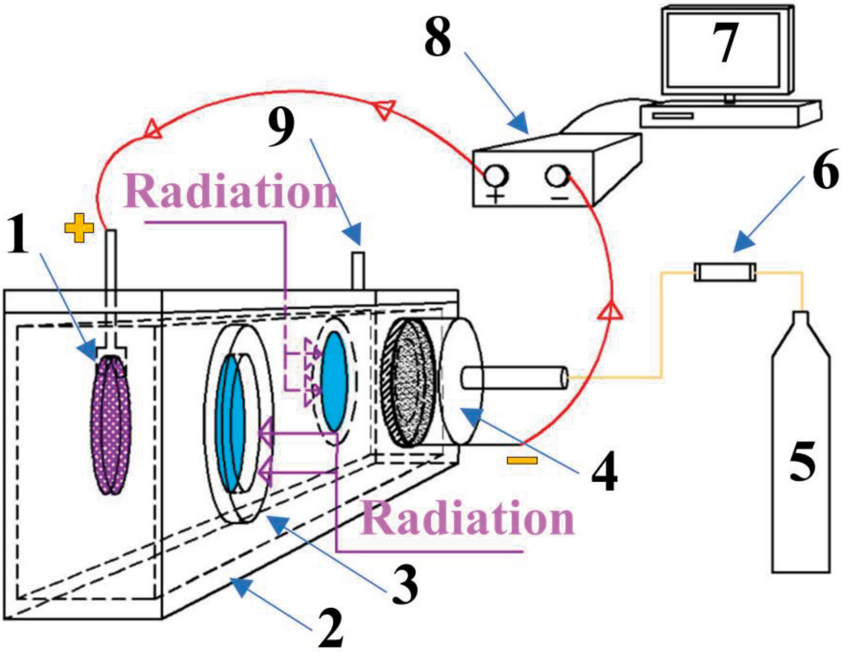

Fig. 4. Schematic diagram of the PEC reaction system in this study. (1. TSSA anode; 2. PEC reactor; 3. Quartz glass; 4. Air diffusion cathode and its chamber; 5.O_2 gas holder; 6. Gas flowmeter; 7. Personal computer; 8. Constant power sourcer; 9. Sampling port.)

In PEC system (Fig. 4), due to the involvement of photo radiation, the reactor was re-designed. Briefly, a PTFE cuboid reactor (11.1 cm×5.0 cm×8.1 cm) was designed with cathode and anode settled on diagonal positions. Two circle quartz glasses with diameter of 3.6 cm were located on the opposite sides against the two electrodes, respectively, for the light transmission. On the cathode side, a cylindroid gas chamber outside the cathode was used for the storage of O_2 which could diffuse into CL through DL of the cathode. The diagonal settlement allowed the direct UV radiation onto the two electrodes simultaneously through the quartz glass, subsequently accelerated the production of oxidant agent in the reactor. In PEC system, a solar simulator with visible light filter was employed for photo radiation, providing UV light with wavelength between 200 to 390 nm. The solar simulator was warmed up for 15 min to guarantee the stable radiation before the experiment. The launching, sampling and monitoring of experiment was the same as in EC system. The pictures of corresponding materials and apparatuses in EC and PEC degradation in this study were as shown in Fig. 5.

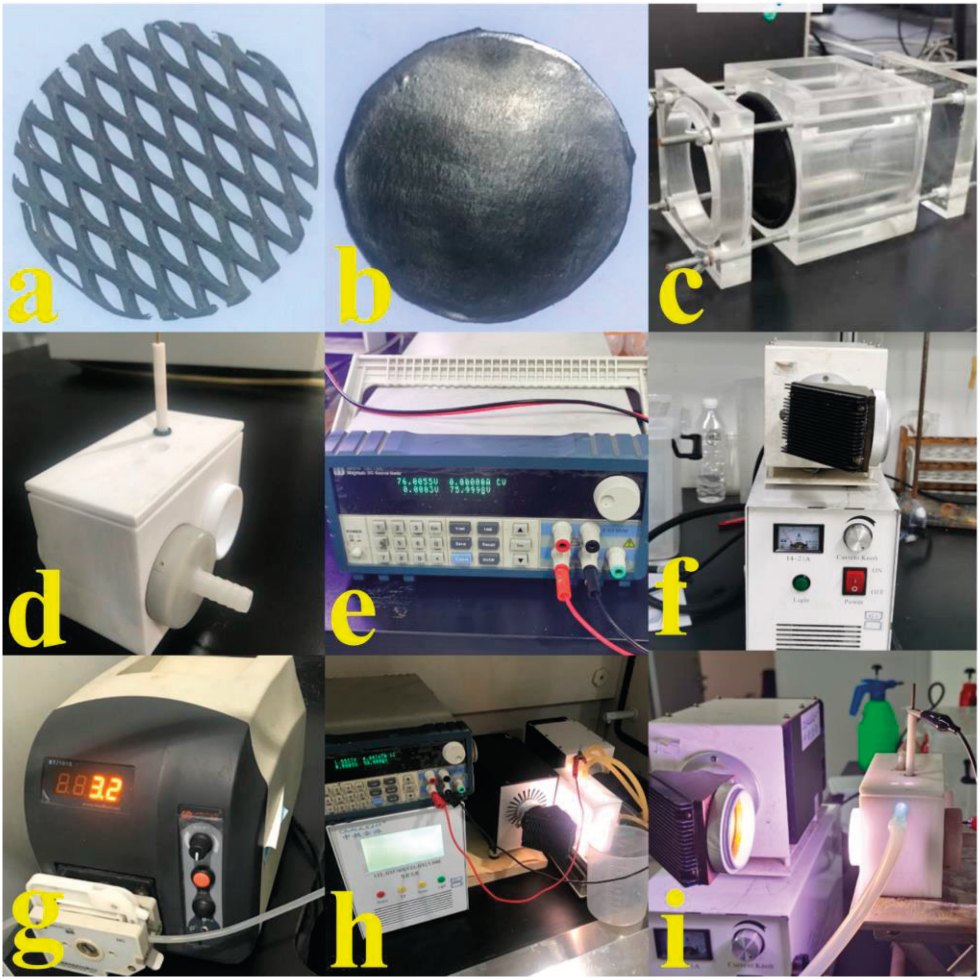

Fig. 5. The pcitures of corresponding materials and apparauses in EC and PEC degradation work. ((a) TSSA anode; (b) Carbon black air diffusion cathode; (c) EC reactor; (d) PEC reactor; (e) Constant power source; (f) UV light source; (g) Peristaltic pump; (h)-(i) The ongoing experiments of photo-electro degradation.)

3.3 Characteristics and measurement

3.3.1 Physical, electrochemical and photo characteristics for electrodes

The phase composition of electrodes was tested by X-ray diffraction with Cu Ka (XRD, Ultima-IV 185, Rigaku., Japan). The chemical states and surface composition were examined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific., USA). While a scanning electron microscopy (SEM, S-3500N, Hitachi, Japan) was employed for investigating the morphology of the electrode materials. The molecular structure and chemical bond were determined by an infrared spectroscopy (TENSOR 37, BRUKER, German). The photo/electrochemical catalysis activities of the anode including cyclic voltammetry (CV), linear sweep voltammetry (LSV), Electrochemical Impedance Spectroscopy (EIS) and photo-current test were determined by electrochemical working station (CHI660D, Chenghua., China) coupled with a solar light simulator (CEL-HXUV300, Jiaojin., China).

3.3.2 Components measurement in wastewater

The free chorine was measured by two methods: (1) N,N-diethyl-p-phenylenediamine (DPD) method using 1 g $L^{-1}$of DPD solution and phosphate buffered solution (pH 6.5), measured by a visible spectrophotometer (T6 Xinrui, Puxi., China) at a wavelength of 515 nm; (2) a free chorine analyser (INST.38, Palintest., Britain). The concentrations of H_2O_2 were determined using potassium titanium (IV) oxalate method (Sellers, 1980) by the same visible spectrophotometer at a wavelength of 400 nm. An electron spin resonance (ESR) apparatus (MiniScope-400, Magnettech., German) was employed for the investigation of the possible created •OH during the experiments, with 5,5-dimethyl-1-pyrroline n-oxide (DMPO) as scavenger. pH value of the electrolyte was monitored using a pH supervision instrument (Rex PHS-3C, INESA., China).

The TOC concentration in the electrolyte was determined by a TOC analyser (TOC-VCPH, Shimadu., Japan). The biodegradability was evaluated by the synthesis working of a COD analyser (5B-3F, Lian-Hua Technology., China) and a BOD analyser (LY-1A, LvYu Environment., China). MO concentrations were analysed directly at a wavelength of 464 nm with visible spectrophotometer. A high performance liquid chromatography (HPLC,1200 series, Agilent., USA) was employed for the measurement of NOR concentration at wavelength of 274 nm, with 0.05% (v/v) Phosphoric acid/acetonitrile as mobile phase (chromatographic column: Eclipse XDB-C185 mm 4.6 _ 150m). The degradation intermediate products were detected by a HPLC-Mass (Xevo TQ-S, Water., USA) in positive ionization mode, with N_2 flow rate of 11 L min^{-1}. The anions concentrations in electrolyte were determined by ion chromatography (ICS 5000, ThermoFisher., USA, detector: As110HC) with 3.54 g L^{-1} KOH as mobile phase and flowrate of 1.2 mL min^{-1}. In addition, ICP-OES (ICP Optima 8300, PerkinElmer., USA) was employed for the measurement of cations concentration in the electrolyte.

3.4 Analysis

3.4.1 Statistics

In this study, to better investigate the mechanisms, features and relations between various factors in the catalysis processes, two statistics methods, grey relation analysis (GRA) and principal component analysis (PCA), were involved in data analysis. This is due to their abilities to show influence degree between parameters and determine the main behaviours in the reaction system. GRA is to measure the relation quantities of factors (G. L. Zhou, 2009), the change of grey correlation degree value reflects the change of relation between these factors. In particular, the involved data was standardized before calculation. The two sequences of data were then calculated for their minimum and maximum differences firstly, as shown below:

$$Max = \max\left(|V_{1\mathrm{i}} - V_{2\mathrm{i}}|\right) \tag{14}$$

$$Min = \min\left(|V_{1\mathrm{i}} - V_{2\mathrm{i}}|\right) \tag{15}$$

Where Max and Min referred to the maximum and minimum values of the difference between one value in the first sequence (V_1) and its corresponding value in the second sequence (V_2). The i is the position of the value in one sequence of data.

The correlation coefficient of each pair of value was shown as below:

$$k_{\mathrm{e}} = (Min + k_r * Max)/(|V_{1\mathrm{i}} - V_{2\mathrm{i}}| + k_r * Max) \tag{16}$$

k_{e} referred to the correlation coefficient with k_{r} represented the resolution degree of the calculation. k_{r}, in the range of 0-1, is usually valued as 0.5. The correlation degree values are distinguished better with lower k_{r}.

The final grey correlation degree was determined by calculating the average of each correlation coefficient.

$$k_{\mathrm{g}} = \frac{1}{m}\sum_1^m (k_{\mathrm{e}}) \tag{17}$$

Where k_g was the grey correlation degree, *m* referred to the number of values in the corresponding sequence of data.

PCA was conducted for the determination of main effect factors in the reaction system as well as showing the relationships between factors visually. PCA is a statistic method for simplification of data set. In this work, factors like degradation efficiencies in various systems, active chlorine concentration, hydrogen ions concentration and NOR concentration were involved in PCA analysis.

3.4.2 Modelling

In this work, the modelling mainly focused on the reaction kinetics to evaluate the degradation performances, mechanisms and contributions of various agents during degradation processes. The classical first and second order laws in reaction kinetics were as the basis:

$$R_1 = k_{\text{fir}}[C] \tag{18}$$

$$R_2 = k_{\text{sec}}[A][C] \tag{19}$$

Where R_1 and R_2 referred to the reaction rate of first and second order laws, respectively. k_{fir} (min^{-1}) was the reaction coefficient of first order law, with k_{sec} (min^{-2}) represented to the coefficient of degradation agent *A* to the pollutant *C*. The bracket referred to the concentration of a certain component.

In this work, we aimed to study the degradation performance by various electrodes (anode and cathode) and various routes (direct and indirect). For a better description, NOR degradation by due anode and cathode was taken as example. The degradation performance was represented by TOC removal ratio.

$$C/C_0 = exp(-k_{\text{f}} * t) \tag{20}$$

Where *C* and C_0 refer to real-time and initial TOC concentrations (mg L^{-1}) respectively. *t* is the experiment running time (min).

In the cathode side, when assuming the generation of •OH from H_2O_2, the •OH generation ratio can be expressed as below:

$$C_1' = k_2 \int k_1 - 0.5 * C_1' \, dt \tag{21}$$

Resulted in:

$$C_1' = -(0.5 * k_1) * \exp(-0.5 * k_2 * t) + 0.5 * k_1 \tag{22}$$

Where C_1' is the •OH generation rate (mg L^{-1} min^{-1}), k_1 refers to the H_2O_2 generation rate (mg L^{-1} min^{-1}), with the constant stable current density, UV light source and oxygen supply. In addition, k_2 (min^{-2}) refers to the second order reaction coefficient of the transformation from H_2O_2 to •OH.

The degradation kinetic equations followed the second order law as shown below:

$$C_2' = k_3[\bullet\ \mathrm{OH}] * [TOC] \tag{23}$$

Where C_2' referred to the degradation rate (mg L^{-1} min^{-1}) of NOR, k_3 is the second order coefficient in the NOR degradation reaction. [•OH] and [NOR] refer to the concentrations of •OH and NOR in the solution, respectively. However, •OH would transfer and disappear instantly as its high reaction activity. Hence, the accumulation of •OH in the solution should not be expected and the concentration should be consistent to the generation rate C_1'.

As a result, the equation can be expressed as follows:

$$-C_2' = k_3[-(k_1) * \exp(-0.5 * k_2 * t) + k_1] * [TOC] \tag{24}$$

On the other hand, on the anode side, Eq. 3-5 and Eq. 6-9 may take place before degradation. Compared to the two steps generation of •OH on cathode from O_2, the generation of free radicals on anode can be considered as one step reaction. This is because the electrochemical and photo radiation enhance the oxidation reaction on anode together, resulting in the production of free radicals directly. Whereas, on cathode side, the electrons charged to cathode surface interrupted the direct generation of holes on it, the free radicals are more likely transferred from H_2O_2 produced by EC. Therefore, the photo- electro catalysis on anode can be integrated as one process, represented by a total coefficient of s (mg L^{-1} min^{-2}). This differed the expressions of anode and cathode degradation processes in formulas, by which the contribution of anode and cathode on degradation can be distinguished.

The kinetic equation can be then descripted as below:

$$C_2' = s * [TOC] \tag{25}$$

Subsequently, for simulating the interruption and competition between anode and cathode of reaction with NOR, the characteristics of anode and cathode reaction would participate in the final equation in the coefficient mode, by which the competition and interruption of NOR degradation from both sides would be included. The entire equation can be expressed below:

$$-C_2' = [-(k_1 k_3) * \exp(-0.5 * k_2 * t) + k_3 k_1 + s] * [TOC] \tag{26}$$

Resulted in:

$$C_2 = -C_0 * exp[-2(w/k_2) * e^{(-0.5*k_2*t)} - w * t - s * t + 2(w/k_2)] \qquad (27)$$

Where w=k_1*k_3, C_0 refers to the initial TOC concentration (mg L^{-1}) in the solution before the experiment. After simulating experiment data by Eq. 27, the contribution of anode and cathode side for the entire degradation can be therefore distributed.

When considering the possible changes of coefficient values due to the complexity of degradation system, differential equations can be employed for the simulation work.

This was conducted to evaluate the degradation performances of direct and indirect routes in this work.

For direct route, first order law was applied:

$$C_2' = k_1[TOC] \qquad (28)$$

$$\Delta k_1 = \Delta k_{\mathrm{f}} - \Delta k_{\mathrm{b}} + \Delta k_{\mathrm{ad}} + \Delta k_{\mathrm{cg}} \qquad (29)$$

Where C_2 is the concentration of TOC as mentioned above. k_1 is the net kinetic coefficient of the direct degradation (min^{-1}). However, k_1 can't retain constant because of the influence from gradients of forward reaction (Δk_f), backward reaction (Δk_b), attenuation of adsorption ability (Δk_{ad}) and concentration gradient (Δk_{cg}).

