MODIFICATION OF BISMUTH FERRITE THROUGH CALCIUM- AND COPPER-DOPING FOR ENHANCED ANTIBIOTICS REMOVAL VIA CATALYTIC PEROXYMONOSULFATE ACTIVATION

KOO POOI LING

UNIVERSITI SAINS MALAYSIA

2023

MODIFICATION OF BISMUTH FERRITE THROUGH CALCIUM- AND COPPER-DOPING FOR ENHANCED ANTIBIOTICS REMOVAL VIA CATALYTIC PEROXYMONOSULFATE ACTIVATION

by

KOO POOI LING

Thesis submitted in fulfilment of the requirements
for the degree of
Master of Sciences

January 2023

ACKNOWLEDGEMENT

I would like to express my gratitude as well as utmost appreciation for the assistance and guidance I have humbly received towards the completion throughout my research. First and foremost, I wish to convey my contentment and recognition towards my supervisor, Dr. Oh Wen Da for his valuable guidance and advice in aiding me to complete my research for Master Degree. His suggestions and ideas have provided the impetus for me to conduct the laboratory experiments smoothly, objectively as well as precisely. From here, I was enlightened by new concepts and abstractions which are immeasurably beneficial towards the scientific development of my laboratory skills and my theoretical perception on the idea of environmental pollution and catalytic degradation. Furthermore, I would like to thank the PhD research student, Mohamed Faisal Gasim as well as the master research student, Choong Zheng Yi which have supported me immensely in my numerous experiments. Furthermore, I would like to acknowledge the financial support provided by Universiti Sains Malaysia (USM). In the nutshell, I wish to thank the School of Chemical Sciences, Archaeology, School of Materials & Mineral Resources Engineering and Science and Engineering Research Centre (SERC), USM, Penang in providing me with various services and necessities towards the fulfilment of my Master Degree Project.

TABLE OF CONTENTS

APPENDICES

LIST OF PUBLICATIONS

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF SCHEMES

LIST OF SYMBOLS

$SO_4^{\bullet -}$	Sulfate radical
$Bi_2Fe_4O_9$	Bismuth ferrite mullite
$^{\bullet}OH$	Hydroxyl radical
$^1O_2$	Singlet oxygen
$O_2^{\bullet -}$	Superoxide radical
c-Cu_2O	Cubic Cu_2O
h-BN	Hexagonal boron nitride
E_{VB}	Valance band energy
E_{CB}	Conductive band energy
h^+	holes
S_{BET}	BET specific surface area
k_{app}	Pseudo first-order rate constant
k	Second-order rate constant

LIST OF ABBREVIATIONS

POPs	Persistent organic pollutants
CIP	Ciprofloxacin
GAT	Gatifloxacin
PMS	Peroxymonosulfate
AOP	Advanced oxidation process
WHO	World Health Organization
FTIR	Fourier transform infrared spectrometry
BET	Brunauer-Emmett-Teller
SEM	Scanning electron microscope
EDX	Energy dispersive X-ray analysis
TEM	Transmission electron microscope
HRTEM	High resolution transmission electron microscope
SR-AOP	Sulfate radical-advanced oxidation process
$^{\bullet}$OH-AOP	Hydroxyl radical-advanced oxidation process
NHE	Normal hydrogen electrode
DOM	Dissolved organic matter
ZVI	Zero valent iron
ATZ	Atrazine
SMX	Sulfamethoxazole
UV	Ultraviolet
US	Ultrasound
RB5	Reactive Black 5
BC	Biochar

CAP	Chloramphenicol
BPA	Biphenol A
AO7	Acid orange 7
2,4-DCP	2,4-Dichlorophenol
TNTs	Titanate nanotubes
LDHs	Layered double hydroxides
PBA	Prussian blue analogs
MOF	Metal-organic framework
TCH	Tetracycline hydrochloride
TC	Tetracycline
MO	Methyl orange
LFX	Levofloxacin
RhB	Rhodamine B
BPAF	Biphenol AF
NFC	Norfloxacin
VL	Visible light
DCF	Diclofenac
LOM	Lomefloxacin
XPS	X-ray photoelectron spectroscopy
UV-Vis	Ultraviolent-visible light
UPLC	Ultra-performance liquid chromatography
MS	Mass spectrometry
TOC	Total organic carbon
AAS	Atomic absorption spectroscopy
ICP-OES	Inductively coupled plasma – optical emission spectrometry

LIST OF APPENDICES

PENGUBAHSUAIAN FERIT BISMUT MELALUI PENDOPAN KALSIUM DAN KUPRUM UNTUK PENYINGKIRAN ANTIBIOTIK YANG DIPERTINGKATKAN MELALUI PENGAKTIFAN PEMANGKIN PEROKSIMONOSULFAT