For indirect degradation, second order law was conducted because of the accumulable oxidant agent reacting with NOR:

$$C_2' = k[\bullet \mathrm{Cl}][TOC] = x[TOC] \qquad (30)$$

Where [•Cl] is the concentration of •Cl (mg L^{-1}), with k as second order coefficient (L mg^{-1} min^{-1}). To reduce the number of coefficient and simplify the system, k and [•Cl] was intergraded as x (min^{-1}), an equivalent concentration of •Cl. The accumulation rate was represented by the follow equation:

$$\Delta(Dx/Dt) = \Delta k_{\mathrm{f2}} - \Delta k_{\mathrm{b2}} + \Delta k_{\mathrm{dr}} + \Delta k_{\mathrm{rs}} = \Delta k_2 \qquad (31)$$

Where Dx/Dt (min^{-2}) refers to the net accumulation rate of x, affected by gradients such as forward reaction (Δk_{f2}), backward reaction (Δk_{b2}), consumption by degradation reaction (Δk_{dr}) and recombination/side reactions (Δk_{rs}) (Eq. 32 and 33). This accumulation rate was finally summarized into one coefficient k_2 (min^{-2}), which expressed the net accumulation rate of the equivalent value of •Cl concentration.

$$\bullet Cl + \bullet Cl \rightarrow Cl_2 \qquad (32)$$

$$\bullet \mathrm{Cl} + O_2 \rightarrow ClO_2 \qquad (33)$$

For both k_1 and k_2, the values of detailed gradients are inconstant. Besides, their relationship with time retains unclear. This made the integration of the final equation (Eq. 34) impossible.

$$DC/Dt = (k_1 + x)[TOC] \qquad (34)$$

Therefore, kinetics was simulated by fitting the data with differential equation group (Eq. 28, 30 and 34).

Besides physical models, artificial neural network (ANN) was also employed in this work for prediction purpose. In experimental research, the limitation of data scale is always inevitable, which interrupts further analysis by modelling. Therefore, a proper method for simulation and data enrichment emerges as necessity. Unlike physical models, ANN provides satisfied simulation in many areas with no need of theoretical equations. In the area of organic matter treatment by AOPs, ANN has proved its competence for analysis and prediction work in electro-Fenton (Alavi et al., 2019; Radwan, Alalm, & Eletriby, 2018), photo-Fenton (Tolba et al., 2019) and pure electro catalysis (Basha et al., 2010; Belkacem, Bouafia, & Chabani, 2017). In this study, a back propagation (BP) ANN was employed for the simulation for degradation ratio in photo-electro catalysis process before the physical model being conducted. A combined BP-ANN-physical modelling process (BP-ANN-P) was used for the simulation, modelling and analysis of degradation performance.

4. Results and discussions

4.1 Degradation performance of new EC systems

This section aims to investigate the performance of MO/NOR degradation by the new duo-working-electrode system. The sol-gel prepared TSSA was employed as anode. While for cathode, both ADCs formatted by carbon black (CB-ADC) and activated carbon (AC-ADC) were prepared. Stainless steel mesh cathode and Pt/C cathode were used for comparison.

4.1.1 Initial study of degradation performance (paper I)

For the initial study, TSSA coupled with CB-ADC (TS-CB) was applied in the dynamic experiment system. TSSA with stainless steel mesh cathode (TS-SS) was as control. 20 mg L^{-1} MO dissolved in 31 g L^{-1} NaCl was used as simulated HSW.

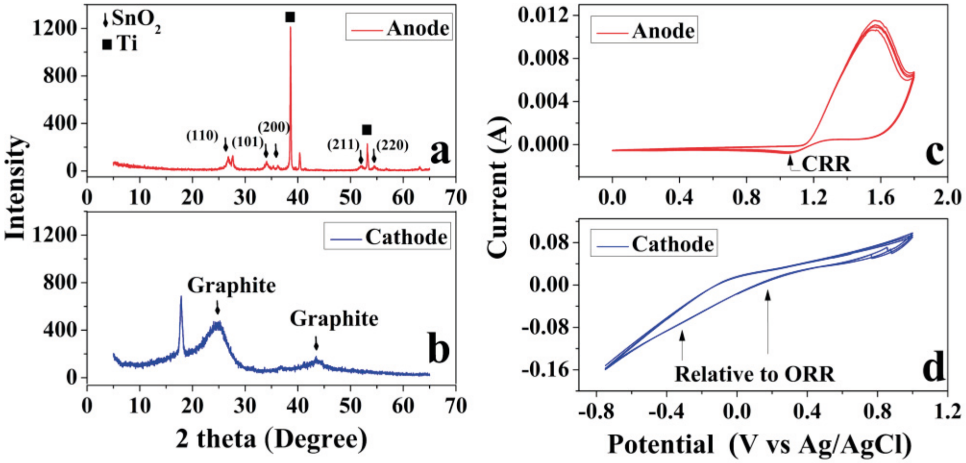

Fig. 6. The characteristics of anode and cathode materials. ((a) XRD test for TSSA anode; (b) XRD test for CB-ADC; (c) CV test for TSSA anode, scan rate: 0.02 V s^{-1}, electrolyte: 31 g L^{-1} NaCl; (d) CV test for CB-ADC, scan rate: 0.02 V s^{-1}, electrolyte: 31 g L^{-1} NaCl.)

The characteristics for both anode and cathode materials were firstly determined, as shown in Fig. 6. The XRD patterns of the TSSA and CB-ADC materials was shown in Fig. 6 (a) and (b). In Fig. 6 (a), the characteristic peaks corresponding to lattice planes of (1 1 0), (1 0 1), (2 0 0), (2 1 1) and (2 2 0) showed a successful formation of tetragonal rutile structure of SnO_2 (Benrabah, Bouaza, Kadari, & Maaref, 2011). Except those for SnO_2 and Ti, none other peaks were found, suggesting all Sb elements were embedded into the crystal lattice of SnO_2 during Sb-doped SnO_2 formation. While in Fig. 6 (b), two characteristic peaks at 25.18º and 43.48º was found for CB-ADC, indicating graphite structure on the cathode surface (Shang, Yang, & Tao, 2009). This suggest the successful attachment of carbon black and carbon nano tube (CNT) on the CL layer of cathode.

The electrochemical characteristics of both electrodes were carried out by CV test. In TSSA test (Fig. 6 (c)), the current lifting in the range of 1.2-1.5 V suggested a CER reaction, producing Cl_2/ClO^-/HClO. Meanwhile, the reduction peak at 1.08 V referred to the chlorine reduction reaction (CRR) from Cl_2/ClO^-/HClO to Cl^-. In CB-ADC test (Fig. 6 (d)), when scanning negatively, the rapid current decrease between 0.1 to -0.3 V reflected ORR reaction, transferring O_2 to H_2O_2 and H_2O. No peaks of ORR were found, this suggested the continuous diffusion of O_2 into water from air through air diffusion cathode, which retained the concentration of dissolved O_2 and its diffusion rate towards cathode surface. Overall, the characteristic tests determined the formation of targeted anode and cathode. Meanwhile, both electrodes showed the expected features as working electrodes in EC.

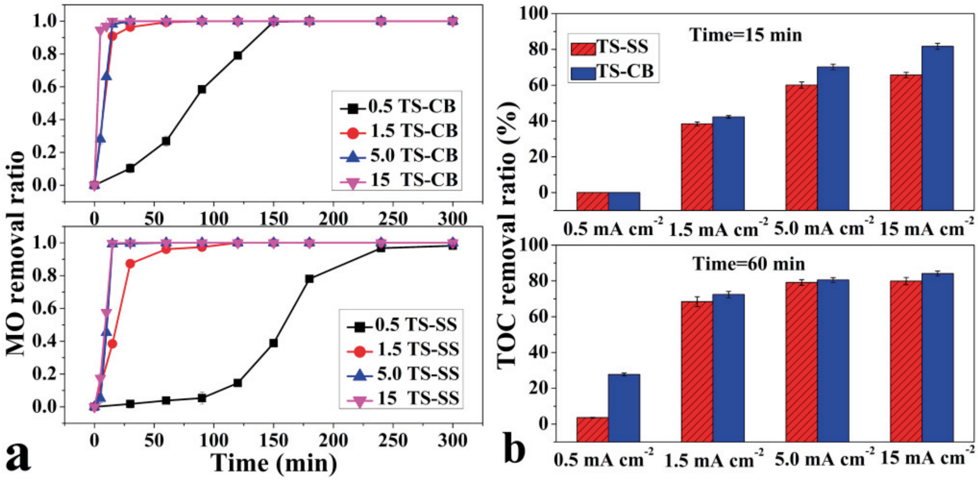

Fig. 7. The MO removal and degradation performances of TS-CB and TS-SS systems in the function of current density. ((a) MO removal ratio; (b) TOC removal ratio; initial pH=6.0, electrolyte: 20 mg L^{-1} MO+31 g L^{-1} NaCl.)

The degradation performances were indicated by both MO and TOC removal ratios for TS-CB and TS-SS systems, as shown Fig. 7. Both systems showed effectiveness for MO treatment. This should be due to the oxidation reactions between EC produced agents ($Cl_2/ClO^-/HClO$ and H_2O_2, etc.) and MO, leading to the decomposition of MO into simpler structures. The MO removal ratio was in the order of 15 mA cm^{-2}>5 mA cm^{-2}>1.5 mA cm^{-2}>0.5 mA cm^{-2} in both systems, indicating an accelerated generation of degradation agents with higher current density. However, compared with TS-SS with single working electrode (anode), the TS-CB system yielded significant improvement in the MO removal ratio (Fig. 7 (a)), where 95% removal of MO was found at 144, 23, 14.5,7.5 min in average at the current densities of 0.5, 1.5,5, 15 mA cm^{-2}, 23.7–51.1% less than that in TS-SS system. In addition, Fig. 7 (b) showed clear improvement of TOC removal in the TS-CB system. TOC removal ratio from 27.7% to 84.1%were reached after running for 60 min in the TS-CB system at the current densities from 0.5 to 15 mA cm^{-2} in average, 1.0–7.7 times higher than those in the TS-SS system, respectively. This should be attributed to the participation of EC produced H_2O_2 on cathode to the MO degradation work.

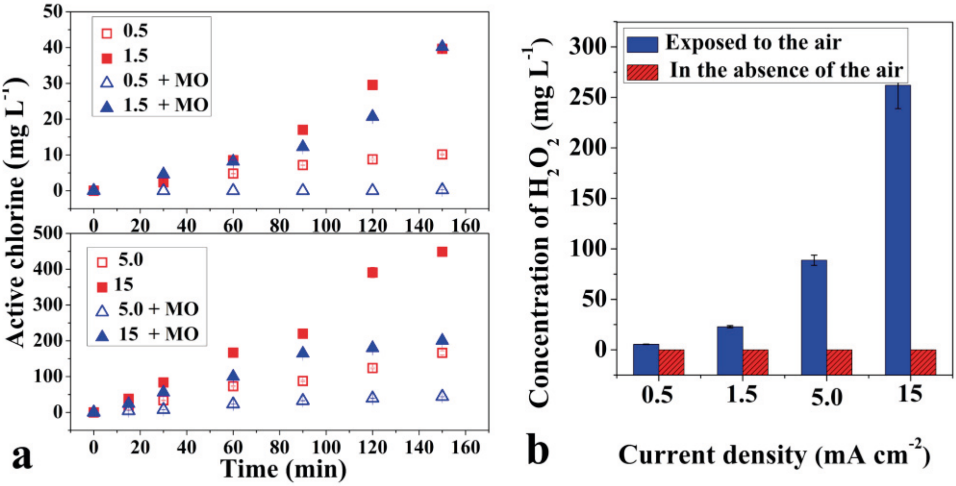

Fig. 8. Test of degradation agents during the experiment. ((a) concentration of active chlorine; (b) concentration of H_2O_2; Initial pH=6.0, electrolyte: 31 g L^{-1} NaCl, 20 mg L^{-1} MO was involved when needed.)

To further confirm the degradation mechanisms, the degradation agents produced during experiment were determined, as shown in Fig. 8. In Fig. 8 (a), in the conditions with and without MO, the production of active chlorine was accelerated by higher current density, consistent with the order of MO removal and degradation performance. In addition, the significant gap of active chlorine concentration between two conditions with and without MO indicated the consumption of it during MO degradation. This proved a major contribution of active chlorine in degradation work. Meanwhile, Fig. 8 (b) confirmed the function of CB-ADC for H_2O_2 production. Significant production of H_2O_2 was determined when the DL of CB-ADC was exposed to the air, with 261.9 mg L^{-1} H_2O_2 detected as highest. However, without exposure, the signal of H_2O_2 can be ignored. This suggested the adsorption-diffusion-transformation route from O_2 in air to H_2O_2 in water by CB-ADC under EC.

Table 1. pH value of the HSW during the experiments in the two degradation systems.

Time (min)	pH value of the HSW					
	0.5 mA cm^{-2}		5.0 mA cm^{-2}		15 mA cm^{-2}	
	TS-SS	TS-CB	TS-SS	TS-CB	TS-SS	TS-CB
60	6.4	6.0	7.5	6.2	9.2	6.2
120	6.4	6.0	9.0	6.3	9.4	6.4
180	6.6	6.0	9.3	6.4	9.4	6.4

The test of pH value in the HSW also differed the two systems, as shown in Table 1. In TS-SS system, generally, the pH variated in the range of 6.0 to 9.4. Theoretically, with HER on cathode and CER on anode, the balanced H^+ and OH^- production keeps the pH stable. However, incomplete transformation from Cl_2 to ClO^- is unavoidable. Therefore, the unconsumed OH^- ions by Cl_2 contributed to the raised pH value. However, in TS-CB system, the values were nearly constant. It should be due to the inhibition of HER by using CB-ADC. The produced H_2O_2 by ORR instead performed as a buffer, releasing H^+ in alkaline environment (Santos, Pereira, Faria, & Orfao, 2009).

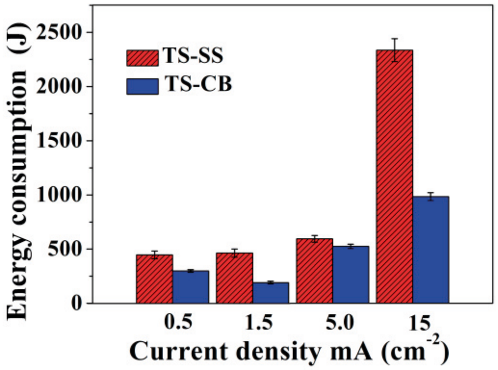

Fig. 9. Energy consumption at the time of 95% MO removal ratio in TS-CB and the TS-SS systems. (initial pH 6.0, electrolyte: 31 g L^{-1} NaCl + 20 mg L^{-1} MO solution.)

The energy consumption was another critical factor to be considered, as shown in Fig. 9. For both systems, the energy consumption for 95 % removal ratio increased with higher current density. This could derive from the redundant agents produced under high current density, which hadn't been used for degradation. The unexpected reactions like oxygen evolution reaction (OER) could also share the electric energy but contribute zero to degradation work. A less energy consumption (11.7–58.8%) in TS-CB system, compared to that in TS-SS system, was due to the extra degradation kinetic from the support of CB-ADC.

Overall, the EC with TSSA and CB-ADC as working electrode has shown its effectiveness in MO removal and degradation in HSW. Compared to the single-working TSSA, the TS-CB system with duo working electrodes showed advantages in degradation performance, pH stability, energy saving, etc. This is due to the utilization of current quantities passing cathode by a CB-ADC. This new EC system, as a method and a concept, proved its value for further investigation.

4.1.2 Critical factors of MO removal (paper II)

To further investigate the removal and degradation performance of the new EC system, critical factors in the experience were studied for their effects to the MO removal ratio. The factors included initial MO concentration, NaCl concentration, pH value and various cathode materials. In this case, a new activated-carbon air diffusion cathode (AC-ADC) was developed for the comparison. The three systems involved in this section were TS-AC, TS-CB and TS-SS. The MO removal ratio in the function of various factors was as shown in Fig. 10.

In Fig. 10 (a), the effect of the initial MO concentration on the MO removal was shown. The MO concentration removal ratio increased with lower initial MO concentration in all conditions, this ratio was in the order of TS-AC>TS-CB>TS-SS. The initial removal rate (mg L^{-1} min^{-1}) was found 51.65 to 110.73 mg L^{-1} min^{-1} for TS-AC system with initial MO concentration ranging from 100 to 300 mg L^{-1}. This was 105.8% to 174.6% higher than those in TS-SS and 66.5% to 93.6% higher than those in TS-CB systems, respectively. The decrease in the MO removal ratio with higher MO concentration derived from an increase in the MO loading on the unit oxidant. However, this negative effect was obviously restrained in TS-AC. A minimum reduction in the MO removal ratio was observed in the TS-AC system (↓ 8.9%), suggesting better adaptability to high organic matter loading of TS-AC.

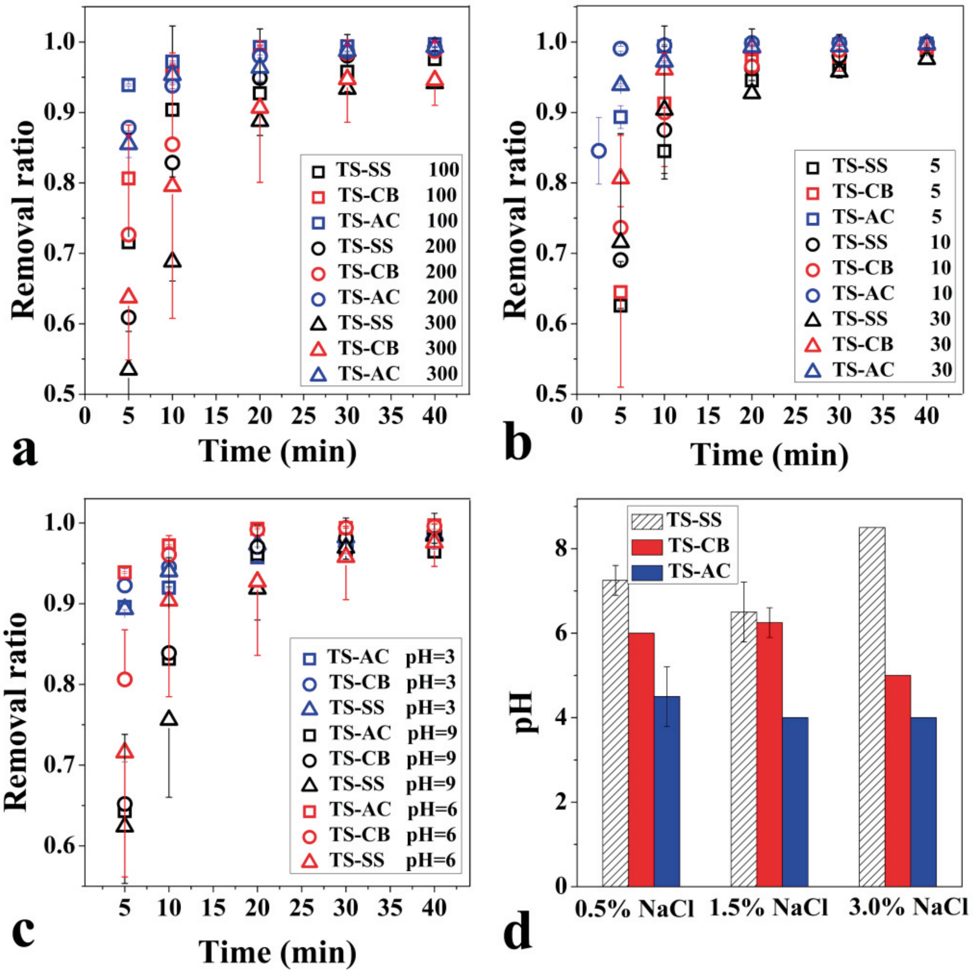

Fig. 10. Effects of critical factors on the MO removal ratio and pH value variation during the experiment in various systems. ((a) effect of initial MO concentration (mg L^{-1}), initial pH=6.0, initial NaCl=30 g L^{-1}, current density=1 mA cm^{-2}; (b) effect of initial NaCl concentration (g L^{-1}), initial pH=6.0, initial MO concentration=100 mg L^{-1}, current density=1 mA cm^{-2}; (c) effect of initial pH value, initial MO concentration=100 mg L^{-1}, initial NaCl=30 g L^{-1}current density=1 mA cm^{-2}; (d) pH values at running time of 10 min, initial pH=6.0, electrolyte: 100 mg L-1 MO+30 g L-1 NaCl.)

Fig. 10 (b) descripted the effect of initial NaCl concentration to the MO removal performance. Same order of performance was found for three systems as mentioned above. Meanwhile, as the concentration of NaCl was increased, higher MO removal was obtained. It probably mainly resulted from an increased active chlorine (HClO/ClO$^-$) produced by TSSA with higher Cl$^-$ content. In addition, with higher initial NaCl concentration, larger increase in the MO removal ratio was found in both the TS-SS and TS-CB systems (14.4% and 25.0% at running time of 5 min, respectively), which are 2.82 and 4.90 times of that in the TS-AC system. Hence, compared to the TS-AC system, the removal performance of TS-SS and TS-CB systems showed higher sensitivity to NaCl concentration.

The effect of initial pH value to the removal ratio was as shown in Fig. 10 (c). A rapid MO removal (~90% removal ratio within 20 min) was achieved in all the three systems with an initial acidic condition (pH=3). However, a significant dropping of the ratio was obtained when pH value lifted towards the basic condition. This was due to that in the active chlorine species, HClO was proved as more active than ClO$^-$, which was mainly formed in acidic condition (Galajda, Fodor, Purgel, & Fabian, 2015; Tolleson et al., 2012). Besides, compared to TS-SS and TS-CB, non-significant dropping of removal ratio was found in TS-AC system when pH value rose from 3.0 to 6.0. According to the coefficient of variation of running time for 90% removal ratio, the performance gap was 4.29 times in three systems at initial pH=6.0, compared to that at initial pH=3. This phenomenon indicated a linkage between high performance of TS-AC and its possible influence to the pH.

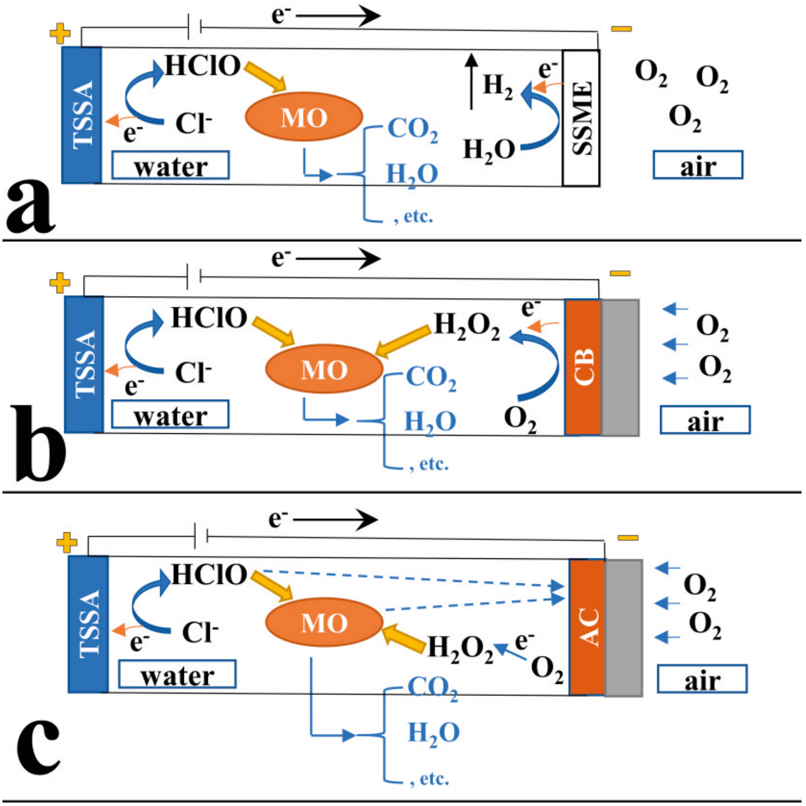

Fig. 11. Degradation mechanisms of various EC systems ((a) TS-SS; (b) TS-CB; (c) TS-AC.).

To verify this hypothesis, the pH values during experiment with initial pH=6.0 was carried out, as shown in Fig. 10 (d). In TS-AC system, the lowest pH values were observed. Cl_2 can be regarded as a main scavenger for HO^- in the three systems (Eq. 4). Hence, the lowest pH values may be corresponding to the adsorption of active chlorine on the activated carbon surface (Lian et al., 2012; Ogata et al., 2013), which efficiently lowered the bulk concentration of $HClO/ClO^-$ and thus accelerated the transformation from Cl_2 to $HClO/ClO^-$ by consuming OH^- (Eq. 4). No desorption mass of MO from the AC surface was obtained. It should be corresponding to the reaction between MO and $HClO/ClO^-$ adsorbed on the AC-ADC surface. Therefore, the high performance of TS-AC should be corresponding to its (1) pH controlling, which retained rich content of HClO in wastewater and (2) the adsorption-degradation of MO on cathode surface. According to the discussions in Section 4.1.1 and 4.1.2, the mechanisms of MO removal and degradation in various systems can be summarized, as shown in Fig. 11.

4.1.3 NOR degradation by the new EC system (paper III)

The new EC systems with duo working electrodes (TS-CB and TS-AC) have shown significant potential for organic matter degradation. To further investigate the new EC systems in the wider area for application, one typical antibiotics NOR dissolved in NaCl electrolyte was selected as targeted HSW in this section. This section aimed to evaluate the performance of the new EC system for NOR degradation in HSW, a TS-Pt system with Pt/C cathode was as control. The state reaction system was employed for the efficiency of experiment.

Fig. 12 descripted the removal ratio of NOR by TS-CB and TS-Pt systems. The rapid removal ratios were found in both systems (mostly over 80% removal ratio within 5 min). In addition, the removal ratio lifted with the lower NOR loading (Fig. 12 (a)) and higher current density (Fig. 12 (b)). This should derive from the same mechanisms as discussed in Section 4.1.2. However, as a rapid removal processes, the removal performances of two systems showed no significant distinction with each other in the same experiment condition. In the slow reaction mode with NaCl concentration=10 g L^{-1} and current density=0.18 mA cm^{-2}, the distinction can be finally found (Fig. 12 (c)). Higher initial and mean removal rates (3.28 and 1.75 mg L^{-1} min^{-1}) obtained in TS-CB system were 31.1% and 12.2% higher than those in TS-Pt system. This was consistent with the results in MO degradation, indicating significant contribution of CB-ADC as working electrode for degradation work.

The degradation performances were further investigated by BOD and COD test, where the ratio of BOD/COD referred to the biodegradability, as shown in Fig. 12 (d). In the initial solution, the biodegradation can be ignored with the BOD/COD

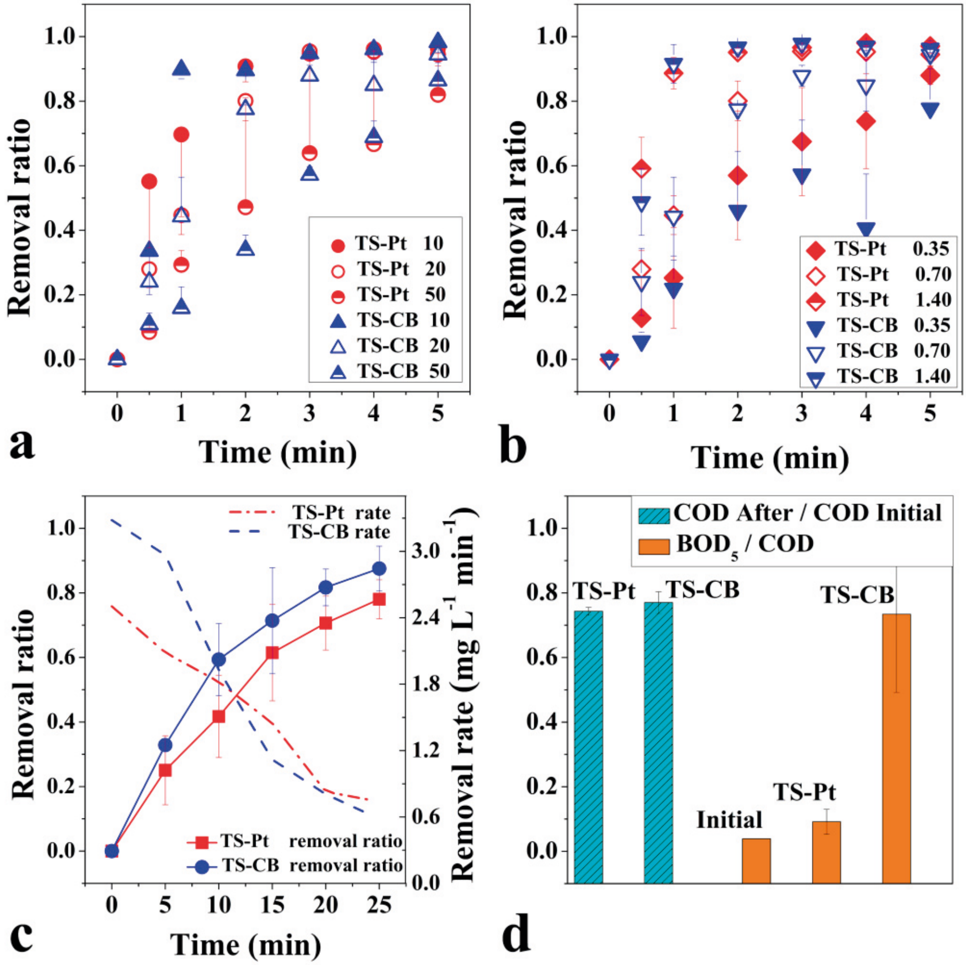

Fig. 12. NOR removal and degradation performance in various EC systems. ((a) Removal ratio in the function of initial NOR concentration (mg L^{-1}), initial pH=7.2, current density=0.70 mA cm^{-2}, NaCl concentration=30 g L^{-1}; (b) Removal ratio in the function of current density (mA cm^{-2}), initial pH=7.2, NOR concentration=20 mg L^{-1}, NaCl concentration=30 g L^{-1}; (c) Removal ratio and rate in slow reaction mode, initial pH=7.2, NOR concentration=20 mg L^{-1}; (d) The BOD and COD relationships before and after the running time of 25 min in TS-CB and TS-Pt systems. initial pH=7.2, current density=0.70 mA cm^{-2}, NaCl concentration=30 g L^{-1}, NOR concentration=20 mg L^{-1}.)

of 3.9%. After the electrolysis of 25 min, similar COD removal ratios was obtained in both systems (25.7% and 23.0% for TS-Pt and TS-CB, respectively). However, in terms of biodegradability, TS-CB system showed the in average 73.4% BOD/COD ratio after 25 min of running, compared to that of 9.1% in TS-Pt system, indicating a considerable higher potential of bio-mineralization after the treatment. This should be attributed to the synergistic effect between CB and TSSA during under EC, leading to extra degradation mechanisms. However, considering COD removal as a standard of degradation degree, the performance of TS-CB was still limited, which need further improvement and extra assistance. This should be due to the complex construction of NOR and its high stability.

The degradation pathway is also significant to illustrate the degradation processes of organic matter in detail. Therefore, the HPLC-MS test was employed for this purpose. The result was displayed in Fig. 13. Basically, the removal of NOR followed two possible cross pathways: P1: the direct destroy of piperazine ring by the oxidation agents and P2: the substitution of hydrogen by chloride on both benzene and piperazine rings. In the TS-Pt system, the negligible increasing of BOD/COD ratio should be attributed to the dominated degradation pathway 2. However, in TS-CB system, the cross reactions between the pathway 1 and 2 were assumed, which led to the entire piperazine ring destruction. However, in either pathway, the completed degradation can’t be achieved.