ABSTRAK

Kaedah pengaktifan peroksimonosulfat (PMS) biasanya digunakan untuk penyingkiran bahan pencemar organik dalam air. Pengaktifan PMS menghasilkan radikal seperti $SO_4^{\bullet-}$ dan $^{\bullet}OH$. Selain itu, spesis bukan radikal seperti $^1O_2$ didapati terhasil daripada tindak balas antara PMS dan kekosongan oksigen di permukaan pemangkin. Pemangkin berasaskan logam heterogen mempunyai aktiviti pemangkin yang tinggi dalam pengaktifan PMS. Mullit ialah pemangkin yang berpotensi untuk mengaktifkan PMS kerana mullit mempamerkan banyak kekosongan oksigen dan kesan sinergistik antara logam peralihan. $Bi_2Fe_4O_9$ ialah pemangkin mullit yang biasa digunakan sebagai fotomangkin kerana sifat multiferoiknya. Walau bagaimanapun, kekurangan kajian terhadap pemangkin $Bi_2Fe_4O_9$ untuk pengaktifan PMS telah disiasat. Objektif utama penyelidikan ini adalah untuk menambah baik aktiviti pemangkin $Bi_2Fe_4O_9$ melalui penambahan dopan untuk penyingkiran antibiotik fluorokuinolon melalui pengaktifan PMS. Dalam bahagian pertama kajian ini, $Bi_2Fe_4O_9$ dan satu siri $Bi_2Fe_4O_9$ terdop Ca dengan pelbagai %w/w Ca telah disediakan melalui kaedah hidroterma untuk mendapatkan $Bi_{2X}Ca_{2(1-X)}Fe_4O_9$ (ditandakan sebagai BFOCa-X, where X = 1, 0.95, 0.90, 0.80, 0.50). Pemangkin BFOCa-X telah dikaji dengan analisis pembelauan sinar-X (XRD), spektrometer inframerah transformasi Fourier (FTIR) dan porosimeter dan keputusan menunjukkan bahawa pemangkin disediakan terdiri daripada $Bi_2Fe_4O_9$ fasa tulen dengan saiz nano. Pemangkin BFOCa-X yang disediakan telah digunakan sebagai pengaktif PMS untuk menyingkirkan gatifloxacin (GAT). Aktiviti pemangkin dalam penyingkiran GAT menurun dengan urutan berikut: BFOCa-0.8 (90.2 % kecekapan penyingkiran GAT dalam 45 min, k_{app} = 0.084 min^{-1}) > BFOCa-0.95 > BFOCa-0.9 > BFOCa-0.5 > $Bi_2Fe_4O_9$, keputusan ini menunjukkan bahawa BFOCa-0.8 mempunyai tapak aktif yang optimum untuk pemangkinan. Spesis oksigen reaktif (ROS) dominan telah dikenal pasti dan $SO_4^{\bullet -}$, $^1O_2$ dan $^{\bullet}OH$ menyumbang dengan ketara kepada penyingkiran GAT. Berdasarkan kajian spektrometri fotoelektron sinar-X (XPS), kitaran redoks Fe^{2+}/Fe^{3+} dan kekosongan oksigen atas pemangkin menghasilkan $SO_4^{\bullet -}/^{\bullet}OH$ dan $^1O_2$, masing-masing untuk pengaktifan PMS. Selain $Bi_2Fe_4O_9$ terdop Ca, pemangkin $Bi_2Fe_4O_9$ terdop logam peralihan juga telah dikaji dalam bahagian kedua kajian ini. Kaedah hidroterma telah digunakan untuk menyediakan $Bi_2Fe_4O_9$ terdop M (M = Zn, Cu, Co dan Mn) sebagai pengaktif PMS untuk menyingkirkan siprofloksasin (CIP). Ciri-ciri $Bi_2Fe_4O_9$ terdop M telah disiasat menggunakan pelbagai alat pencirian termasuk XRD, FTIR dan porosimeter. Keputusan didapati bahawa $Bi_2Fe_4O_9$ terdop M berstruktur ortorombik segi empat sama yang bersaiz nano. Aktiviti pemangkin $Bi_2Fe_4O_9$ terdop M telah dibandingkan dalam kaedah yang sama dan keputusan menunjukkan bahawa $Bi_2Fe_4O_9$ terdop 0.08 wt.% Cu mempunyai aktiviti pemangkin tertinggi (k_{app} = 0.085 min^{-1}) berbanding dengan $Bi_2Fe_4O_9$ terdop logam yang lain. Interaksi sinergistik antara Cu, Fe dan kekosongan oksigen adalah faktor utama yang meningkatkan prestasi $Bi_2Fe_4O_9$ terdop logam. ROS yang dominan telah dikenal pasti dan $SO_4^{\bullet -}$, $^1O_2$ dan $^{\bullet}OH$ memainkan peranan utama dalam penyingkiran CIP. Keseluruhannya, kajian ini menunjukkan bahawa $Bi_2Fe_4O_9$ terdop Ca dan M berpotensi menjadi pengaktif PMS untuk penyingkiran fluorokuinolon.