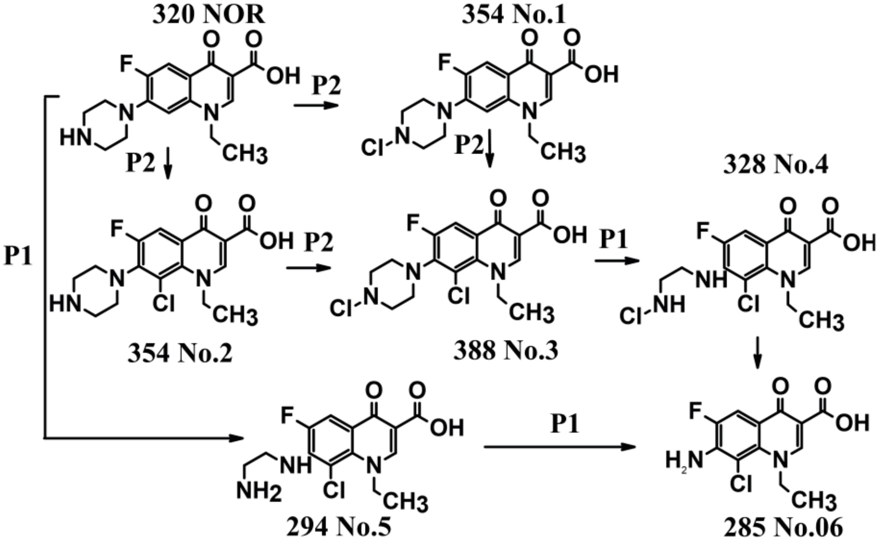

Fig. 13. The possible degradation pathway of NOR in EC systems.

In this section, a considerable NOR removal and degradation ability was determined for the new EC system with duo working electrode (TS-CB). A rapid NOR removal in 5 min and a significant lift of NOR biodegradability was obtained. However, due to the high stability and complex construction of NOR, the degradation performances were still limited with single EC, which required further development and improvement.

4.2 Degradation performance of new PEC systems

PEC has emerged as a new potential degradation method for organic matters in wastewater. This is due to the synergistic work between photo and electrochemical catalysis, resulting in the efficient generating of high activity free radicals (•Cl/•OH, etc), as mentioned in Section 2.3. Therefore, in this section, a new PEC system was designed to develop the degradation performance of the simple EC system. This new PEC system (PEC-D, as shown in Fig. 4) contained duo working anode (TSSA) and cathode (CB-ADC), with photo and electrochemical catalysis applied simultaneously on both electrodes in degradation work. Single photo catalysis (SPC), single electrochemical catalysis (SEC) and PEC system with single working anode (PEC-S) were for comparison. This experiment was conducted in the state reaction system. For the wide existence of antibiotics in mariculture, the target HSW was formatted by dissolving a certain amount of NOR (20 mg L^{-1}) into filtered seawater from Bohai sea in China. 21.3 g L^{-1} Cl^-, 0.338 g L^{-1} K^+, 0.332 g L^{-1} Ca^{2+}, 1.37 g L^{-1} Mg^{2+}, pH of 7.63 and 19.7 g L^{-1} TOC were determined in the HSW before treatment in the reactor.

4.2.1 The initial study of degradation performance (paper IV)

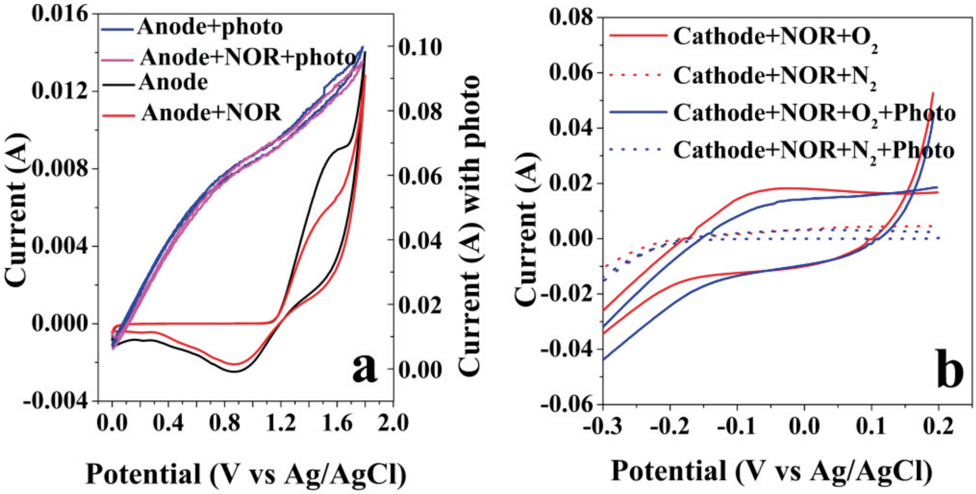

Fig. 14. CV tests under photo radiation for anode and cathode. ((a) CV test for TSSA anode; (b) CV test for CB-ADC cathode; Scan rate=0.02 V s^{-1}, NaCl concentration=31 g L^{-1}, MO concentration=20 mg L^{-1} when added.)

Before degradation work, the photo-electro catalysis characteristics for both anode and cathode were determined by CV test, as shown in Fig. 14. Fig. 14 (a) showed the effect of UV radiation and NOR to the CV curves. With no radiation, the addition of 20 mg L^{-1} of NOR performed no remarkable effect on the CER. A little decrease of reduction peak area (at E≈0.9 V) with additional NOR indicated a consumption of active chlorine by NOR, leading to fewer amount of active chlorine reduced back in reduction reaction. The pure capacitance area was found between 0-1.2 V with little current variation, suggesting no reaction happened in this range. Meanwhile, the rise of current was obtained when TSSA was radiated by UV either with or without NOR. This can be explained as photogenerated current. With UV radiation on TSSA, the electron was transformed to the exacted state with photo-generation hole left, which led to the easier release of electrons from material surface, resulting in the rapid increasing of current. The photo-generated hole on the TSSA can be utilized for oxidation reaction to generate free radicals. The photo-electro characteristics of CB-ADC cathode was shown in Fig. 14 (b). No significant effect of UV radiation on the current in CV test of CB was found. This is due to the reduction reaction on cathode side, the faster electron release by UV radiation can't accelerate this process. However, the conditions with extra O_2 by aeration showed significant larger redox area, compared to those with N_2, this indicated the CER and ORR reactions occurred on the cathode side.

Generally, on cathode side, little direct photo-electro synergistic work can be found. Whereas on anode side, the high current by the combination of photo and electrochemical catalysis may indicate the enhanced oxidation activity by the direct synergistic effect on anode.

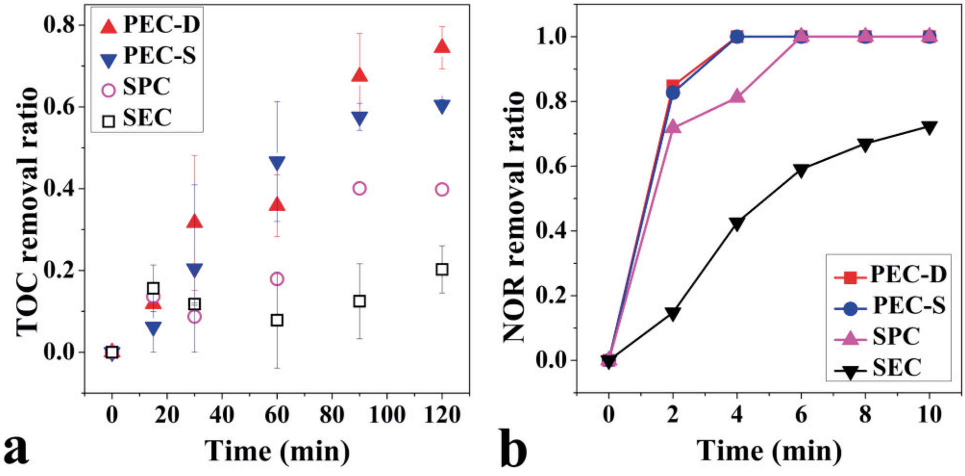

Fig. 15. NOR degradation and removal performances. ((a) TOC removal ratio; (b) NOR removal ratio; initial NOR concentration=20 mg L^{-1}; current density=5.2 mA cm^{-2}, initial Cl^- concentration=21.3 g L^{-1}.)

The degradation performances were carried out, as shown in Fig. 15. After the 120 min of experiment, the TOC removal ratio was found in the order of PEC-D>PEC-S>SPC>SEC. This order agreed with the test of NOR removal ratio. The highest TOC removal ratio of 74.4% was obtained in PEC-D at 120 min, 23.0% higher than that in PEC-S system and 267% higher than that in SEC system. The TOC removal ratios achieved in PEC systems (>60%) were higher than those from SPC and SEC combined. This indicated the synergistic effect of electrochemical catalysis and photo radiation in PEC systems, rather than the individual work from photo or electrochemical catalysis. In particular, this should be attributed to the accelerated generation of free radicals (•OH, •Cl, etc) by the photo-electro synergistic effect. The highest degradation ratio found in PEC-D system could be mainly ascribed to •OH produced via electro-generated H_2O_2 decomposition under UV radiation on the cathode side.

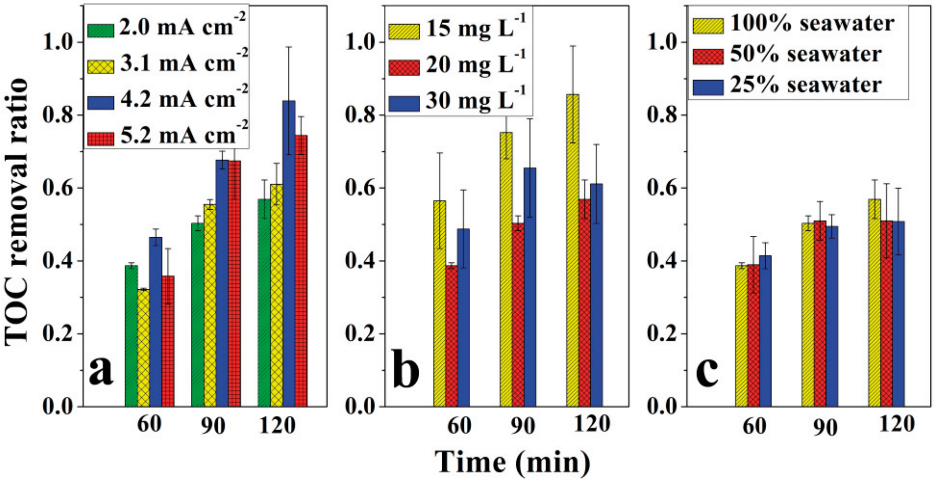

Fig. 16. Effect of critical effect factors on the NOR degradation ratio by PEC-D. ((a) effect of current density, in where the initial NOR concentration=20 mg L^{-1}; initial Cl^- concentration=21.3 g L^{-1}; (b) Effect of initial NOR concentration, in where the current density= 2.0 mA cm^{-2}; initial Cl^- concentration=21.3 g L^{-1}; (c) Effect of initial Cl^- concentration, current density=2.0 mAcm^{-2}; initial NOR concentration=20 mg L^{-1}.)

To further investigate the PEC-D system, the critical effect factors were studied in the NOR degradation process by PEC-D system, as shown in Fig. 16. In Fig. 16 (a), the rise of TOC removal ratio was found with current density changing from 2.0 to 4.2 mA cm^{-2}, which can be attributed to the faster free radical generation on both anode and cathode, with the highest TOC removal ratio of 83.9%. However, no increased removal ratio was obtained when the current density increased to 5.2 mA cm^{-2}. This may derive from accelerated side reactions (OER on anode, for instance) with high current density or the replacement of controlling role of current density by other factors like molecular diffusion rate. The effect of initial NOR concentration was shown in Fig. 16 (b). The highest TOC removal ratio was found with the initial NOR concentration of 15 mg L^{-1}. However, no removal ratio dropping was found when increasing initial NOR loading from 20 mg L^{-1} to 30 mg L^{-1}, indicating the adaptive capacity of high organic matter loading in PEC-D system. The effect of Cl^- concentration showed the highest TOC removal ratio in 100% seawater Cl^- concentration (21.3 g L^{-1} Cl^-) after running of 120 min (Fig. 16 (c)). However, the difference between the three performances was kept within 12.3% by raising Cl^- concentration by 4 times. This difference can be ignored when comparing to the conditions of single EC degradation. The photo-electro synergistic work may reduce the dependency on ion concentrations in traditional EC systems.

4.2.2 Analysis and modelling for degradation performance (paper IV)

The relevancy analysis on the degradation performance among different systems were conducted by GRA and PCA, as shown in Table 2.

Table 2. The results in statistical analysis of NOR degradation performances in vary systems. ((a) grey relation analysis (GRA); (b) principal component analysis (PCA)).

(a) Grey Relation Analysis				
Reference	Relational Grade			
	PEC-D	PEC-S	SPC	SEC
PEC-D	---	0.776	0.672	0.604
PEC-S	0.743	---	0.656	0.581
SPC	0.591	0.604	---	0.705
SEC	0.604	0.617	0.774	---

(b) Principle Component Analysis				
Component	Explained Variance			
	PEC-D	PEC-S	SPC	SEC
1	0.98	0.934	0.975	0.768
2	-0.136	-0.32	-0.059	0.638

The overall grey relational grades (γi) of GRA after calculation were shown in Table 2 (a). The TOC removal ratio obtained from SEC and SPC systems can be seen as two reference sequences, considering pure electrochemical and pure photo degradation as two independent processes. The degradation performance in both PEC-D and PEC-S systems showed almost equal considerable degree of correlation (γi>50%) to SEC and SPC systems. However, high γi between PEC-D and PEC-S systems were obtained when they performed as reference. In this case, the γi between PEC systems and none-PEC systems were significant lower. This suggested the two PEC systems showed closer degradation behaviour (the regulation of TOC value variating) with each other, than with the others. Meanwhile, the PCA showed 84% of variance explained in component 1 with 15% of that explained in component 2, indicating component 1 as the premier dominating factor. Variances of 0.980, 0.934, 0.975 and 0.768 were found to component 1 for PEC-D, PEC-S, SPC and SEC systems, respectively (Table 2 (b)). This should be corresponding to the approximate positive correlation between time and TOC removal ratio in the four systems. PEC-D, PEC-S and SPC systems can be considered as the three main contributors to component 1 by showing larger variances to component 1. While SEC system was found obvious independent from component 1 and should be considered as the main contributor to component 2. This can be attributed to the significant fluctuant type of TOC removal in the SEC system, as shown in Fig. 15 (a), reflecting limited degradation activity by simple EC. In contract, the component 1 formed by the three photo-relative processes referred to the pure-photo or electro-enhanced photo catalysis processes, resulting in the generation of free radicals and the rapid continuous NOR degradation. Assuming the HClO/ClO^-/H_2O_2 produced by electrochemical catalysis as component 2 and free radical generated under photo catalysis as component 1, the PEC systems in this work were found closer to component 1.

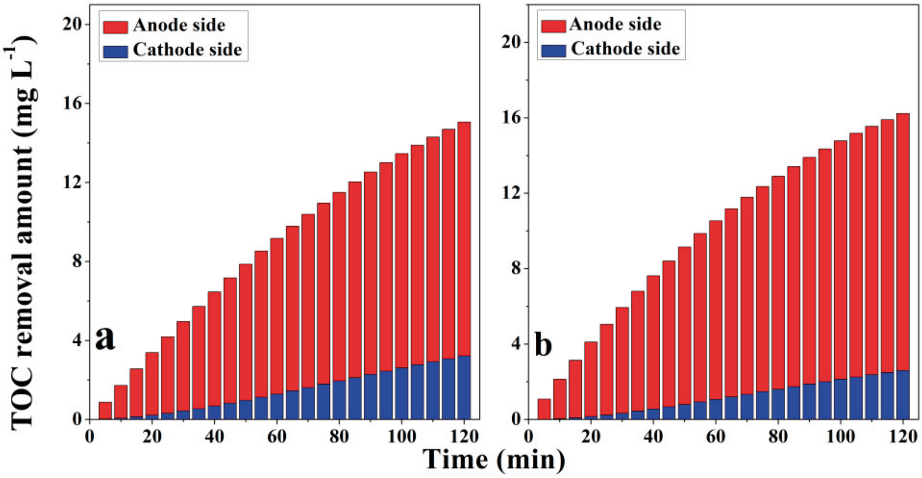

Fig. 17. The simulated contribution of degradation from anode and cathode with current density of (a) 5.2 mA cm^{-2} and (b) 4.2 mA cm^{-2}.

The modelling and simulation were carried out to explore reaction kinetics and distinguish the contribution of anode and cathode sides to the total degradation performance in PEC-D system. As mentioned in Section 4.2.1, the direct enhancement of EC by UV radiation occurred on anode, with indirect O_2-H_2O_2-•OH transformation on cathode. The degradation agent production on anode was integrated as one step with that on cathode as two steps. The simulation work was conducted according to Eq. 27 in Section 3.4.2, with results shown in Fig. 17.

The considerable fittings were obtained with current density equals to 5.2 and 4.2 mA cm^{-2}, with R^2 equals to 0.961 and 0.903, respectively. The contributions of anode and cathode for the degradation ratio were carried out and showed similar trends in both current densities, as shown in Fig. 17 (a) and (b). The anode side yielded dominating contribution at the beginning of the experiment, however, the contribution ratio of cathode side rose with longer running time, resulting in 21.4% and 16.0% of final degradation contribution at the current density of 5.2 mA cm^{-2} and 4.2 mA cm^{-2}, respectively. This was due to the stepwise accumulation of H_2O_2 and its subsequent transformation •OH. Whereas on anode, the direct photo-electro synergistic work immediately generated degradation power. Overall, the anode and cathode sides both functioned significantly during the degradation.

To understanding degradation process in detail, the degradation pathways of NOR by PEC-D were carried out by intermediate products test, as shown in Fig. 18. The oxalic acid was found as lowest molecular-weight intermediate in this work, indicating that the NOR can be degraded to simple organic matter with single structure and small molecular-weight. Five possible intersecting degradation pathways of NOR (P1-P5) was determined including P1: the ring-opening reaction of piperazine ring; P2: substitution reaction of F on benzene ring; P3: submission of H by Cl in benzene ring; P4: ring-opening reaction of C-N hexatomic ring; P5: dicarboxylic reaction. Generally, the degradation of NOR took place under the combined contribution of P1, P2, P3, P4 and P5. The final compound No.13 can be further degraded to CO_2, H_2O and NH_4^+. Meanwhile, the No.16 (oxalic acid) with lowest molecular weight found in this test was supposed to be obtained by P4 and P5 processes from the original NOR, indicating the importance of P4 and P5 in the degradation. Furthermore, it can be also assumed that P1, P4 and P5, which correlated to the decomposition process, contributed more in NOR degradation than P2 and P3 of single substitution reactions. Compared to the simple EC in Section 4.1.3, smaller intermediate molecular was detected with PEC-D treatment, indicating a higher degradation degree with duo photo-electro catalysis.

In summary, the new PEC-D system was developed for the NOR degradation in HSW. Due to the synergistic effects of photo-electro catalysis, the PEC systems showed significant higher degradation efficiency than individual photo or electrochemical systems. The advantage of PEC-D derived from the extra degradation power from the cathode side with combined photo-electro catalysis. Low-molecular-weight oxalic acid was detected as smallest intermediate in this degradation process, suggesting a strong reaction activity and decomposition ability of the new system. By GRA and PCA analysis, the PEC systems were confirmed to

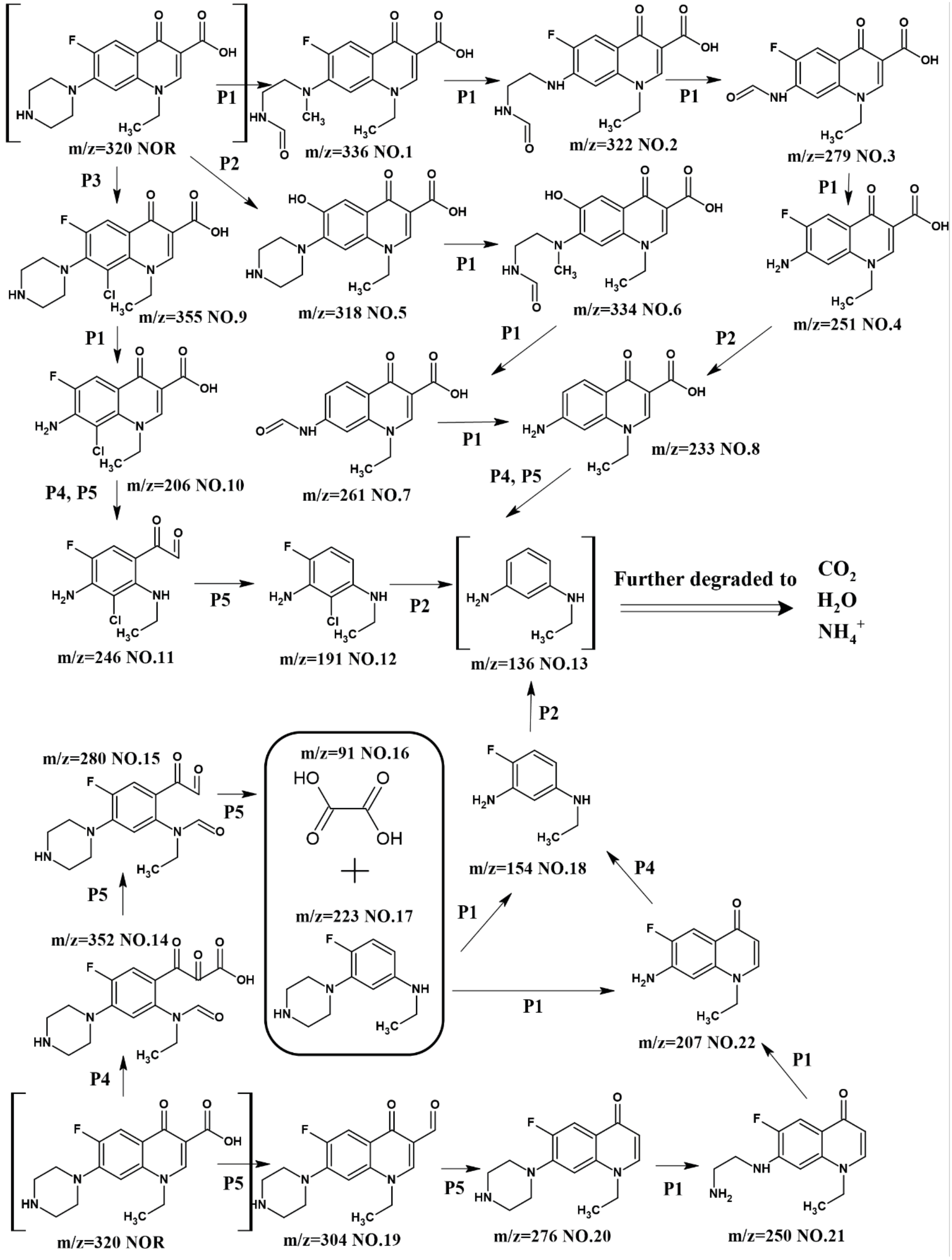

Fig. 18. Possible degradation pathways of NOR in PEC system.

act as an electrochemical-enhanced photo catalysis, rather than a photo-enhanced electrochemical system. The simulation showed a more significant contribution of degradation on the cathode-side catalysis with longer running time, whereas in shorter terms, it was dominated by the anode side. In the PEC-D system, both electrodes contributed significantly for degradation work, with anode as the main degradation driving force.

4.2.3 Improvement and further investigation of the PEC system (paper V)

This section aimed to improve and further investigate the PEC system for NOR degradation in HSW. The new PEC-D showed high degradation performance with synergistic effect of both anode-cathode and photo-electro. The anode side was suggested as the main degradation contributor which owned immediate reaction activity when the treatment started. Therefore, in this section, the improvement focused on anode side, an efficient urea precipitation method (Rao, Reddy, Jayalakshmi, Jaya, & Sridhar, 2005) was employed to format a novel porosity TSSA (UTS) for degradation work. For factor controlling, the PEC system with new TSSA (PEC-UTS) was tested with no assistance from cathode. The PEC system with traditional TSSA (PEC-TS) was for comparison. The degradation agents were tested and analysed to confirm the theory in Section 4.2.3. A novel BP-ANN-P modelling was employed for the further evaluation and analysis for the degradation performances and behaviours.

Physical characteristics of anodes was firstly carried out, as shown in Fig. 19. The XRD patterns of UTS and TSSA were shown in Fig. 19 (a). The characteristic peaks for tetragonal rutile structure of SnO_2 were found at 26.66°, 33.94°, 38.06°, 51.88° and 54.78° on both anodes, referring to the lattice planes of 110, 101, 200, 211 and 220, respectively. The lattice parameters were found a=b=4.730Å, c=3.187Å on UTS, while a=b=4.735 Å，c=3.182 Å on TSSA, with unit cell volume of 71.30 Å and 71.34 Å, respectively. They were both smaller than the standard (a=4.829, b=4.835 Å, c=3.243 Å, and unit cell volume=75.73 Å), indicating a lattice distortion on both anodes. The Sb oxide could not be observed in XRD patterns, which could be attributed to the insertion of Sb into SnO_2 lattice. In addition, slight peaks for Ti on both anodes indicated considerable coating of SnO_2-Sb onto the substrate.

The composition of elements and their valance state on both anodes were studied by XPS analysis, shown in Fig. 19 (b). No peaks at 464.0 eV (TiO_2) and 458.3 eV (Ti) were found, consistent with the result in XRD test. The electron peaks at 487.0 eV and 496.0 eV corresponded to $Sn3d_{5/2}$ and $Sn3d_{3/2}$, respectively, in which the peak at 487.0 eV showed the existence of SnO_2 structure. However, more intensive coating of SnO_2 layer on Ti substrate was indicated by the higher electron peaks intensity on UTS. Electron peaks around 531.0 eV and 540.0 eV were attributed to $Sb3d_{5/2}$ and $Sb3d_{3/2}$, respectively, indicating the existence of Sb on the formatted anodes. In both XRD and XPS tests, significant higher signal for SnO_2 structure on

UTS was found, compared to that on TSSA, indicating a more intensive coating of SnO_2 on Ti substrate on UTS.

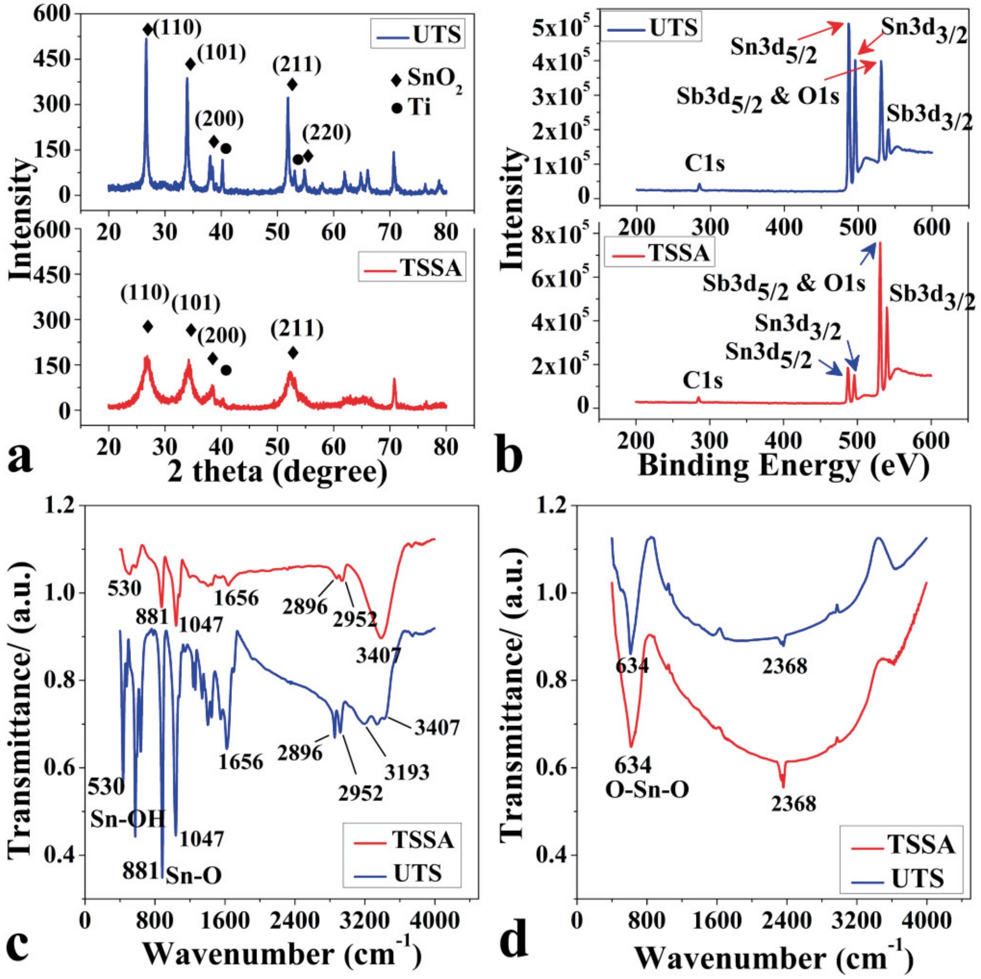

Fig. 19. Physical characteristics of UTS and TSSA anodes. ((a) XRD test; (b) XPS test; (c) Infrared spectroscopy before calcination; (d) Infrared spectroscopy after calcination.)

Infrared spectroscopy test was conducted before and after calcination for both anodes to track the SnO_2-Sb formation procedure, as shown in Fig. 19 (c) and (d). The absorption peaks of Sn-OH band at 530 cm^{-1} and Sn-O band at 881 cm^{-1} confirmed Sn precipitation with -OH derived from urea hydrolysis on UTS (Fig. 19 (c)), while on TSSA, these bands are the result of electrochemical reduction reactions. After calcination, all C-O (1047 cm^{-1}), C-H (2952 cm^{-1}) and –OH (3407 cm^{-1}) absorption peaks disappeared with the appearance of a new vibrating peak at

634 cm^{-1} for O-Sn-O, indicating the formation of SnO_2 (Fig. 19 (d)) and the purification of purified SnO_2-Sb layers by calcination.

The morphology of UTS and TSSA surfaces was studied by SEM test, as shown in Fig. 20. Regular surfaces were obtained for both synthetic methods after 500 °C calcination (Fig. 20 (a) and (d)), suggesting a successful coating on Ti substrate. Notably, a highly porous and fluffy structure was obtained on UTS (Fig. 20 (d) to (f)), compared to that on TSSA (Fig.20 (a) to (c)). After magnifying to 40000 times, dense thin tubular structures were obtained (Fig. 20 (f)). Therefore, the porosity on UTS surface was attributed to the fabrication by tubular units after calcination.

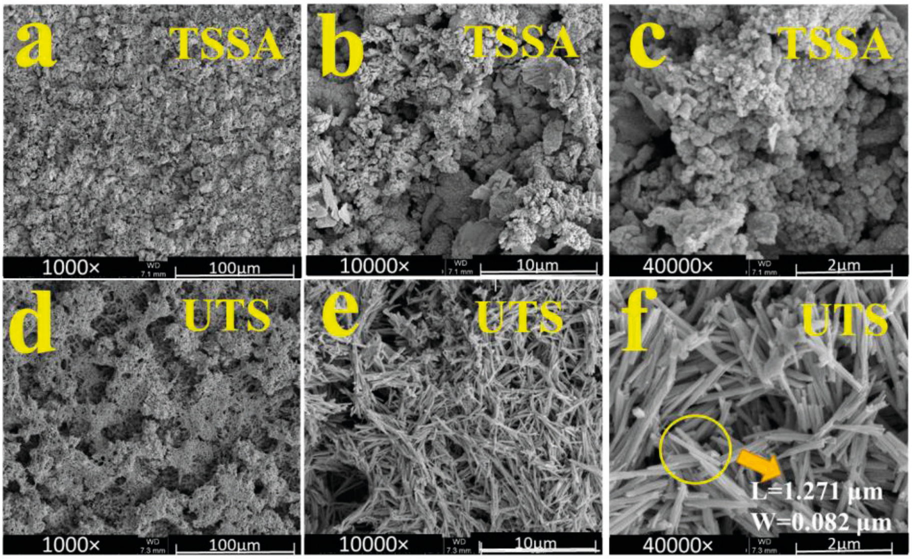

Fig. 20. SEM of UTS and TSSA anodes.

The photo-electro characteristics and degradation performances were summarized on Fig. 21 and Table 3, where LSV, EIS, photo-current and NOR degradation tests were included.

The LSV patterns for both electrodes in NaCl and Na_2SO_4 solutions were shown in Fig. 21 (a) and (b). A smaller onset potential for CER were obtained in UTS (at 1.32 V vs Ag/AgCl) in Fig. 21 (a) with higher reaction current, compared to that in TSSA (at 1.645 V vs Ag/AgCl). This confirmed an accelerated production of active chlorine with lower potential required on UTS. Similarly, in Na_2SO_4 solution (Fig. 21 (b)), UTS also showed a smaller onset potential for OER compared to that of TSSA.

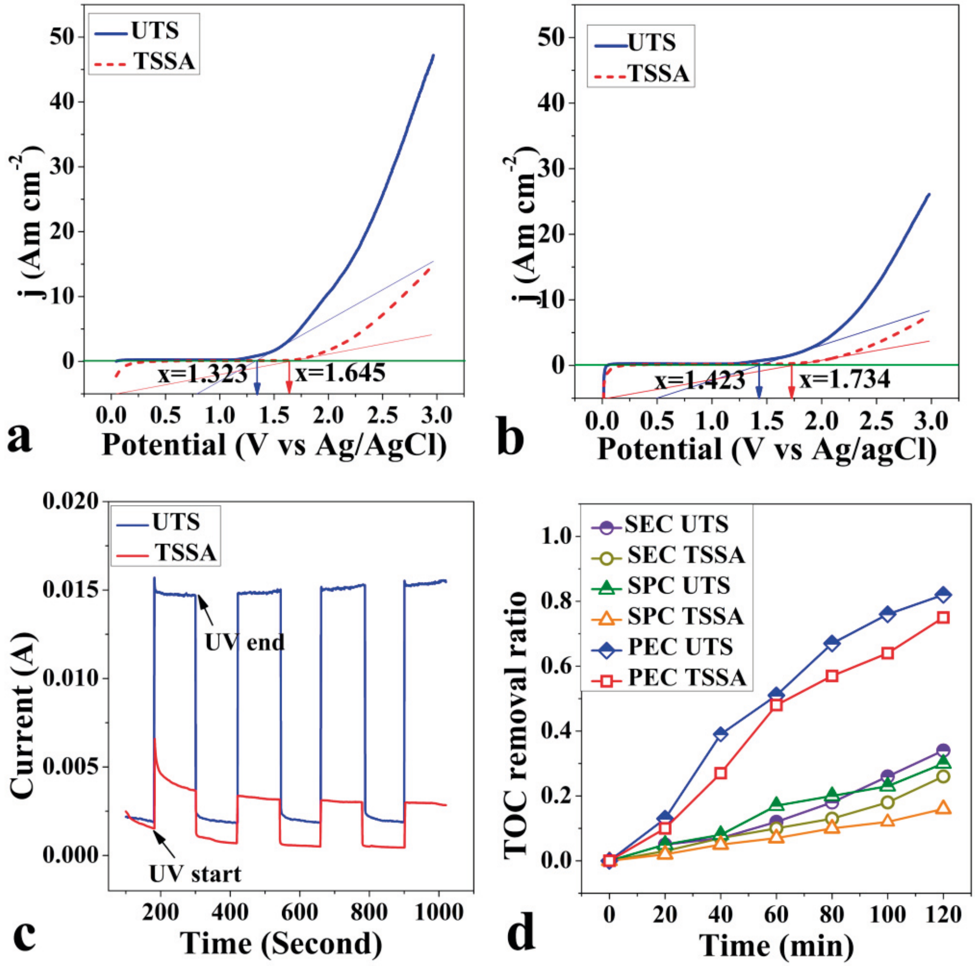

Fig. 21. Photo/electro analysis and degradation tests for both anodes. ((a) LSV for both anodes in NaCl solution, electrolyte: 30 g L^{-1} NaCl, scan rate: 20 mV s^{-1}, range: 0-3.0 V; (b) LSV for both anodes in Na_2SO_4 solution, electrolyte: 30 g L^{-1} Na_2SO_4, scan rate: 20 mV s^{-1}, range: 0-3.0 V; (c) Photo-generated current test for UTS and TSSA, UV light wavelength: 200 to 390 nm, Electrolyte: 30 g L^{-1} NaCl, initial pH=7.0; (d) Performance of NOR degradation in saline NOR with UTS and TSSA as anodes, Electrolyte: 30 g L^{-1} NaCl, current density=10 mA cm^{-2}, UV light wavelength: 200 to 390 nm, initial NOR concentration=30 mg L^{-1}, initial pH=7.0.)

Table 3. Resistance and capacity of UTS and TSSA in saline water.

	R_s (Ω)	C_{dl}(F)	R_{ct}(Ω)	C_i(F)	R_i(Ω)	R(Ω/S$^{0.5}$)
UTS	7.04	0.79	1.63	1.37	3.09	1.7
TSSA	9.32	0.22	4.88	0.72	7.02	2.6

Resistance and capacity of both anodes were tested by EIS, with analysis results listed on Table 3. R_s referred to a resistance between solution and electrode, its value depends on the distance from reference electrode to anode and the conductivity in solution. R_{ct} and C_{dl} were the electron transportation resistance and capacitance within double electrode layer, respectively. Compared to the TSSA, UTS possessed a 66.6% lower R_{ct} and 3.59 times higher C_{dl}, indicating an easier electron transportation and larger active area within double electrode layer. While R_i reflected the interface resistance between Ti and SnO_2-Sb, with C_i as the corresponding capacity. 56.0% lower R_i was obtained in UTS than that in TSSA.

To investigate the photo-catalytic activity of the SnO_2-Sb layer, the photo-current test was conducted with a periodical simulated solar radiation on electrodes (Fig. 21 (c)). Both anodes showed a rapid climb of current under UV radiation from background values. However, 7.51 times higher photo-current was obtained in UTS than in TSSA. Specifically, it may be associated with (a) a lower excitation energy from valence band to conductive band; (b) a larger available surface area; (c) an easier electrode transportation between Ti and SnO_2-Sb.

NOR degradation test was then carried out (Fig. 21 (d)). In single electro catalysis (SEC), 34.0% final TOC removal was obtained in UTS, 30.7% higher than it in TSSA. the higher TOC removal ratio in UTS was due to the faster active chlorine production, which had been confirmed in the CV and LSV tests. Meanwhile in single photo catalysis (SPC), 30.0% of TOC removal was obtained in UTS in 120 min of running, 87.5% higher than it in TSSA. This was associated with the higher UV radiation sensitivity on UTS. In term of photo-electro catalysis, the TOC removal by PEC-UTS and PEC-TS was found 82.0% and 75.0%, respectively. The first order reaction coefficient $k=0.0129\ min^{-1}$ was found by PEC-UTS, 27.0% higher than that of PEC-TS. However, performance gap between two anodes shrank when under photo-electro synergistic effect involved. This may indicate that the photo-electro synergistic effect compensates the gap of degradation efficiency significantly between various catalysis materials with different microstructure.

In brief, higher electro/photo catalysis activity, higher photo/electro/photo-electro degradation performances, lower internal resistance and higher capacitance have been obtained in UTS. This is possibly due to its unique tubular microstructure which formatting larger surface area, denser active site distribution and tighter connection between Ti and SnO_2-Sb.

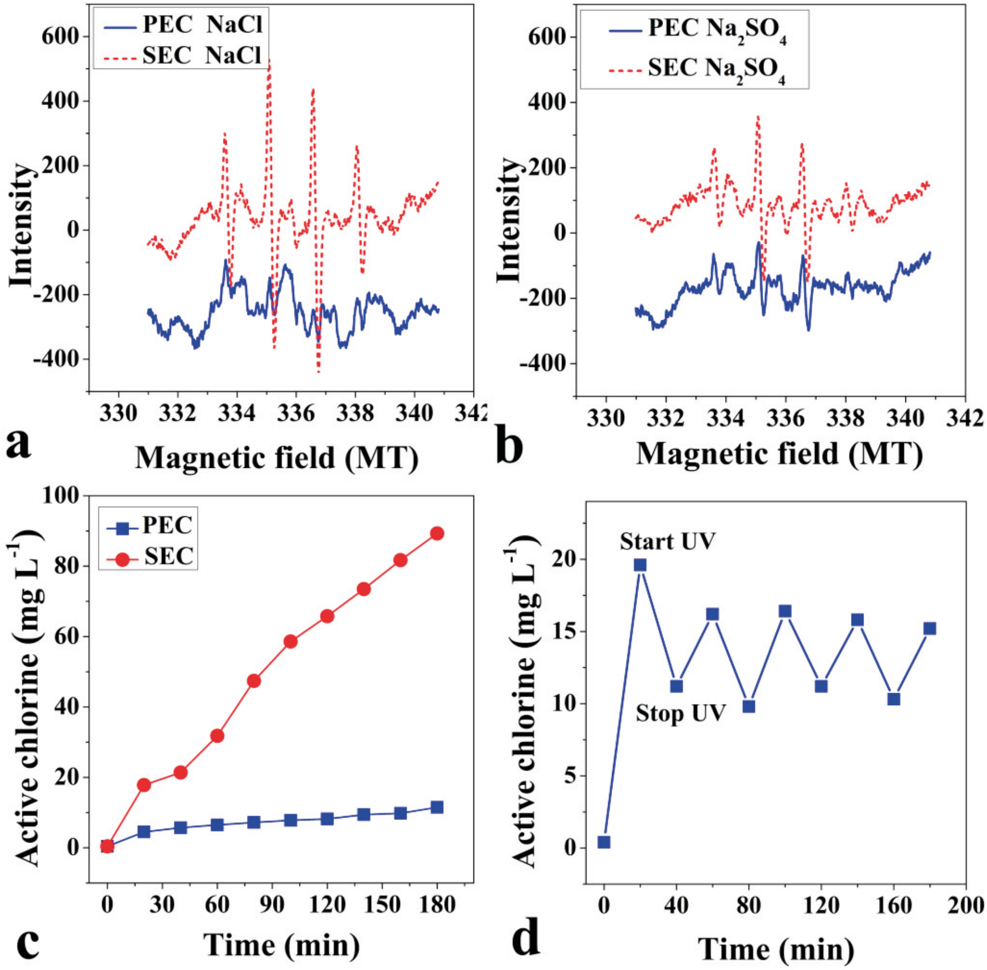

Fig. 22. Test of oxidizing agent created in the experiments with UTS as working electrode. ((a) ESR test for •OH electrolyte=30 g L^{-1} NaCl under photo-electro and electro catalysis; (b) ESR test for •OH in 30 g L^{-1} Na_2SO_4 under photo-electro and electro catalysis; (c) Active chlorine test under photo-electro and electro catalysis, electrolyte=30 g L^{-1} NaCl; (d) Active chlorine test in intermittent UV radiation test under constant electro catalysis; Current density=15 mA cm^{-2} when electro catalysis involved, initial pH=7.0 for all conditions.)

For further investigating the degradation mechanism of the new PEC-UTS system, the produced degradation agents with UTS in PEC and SEC systems were detected, as shown in Fig. 22. The four characteristic peaks in Fig. 22 (a) indicated a generation of •OH under EC in NaCl electrolyte, which disappeared in PEC-UTS system. However, in Na_2SO_4 solution, •OH was determined in both EC and PEC-UTS systems, as shown in Fig. 22 (b). The gap of •OH production in NaCl and Na_2SO_4 should be due to the occupying of holes, active sites and the consumption of •OH by Cl^- in high salinity water (Eq.6-8, 12) (Bruninghoff et al., 2019).

While in Fig. 22 (c), 87.1% less active chlorine found in PEC-UTS system indicated a significant transformation from active chlorine to •Cl by UV radiation. This is supported by the real-time test as shown in Fig. 22 (d), where rapid reduction of active chlorine was found as the UV radiation started. These above suggested the significant generation of •Cl rather than •OH/active chlorine in saline water under PEC in PEC-UTS system. Because of the comparability of •Cl and •OH in the degradation of organic matters (Y. T. Wang, Xue, & Zhang, 2020; Yang, Shin, Jasper, & Hoffmann, 2016), the significant role of •Cl in NOR degradation should be confirmed. Considering the absence of active chlorine and •OH, •Cl retained the premier degradation agent. The pathway (Cl^-)--($HClO/ClO^-$)--(•Cl) can be a main mechanism (Eq. 3-8) of synergistic work between photo and electrochemical catalysis in PEC-UTS system for indirect degradation.

Meanwhile, As the highly porous of the UTS, the in-situ direct adsorption-degradation on it should also be considered (Eq. 10 and 11) as a possibly significant degradation contributor. Due to the difficulty of experimental measurement and distinguishing, the degradation contribution of direct and indirect routes for degradation was determined by the newly developed BP-ANN-P model as explained in Section 3.4.2. The results were shown in Fig. 23 and Fig. 24.

The variation of k_1 and k_2 affected by critical factors in the function of time were as shown in Fig. 23, where k_1 referred to the reaction coefficient of direct route, k_2 represented the equivalent accumulation rate of degradation agent (mainly •Cl) in indirect route. For comparison purpose, the values of k_1 and k_2 were standardized in Fig. 23. Generally, k_1 value remained relevant stable for approximate 20-51 min in most conditions, compared to remarkable slopes from the beginning of the experiments (Fig. 23 (a)-(c)). This phenomenon agreed with a recent experimental study where alginic acid processed direct degradation with a dropping of reaction rate (Chung, Lee, Hong, & Cho, 2019), the negative slope at the beginning of experiment should be associated with (1) the fouling of UTS surface by NOR and its intermediates and (2) the concentration polarization in anode vicinity, etc. Afterwards, k_1 values entered a steady phase when the surface adsorption-degradation and UV radiation performed constant reaction activity to the NOR degradation. The final dropping of k_1 in most conditions may derive from lower values of TOC removal ratio obtained after 80 min of experiments, which can be interrupted by bias significantly. k_1 lifted with higher current density applied Fig. 23 (b)), suggesting stronger electric field accelerates direct degradation. While with the variation of initial pH value (Fig. 23 (c)), the k_1 in neutral condition expressed an absolute advantage compared to those in acidic and alkaline conditions.

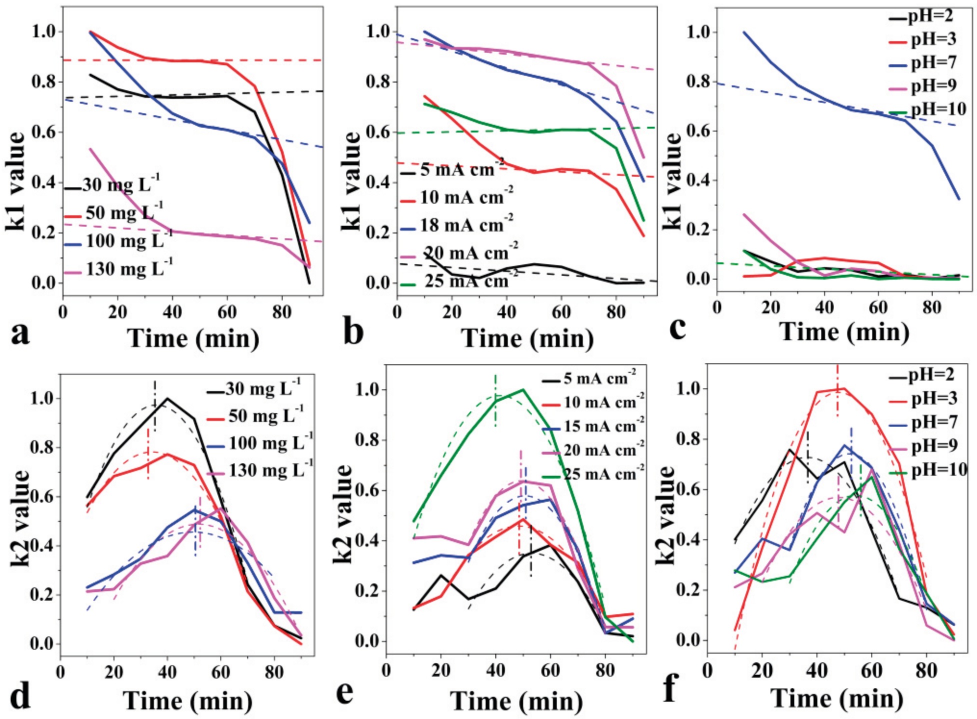

Fig. 23. Variation of kinetic coefficients in direct (k_1) and indirect (k_2) routes of NOR degradation in the function of time with initial NOR concentration, current density, and initial pH value as critical factors.

Compared to k_1, k_2 values showed higher dispersion degree in general (Fig. 23 (d)-(f)). This is due to the consumption of •Cl by degradation reaction, side reaction and recombination of degradation agents during the PEC process. The positive trends of k_2 values at the beginning of experiments were due to the slower agent consumption by less NOR during degradation, while the negative ones derived from faster side reactions and recombination with higher •Cl concentration. This was supported by Fig. 23 (d), where higher k_2 values (net equivalent •Cl accumulation rate) were found with lower initial NOR concentrations. Additionally, consistent to k_1, k_2 also increased with higher current density (Fig. 23 (e)), this suggested that higher current density accelerated both direct and indirect routes for degradation work. Moreover, a significant variation of k_2 was also found with different initial pH values, as shown in Fig. 23 (f), consistent with the dependence of free radical concentration on pH values in other reports (Gao, Gao, Deng, Yang, & Ma, 2012; Huang et al., 2017). Higher k_2 obtained at pH value of 2 and 3, compared to that from 9 to 10, was due to the favoured CER in acidic environment (Tawabini et al., 2020). The two highest $k_{2(pH=3)}$ and $k_{2(pH=7)}$ were associated with the dominating HClO among active chlorine species with pH value between 3 to 8 and its subsequent transformation to •Cl (Eq.

7). Whereas with pH value below 2, Cl_2 emerged as prior (McQuillan, Stevens, & Mumford, 2020).

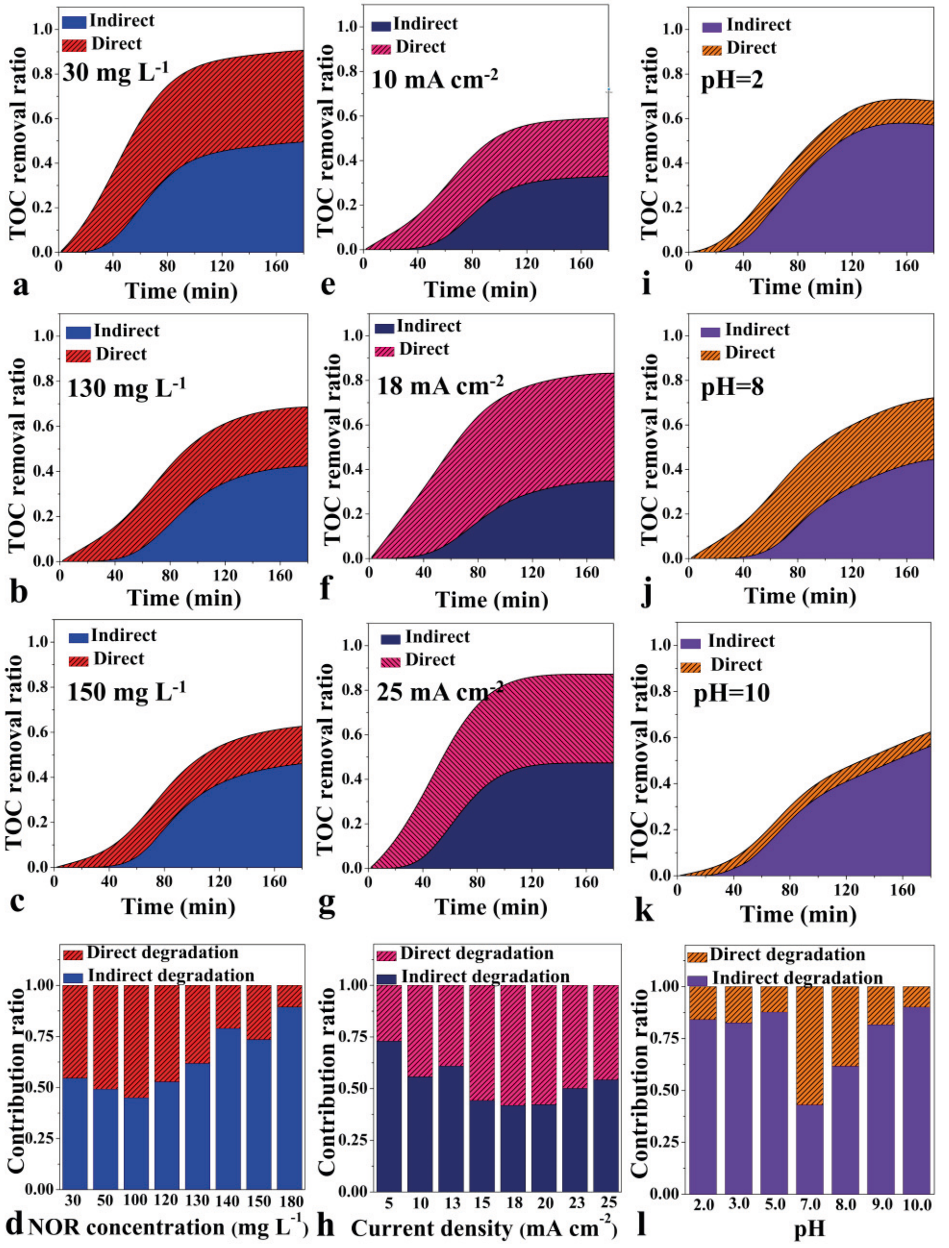

Fig. 24. The contribution ratio of direct and indirect routes to NOR degradation in the function of time with the variation of initial NOR concentration ((a)-(d)), current density ((e)-(h)) and initial pH value ((i)-(l)) as critical factors.

Based on k_1 and k_2, the degradation contribution from direct and indirect route was distinguished, as shown in Fig. 24. In all conditions (Fig. 24 (a)-(c), (e)-(g) and (i)-(k)), the direct route dominated within the first 13-23 min (contribution ratio $\geq$ 99.0%), while indirect route catch up later with experiment time increasing. However, the effect increased with time and resulted in 41.8-90.1% degradation contribution, indicating •Cl as a major degradation agent. This is due to the different mechanisms of direct adsorption-degradation and indirect diffusion-transformation-degradation, sharing the same principle with contribution distribution between anode and cathode in Section 4.2.2. The summarized contribution ratio in Fig. 24 (d), (h) and (I) was the total degradation contribution ratio at the end of 180 min experiment.

In particular, the finite contact surface on UTS led to a dropping of final contribution ratio of direct route (45.4-10.5%) with higher initial NOR concentration was obtained (Fig. 24 (d)). However, indirect route showed better adaptation of high NOR loading because of the continuous diffusion of degradation agent into the entire electrolyte. By the variation of current density (Fig. 24 (h)), a peak of degradation contribution (58.1%) by direct route was found approximately at the current density of 19 mA cm^{-2}. This is due to the significant lift of k_1 with current density from 5 to 20 mA cm^{-2}, whereas, at the range higher than 20 mA cm^{-2}, this trend was blocked with a significant increasing of k_2 (Fig. 23 (e)). In terms of initial pH variation (Fig. 24 (l)), neutral condition showed highest direct route contribution (57.0%), where k_1 was found obvious higher than at other values (3.8-1234.8 times). Compared to which, the variation of k_2 can be ignored. The better degradation performance at pH=7 can be therefore mainly due to the high direct reaction coefficient value at neutral condition. When comparing acidic and alkaline conditions, the direct contribution ratio dropped less with pH increasing than decreasing, this was associated with by-products in alkaline condition which limited the •Cl production.

Overall, UTS anode showed advantage in photo/electro/photo-electro degradation due to its higher photo/electro reaction activities and large available surface. This is attributed to the unique tubular microstructure by urea precipitation. UTS involved PEC-UTS system showed the optimal performance with 91.1% TOC removal ratio, indicating a high degree of mineralization from NOR to inorganic matters. In this case, both direct route (adsorption-degradation, photo radiation) and indirect route (mainly •Cl) contributed significantly, where indirect route shared 41.8-90.1% of total degradation ratio. The kinetics of both routes were enhanced by higher current densities. The kinetics of direct route preferred neutral conditions, with indirect route dominated in the range of pH=3-7. The contribution ratio of indirect route dropped significantly with neutral environment and lower initial NOR loading. While with relatively high loading, indirect route showed better adaptability.

4.2.4 Real pharmaceutical wastewater treatment by PEC-D system (paper VI)

The potential of PEC-D system for organic matters degradation in HSW has been determined. To verify the effectiveness of the new PEC-D system for real HSW treatment, a PW was employed as targeted HSW. This PW was obtained from an antibiotic pharmaceutical factory which mainly produces cefotiam (CTM, $C_{18}H_{23}N_9O_4S_3$) and 7-phenylacetamide-3-chlorormethyl-3-cepham-4-carboxylic acid p-m-ethoxybenzyl ester (GCLE, $C_{24}H_{23}O_5N_2SCl$). Before PEC treatment, the PW was pre-purified to remove suspended solid particles and insoluble organic matter, the parameters before and after the purification were listed on Table 4. In this section, the PEC-D was employed with SPC and SEC as comparison.

Table 4. Water quality parameters before and after pre-treatment of PW.

Condition	Turbidity (NTU)	pH	Salinity (%)	Conductivity ($mS\cdot cm^{-1}$)	SS ($mg\cdot L^{-1}$)	COD ($mg\cdot L^{-1}$)	TOC ($mg\cdot L^{-1}$)
Before	26.1	6.47	0.5	10.63	10	14705	3917
After	15	5.2	0.56	10.26	---	7645	2610

The effects of organic pollutant concentration and current to the degradation performance were first carried out, as can be seen in Fig. 25. PEC-D showed degradation ratios below 5% in the raw PW (Fig. 25 (a)), which increased limitedly when PW was diluted by 16 times at most, with the initial COD dropped to approximately 480 mg L^{-1} (Fig. 25 (b) and (c)). This was due to the high organic matter concentration and finite degradation agent production ratio. Meanwhile, the difference of degradation ratio between various current densities can be hardly distributed, which should be corresponding to the significant effects of bias and errors to small values of experiment data. However, despite the limited performance, the positive trend of degradation ratio performed from Fig. 25 (a) to (c). Therefore, for the efficient reveal of degradation performance, the degradation process was accelerated by 200 times dilution of the raw PW (COD $\approx$ 40 mg L^{-1}). The result was shown in Fig. 25 (d). The highest 95.58% TOC removal ratio was obtained with current=0.08 A at 120 min. This indicated the high degradation degree towards inorganic matters as well as the adaptability to real HSW with complex organic content of PEC-D. The performance increased with higher current applied until 0.08 A, which dropped when the higher 0.11 A was employed. This was consistent to the results in the simulation HSW treatment in Section 4.2.3, which should be due to the controlling role of molecular diffusion when current reached to a high level as well as the occurrence of side reactions. Overall, with 200 times dilution, the experiment was successfully accelerated and almost completed degradation was obtained. Therefore, PW with 200 times dilution was applied in the following tests.

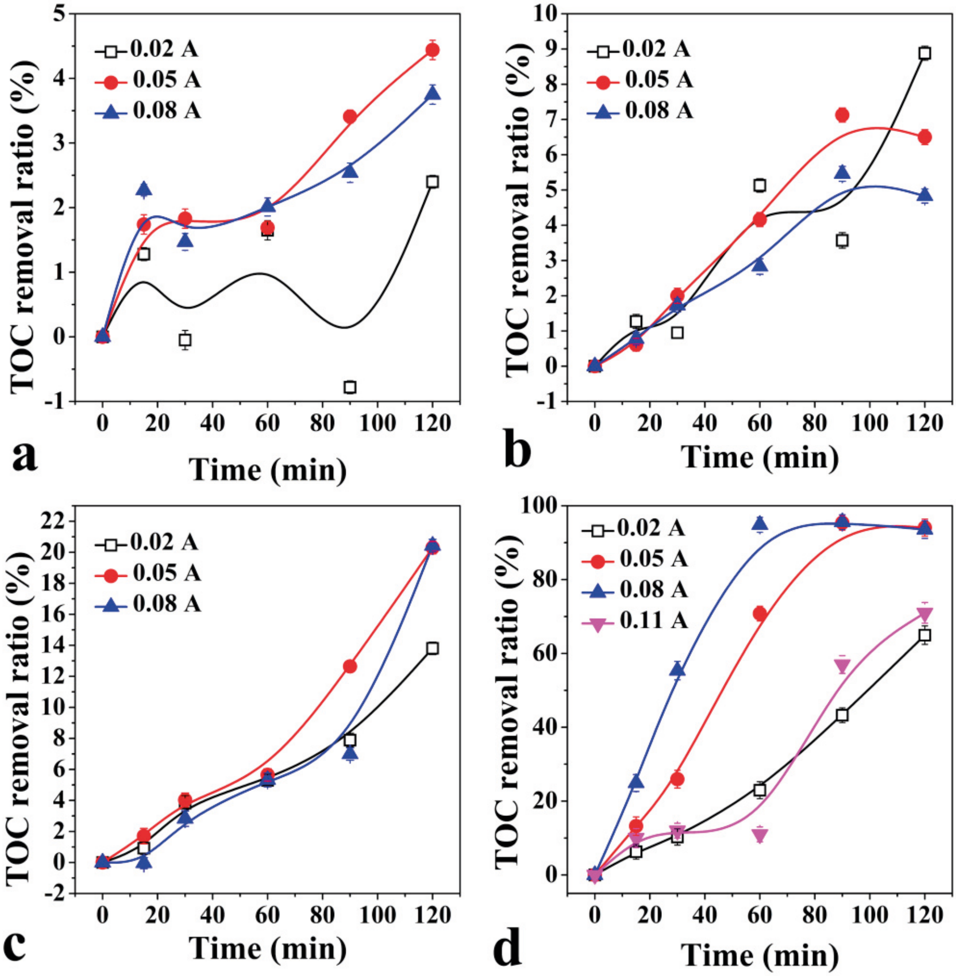

Fig. 25. Degradation performance for PW by PEC-D system in the function of current with various dilution times ((a) Original PW; (b) diluted by 4 times; (c) diluted by 16 times; (d) diluted by 200 times; The variation of ion concentration was compensated by added NaCl.)

The effects of different systems and initial pH values to the degradation performance as well as the biotoxicity in the PW during experiment were as shown in Fig. 26. In general, the trends highly agreed with the results in simulated HSW treatment. The dominating advantages of PEC-D system compared to the SPC and SEC systems was shown in Fig. 26 (a). This was due to the synergistic work between anode and cathode as well as between photo and electro catalysis. The highest performance was found in neutral conditions (Fig. 26 (b)), according to the findings in Section 4.2.3, this should be due to suitability of free radical production and the major occurrence of direct adsorption-degradation in neutral condition. The toxicity of treated PW was carried out by luminescent bacteria method (Fig. 26 (c)).

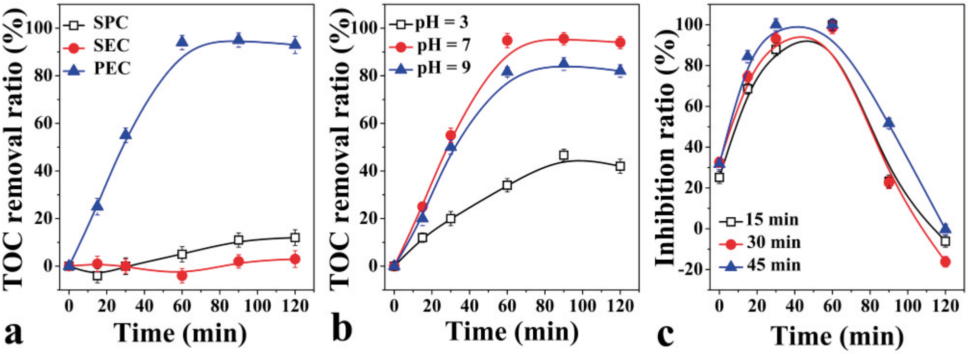

Fig. 26. Effect factors and biotoxicity during the degradation process w. (a) The effect of different systems to the degradation performance; (b) The effect of pH value to the degradation performance; (c) The luminescence inhibition ratio (biological toxicity) of the PW during experiment.(current=0.08 A.)

In general, the biological toxicity increased first and then decreased with the extension of degradation time. Within 30 min, in all contact times of 15, 30, and 45 min, although the TOC of wastewater has been reduced, the toxicity of wastewater increased. This phenomenon might be resulted from the production of toxic intermediates in the initial decomposition stage. When the degradation time exceeds 30 min, the inhibition ratio showed a downward trend until negative values This should be due to the formation of non-toxic organic substances after the fully degradation of wastewater, which can provide energy for the luminescent bacteria.

The organic compounds in PW before and after the PEC-D treatment were as shown in Table 5 and 6, respectively. As can be seen, the untreated antibiotic PW contains organic pollutants with complex composition and high content. Most of these organic pollutants are harmful and toxic to the ecological environment as well as humans. After the treatment, the species and content of organic pollutants in the PW have been greatly reduced. Less-toxic water can be obtained after PEC-D treatment, which further proved the effectiveness of the PEC-D for the biological harmless treatment of HSW.

Overall, high performance of PEC-D for real HSW was confirmed, the biological harmless outflow can be achieved. However, PEC-D showed limited degradation efficiency for high concentration organic matters, However, it was suitable for low concentration refractory organic matters treatment in HSW.

Table 5. The organic compounds in PW before the treatment.

No	Compound	Retention time	Molecular formula	Molecular	Peak area
1	Trisiloxane	8.588	$C_9H_{28}O_3Si_4$	296	85122
2	Undecane	9.651	$C_{13}H_{28}$	284	199436
3	Cyclopentasiloxane	11.188	$C_{10}H_{30}O_5Si_5$	370	83761
4	Nonane	13.115	$C_{13}H_{28}$	284	149630
5	Dodecane	15.996	$C_{14}H_{30}$	198	188495
6	Hexadecane	15.996	$C_{16}H_{34}$	226	172291
7	Eicosane	18.86	$C_{20}H_{42}$	282	232842
8	Eicosane	22.264	$C_{20}H_{42}$	282	280675
9	2-Methylhexacosane	24.34	$C_{27}H_{56}$	380	106043
10	Heptadecane	24.667	$C_{18}H_{38}$	254	281291
11	Heneicosyl acetate	24.892	$C_{23}H_{46}O_2$	354	301252
12	Hexadecanoic acid	25.15	$C_{18}H_{36}O_3$	300	189240
13	Geranyl ethyl ether	26.067	$C_{12}H_{22}O$	182	166788
14	4,6-Hexacosanedione	26.175	$C_{26}H_{50}O_2$	394	123820
15	Dihydrophytol	26.233	$C_{23}H_{50}OSi$	370	221018
16	Tetradecane	26.325	$C_{15}H_{32}$	212	59878
17	Phenol	26.325	$C_{23}H_{32}O_2$	340	4716932
18	Hexadecanoic acid	26.483	$C_{18}H_{36}O_3$	300	190975
19	1,3,5-Trisilacyclohexane	26.662	$C_3H_{12}Si_3$	132	162417
20	2-Ethylbutyric acid	26.756	$C_{26}H_{52}O_2$	396	834137
21	1-Eicosyne	26.983	$C_{20}H_{38}$	278	248392
22	Bis(tridecyl) phthalate	27.125	$C_{34}H_{58}O_4$	530	425345
23	n-Nonadecanoic acid	27.986	$C_{24}H_{52}O_2Si_2$	428	234142
24	Hexanoic acid	28.076	$C_{23}H_{46}O_2$	354	491627
25	1-Octadecanesulphonyl chloride	28.858	$C_{18}H_{37}ClO_2S$	352	431060
26	Octadecanoic acid	29.567	$C_{21}H_{42}O_4$	358	177

Table 6. The organic compounds in PW after the treatment.

No	Compound	Retention time	Molecular formula	Molecular	Peak area
1	Nonane	13.534	$C_{13}H_{28}$	184	39981
2	Decane	16.419	$C_{13}H_{28}$	184	74552
3	Sulfurous acid	16.991	$C_{14}H_{30}O_3S$	278	49075
4	Nonane	19.507	$C_{13}H_{28}$	184	51502
5	Nonane	20.373	$C_{13}H_{28}$	184	36692
6	Phenol	26.92	$C_{23}H_{32}O_2$	340	403413

4.3 Discussion

4.3.1 Performances and mechanisms

The new EC (TS-CB & TS-AC) and PEC (PEC-D & PEC-UTS) systems have shown significant potential for organic matter removal and degradation in HSW. This was due to the new structures and materials applied. In the EC experiments (**paper I**), the higher performance of new EC systems derived from the duo working anode and cathode, compared to the ones with single working anode. This was proved by the detection of produced active chlorine and H_2O_2. The utilization of the current on cathode side accelerated the degradation process and therefore lower the energy consumption. In EC experiments, the adjustment of pH with duo working electrodes was also found. According to the reaction equations, the pH should stay stable when Cl_2 reacted with OH^- by 100 %. For the inevitable uncompleted reaction in reality, the bias towards alkaline condition was obtained in EC system with only working anode. With duo working anode and cathode, however, two different theories of pH controlling should be considered (**paper I and paper II**). By CB cathode, H_2O_2 produced under EC was as buffer agent to retain the neutral condition. By AC cathode, the adsorption of active chlorine on cathode surface consumed more OH^-, which lower the pH value and led to acidic conditions. Because of the higher reaction activity of HClO than ClO^-, the acidic condition was prior for degradation work. In the degradation work of NOR (**paper III**), the rapid NOR removal was also found. However, according to the COD values, the degradation ratio was significantly lower and delayed. This was due to the different reactionary power required by various reactions. The rapid removal can derive from the simple substitution reactions which replaced H or F by Cl on NOR structure. However, this contributed little to the decomposition of the molecular. Due to the limited reactionary power of active chlorine and H_2O_2, the ring opening reactions needed the accumulation of both agents to high concentrations. This caused the longer experiment time and lower degradation ratio. The final 23.0% COD removal was due to the piperazine ring opening, which also lifted biodegradability.

The NOR degradation was significantly enhanced by PEC systems (**paper IV**). In PEC-S with only working anode, the enhancement was mainly due to the assistance of radiation power, accelerating the electron emission and transition. These created holes with high reaction activity produced free radicals or directly decomposed NOR by adsorption-degradation. In the new PEC-D, higher degradation performance should be attributed to •OH transferred from H_2O_2 by duo photo-electro catalysis. The oxalic acid was detected as the smallest intermediate product with molecular weight as 91, indicating a high degradation degree with photo-electro produced free radicals. These radicals participated in the hexatomic ring opening, piperazine ring opening and dicarboxylic reaction. The simulation work suggested significant contribution from both anode and cathode in PEC-D system, with anode as prior. Therefore, the development of TSSA anode was considered as premier in the next work (**paper V**). The urea precipitation prepared TSSA (UTS) showed significant higher degradation performance on NOR compared to the traditional sol-gel prepared one. This was due to the high photo/electro catalysis activity and high conductivity of UTS, which was associated with porosity from the unique tubular microstructure. The •Cl, rather than •OH, was the main contributor to the indirect degradation route. The •Cl was supposed to be produced from active chlorine and •OH. Therefore, the active chlorine from EC was consumed significantly. This reduced the redundant residual chlorine during and after treatment and subsequently lower the environmental risk.

The test of PEC-D method in real HSW treatment (**paper VI**) showed a high performance with low concentration refractory organic matters, whereas, its efficiency was limited for high concentrations. This was due to the finite degradation agents-production speed in PEC-D. Therefore, the performance of PEC methods should be further developed by increasing production rate and involving more efficient degradation mechanisms. So far, this method should aim to deal with the left refractory organic matters after the main degradation process in water treatment plants.

4.3.2 Simulation and modelling

To investigate treatment performances of new methods, the simulation and modeling are always needed. The simple first order and second order laws are simple and effective. The coefficients obtained can illustrate roughly the kinetics in the degradation reaction. However, in complex systems, these methods may not be suitable. Therefore, deduced from these laws, the new models for simulation was developed in this study. The first application in **paper IV** was used directly one equation for the simulation with fixed coefficients to be calculated. Whereas in **paper V**, considering the possible variation of coefficients due to different impacts, differential equations were employed. Both ways resulted in the successful distribution of degradation contribution of anode and cathode. Meanwhile, these models retained simple and applicative for average personal computers. However, accuracy and obtained information from these models were still limited, which need the further explore in the future works. Meanwhile, to establish the whole picture, other factors like pH, intermediates, temperature, radiation intensity and current density should be also involved in the modeling.

4.3.3 Impact on environment and energy

To evaluate new water treatment methods, environmental risk and energy consumption are necessary for discussion. Theoretically, due to the in-situ production of degradation agent from ions and compounds in the water, the new EC and PEC systems can be considered as a "one step treatment" with no need of extra assistance, compared to traditional methods. This means a potential for energy and material saving. As members of AOPs, these methods also avoid negative impacts on degradation performance from biotoxicity and high saline concentration. The PEC systems, especially, are suitable for refractory organic matters degradation due to its extra reactionary power from radiation. However, the applied range of PE/PEC methods should be limited to the organic matters with low biodegradability and high toxicity in small scale. For many other cases, the proven bio treatment shows dominating advantages in economy and energy saving. So far, as our best knowledge, few models for large scale applications of EC or PEC have been figured out. This is due to the requirement of contact between pollutant and electrode surface/degradation agent as well as the exposure to radiation in these methods, which lead to the difficulty for plant design.

Compared with each other, PEC showed less impact to environment due to its cancelation of residual chlorine. The produced free radicals from residual chlorine can be consumed by organic matters with no reaction activity left. However, in EC systems, the residual chlorine can't be avoided in the fast degradation. When attempting to match the content of active chlorine and organic matter, the reaction retains slow. The PEC systems also show high degradation performances, the outflow will be safer for environment and human beings. The final target of PEC method is to utilize solar radiation efficiently, however, this relies on weather conditions and also need further development of catalysis materials and reactor structures, which need future studies.

5. Conclusions

5.1 Discussion and summary

In this study, the new EC and PEC methods with duo working electrodes and economic catalyst materials (anode and cathode) were developed for organic matter degradation in HSW, resulting in considerable performances. In general, new EC and PEC methods (EC-D and PEC-D) showed significant higher removal and degradation efficiency compared to traditional ones with only one work anode (**paper I, paper II and paper IV**). This was due to the synergistic work between anode and cathode in the new systems. Particularly, in EC system, this derived from the adsorption-transformation from O_2 to H_2O_2 on air diffusion cathode (**paper I**). However, the single electrochemical catalysis showed shortage when addressing refractory NOR, this was attributed to the limited reaction activities of active chlorine and H_2O_2 produced under EC (**paper III**). Whereas, in PEC-D system, with synergistic work between photo and electro catalysis as well as between anode and cathode, these agents above were further transferred to highly active free radicals, leading to significant lift of degradation efficiency (**paper IV and paper V**). This transformation process also removed harmful residual chlorine (**paper V**) and resulted in cleaner output. Newly developed models were involved in the mechanism study of degradation performance in this work (**paper IV and paper V**). Conclusively, both anode and cathode contributed significantly with anode as prior. Both direct adsorption-degradation and indirect decomposition by free radicals were proved important, with indirect route as prior. The efficiency of PEC was further improved by the development of anode material. A urea precipitation prepared TSSA (UTS) with tubular microstructure lifted the degradation efficiency, this is due to the high photo and electro catalysis activity, high conductivity and large available surface area (**paper V**). The real application of the new PEC was finally attempted using a real PW as target pollutant (**paper VI**). The results suggested a suitability of PEC to address low-concentration refractory organic matter. However, with high concentrations (for instance, COD>400 mg L^{-1}), the efficiency of PEC dropped. This should be due to the limited degradation agent production rate and diffusion in the water. Therefore, PEC method can be a potential supplement for water degradation after the traditional treatment processes in the treatment plants.

After the discussion above, the potential practical application of these new methods should be then analyzed. Because of the effectiveness of the electrodes both for photo and electrochemical catalysis, the EC and PEC can be integrated as PEC in the real application. The electro/photo degradation works when the corresponding catalysis is available. In terms of regional factor, the areas with clean electric power sources and rich solar radiation are more suitable for EC and PEC plants. This is to guarantee the treatment efficiency and secondary-pollution proof. In the whole HSW treatment system, the application of PEC depends on the concentration and categories of both organic matters and electrolyze. Usually, PEC is suggested to be settled after the main degradation plants to deal with refractory organic matters left. When directly facing high organic concentration, the performance of PEC may be limited, as explained above. In the municipal water treatment plants, on the other hand, EC may lose its power due to the low saline concentration and photo catalysis will therefore play the only main role. The position of PEC plants in municipal water treatment systems is as in HSW treatment system for the same theory.

However, despite the limited conditions for application so far, with the continuous development of EC/PEC systems, the wider application range in many aspects can be expected (discussed in Section 5.3). This requires the further study in this area by researchers.

5.2 Concluding remarks

In this study, new EC and PEC systems (EC-D and PEC-D) with duo-working-electrode structure as well as efficient and economic catalyst materials (anode and cathode) were successfully developed to address organic pollutants in HSW. The detailed conclusions were as follow:

1. In initial experiment, new EC-D system performed higher degradation and removal efficiency, with lower energy cost, compared to EC with single working anode (EC-S). This was due to the active chlorine and H_2O_2 produced on anode and cathode, respectively. The synergistic work between duo working electrodes was initially proved.
2. Single EC method showed shortage dealing with complex and refractory organic matter, such as Norfloxacin (NOR). This should be attributed to the limited reaction activity of EC produced degradation agents. However, by partly decomposing the NOR, biodegradability was improved.
3. PEC system significantly enhanced the performance of EC system due to the synergistic work between photo and electric power, by which the EC produced degradation agents transferred to stronger free radicals.

4. The degradation performance was in general in the order of PEC-D>PEC with single work electrode (PEC-S)>single photo catalysis (SPC)>single electro catalysis (SEC). PEC-D emerge as prior duo to its synergistic work between photo-electro catalysis and between anode and cathode.
5. PEC systems also avoid harmful residual chlorine result in EC systems by transferring them the free radicals. This showed a better prospect of PEC in the view of environment and human health.
6. In general, in PEC system, anode and cathode both contributed significantly to degradation work, with anode as prior. Both direct adsorption-degradation and indirect degradation by agents contributed significantly, with indirect route as prior.
7. Formatting anode by a new urea precipitation method, the efficiency of PEC system lifted importantly. This was due to the high photo/electro reaction activity, high conductivity and large surface area of the new anode, derived from its unique tubular microstructure.
8. PEC-D showed high performance in real HSW treatment with low initial organic matter concentration, the biological harmless outflow can be expected. It’s suitable for the treatment of left refractory organic matters after the main degradation process.

In general, both new EC and PEC showed bright prospects in organic matter removal and degradation in HSW, where the new PEC-D owned best performance. This study also showed limitations of the new systems (discussed in Section 5.3). They should be further developed before application, which left significant space for future study.

5.3 Limitations of current study and plans for future steps

Both new EC and PEC systems showed potential for further study and future application. However, various limitations of them were also discovered:

1. To further study the performances and features, more categories of organic matters should be tested and more critical factors should be considered in the future works.
2. The degradation efficiency and the sustainability of the new methods need further development.
3. A good design of reaction construction for large scale application still retains as a vital issue. The new models require further development to improve the accuracy and yield more useful information.

4. PEC relies on enough solar radiation and simple EC shows less effectiveness for refractory organic matter degradation. The performances of both methods depend on the content of ions in wastewater. Therefore, their application areas and conditions are limited so far. Hence, how to develop these methods towards better adaptability and wider the application fields remains as challenges.

To address these limitations and further develop EC and PEC techniques, several aspects will draw my attention in the future study:

1. More possible degradation mechanisms should be involved and the study of inter-discipline should be considered. The possibility of integrating of EC/PEC with bio-treatments, membrane techniques and intelligent control, etc. should be studied. The multi degradation mechanisms will wider the application fields and enhance the adaptability to various environments.
2. Further selection and development of efficient and economic catalysis materials for EC/PEC degradation will be also focused on. This relies on (1) the selection of potential combination of elements, oxides and other compounds for catalyst (anode and cathode) as well as (2) the usage of novel efficient and environmentally friendly craftmanship for the catalyst formation. The target is to enhance the performances of catalyst with lower cost.
3. The effective design of large-scale plants for real application should be figured out. This needs the cooperation with engineering science. The design requires the efficient utilization of solar radiation and electric power as well as the full contact between water and catalyst in a large scale. This is critical for the real application of EC/PEC in the water treatment.
4. Besides the organic pollutants, other factors like nitrogen, phosphorus and salinity in HSW also cause serious risks. The theory of EC/PEC is to stimulate the charge exchange to achieve a certain purpose. Therefore, the nitrogen/phosphorus removal and desalination by PE/PEC showed potential. For these purposes, one possibility route should be the combination of EC/PEC-degradation, electro-adsorption and membrane filtration (like electroosmosis). The development of the theory, the design of system as well as the exploration during experiment should draw attention in the future work.

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