MODIFICATION OF BISMUTH FERRITE THROUGH CALCIUM- AND COPPER-DOPING FOR ENHANCED ANTIBIOTICS REMOVAL VIA CATALYTIC PEROXYMONOSULFATE ACTIVATION

ABSTRACT

Recently, catalytic peroxymonosulfate (PMS) activation is frequently used for the removal of the organic pollutants in water. The activation of PMS will lead to the generation of $SO_4^{\bullet-}$ and $^{\bullet}OH$. Apart from the formation of radicals, non-radical species such as $^1O_2$ has been found to be produced from the reaction between PMS and oxygen vacancies on the surface of the catalyst. Heterogeneous metal-based catalysts possess higher catalytic activity compared to homogeneous metal-based catalysts in PMS activation. Mullite-based material can be considered as a potential PMS activator as it exhibits abundant oxygen vacancies and synergistic effects between the transition metal ions in the catalyst. Bismuth ferrite ($Bi_2Fe_4O_9$) is a mullite-based catalyst which is commonly used as photocatalyst due to its multiferroic properties. However, limited studies on the application of $Bi_2Fe_4O_9$ as PMS activator have been explored. The main objective of this research is to improve the catalytic activity of $Bi_2Fe_4O_9$ through doping for the removal of fluoroquinolone antibiotics via PMS activation. In the first part of the study, pure $Bi_2Fe_4O_9$ and a series of Ca-doped bismuth ferrite was prepared at various %w/w of Ca via a facile hydrothermal method to obtain $Bi_{2X}Ca_{2(1-X)}Fe_4O_9$ (denoted as BFOCa-X, where X = 0.95, 0.90, 0.80, 0.50). The BFOCa-X catalysts were characterized X-ray diffraction (XRD) analysis, fourier transform infrared spectrometer (FTIR) and porosimeter and the results showed that they consist of pure phase $Bi_2Fe_4O_9$ with nanosheet-like morphology. The as-prepared BFOCa-X catalysts were used as PMS activator for gatifloxacin (GAT) removal. It was found that the catalytic activity decreased in the following order: BFOCa-0.8 (90.2% GAT removal efficiency in 45 min, k_{app} = 0.084 min^{-1}) > BFOCa-0.95 > BFOCa-0.9 > BFOCa-0.5 > $Bi_2Fe_4O_9$ indicating that BFOCa-0.8 has the optimized active sites for catalysis. The dominant reactive oxygen species (ROS) were identified using chemical scavengers, revealing that $SO_4^{\bullet -}$, $^1O_2$ and $^{\bullet}OH$ contributed significantly to GAT degradation. Based on the X-ray photoelectron spectrometry (XPS) study, PMS was activated by the Fe^{2+}/Fe^{3+} redox cycling and oxygen vacancies to produce $SO_4^{\bullet -}/^{\bullet}OH$ and $^1O_2$, respectively. Apart from the doping of Bi by Ca, the catalytic performance of transition metals doped into Fe have also been studied in second part of the research. A facile hydrothermal method was employed to prepare M-doped $Bi_2Fe_4O_9$ (M = Zn, Cu, Co and Mn) as PMS activator for ciprofloxacin (CIP) degradation. The characteristics of the M-doped bismuth ferrites were investigated using various characterization instruments including XRD analysis, FTIR and porosimeter indicating that the M-doped $Bi_2Fe_4O_9$ with nanosheet-like square orthorhombic structure was successfully obtained. The catalytic activity of various M-doped $Bi_2Fe_4O_9$ was compared and the results indicated that the Cu-doped $Bi_2Fe_4O_9$ at 0.08wt.% possessed the greatest catalytic activity (k_{app} = 0.085 min^{-1}) over other M-doped $Bi_2Fe_4O_9$ under the same condition. The synergistic interaction between Cu, Fe and oxygen vacancies are the key factors which enhanced the performance of M-doped $Bi_2Fe_4O_9$. The dominant ROS was identified using the chemical scavengers with $SO_4^{\bullet -}$, $^1O_2$ and $^{\bullet}OH$ playing a major role in CIP degradation. Overall, this study shows that Ca-doped and M-doped $Bi_2Fe_4O_9$ can potentially be the PMS activator in the fluoroquinolone degradation.

CHAPTER 1

INTRODUCTION

1.1 Background of study

The rapid industrialization associated with the modernization of the world has led to unregulated use and release of persistent organic pollutant (POPs) into the environment. POPs are defined as chemicals that are persistent in the environment and their potential for long range transport, ability to bio-accumulate in ecosystem and their impacts on human health have aroused great concern [1]. In particular, POPs such as antibiotics have caught much attention as even small amount of antibiotics will lead to significant negative impacts. Antibiotics such as lymecycline, ciprofloxacin (CIP) and gatifloxacin (GAT) are widely used in numerous fields including agriculture, livestock production and hospitalization [2]. Both GAT and CIP are classified in fluoroquinolone family and the structures are shown in **Figure 1.1a** and **b**, respectively. GAT is mostly used as a medication to treat bacterial conjunctivitis for eye infections [3] while CIP is used to treat numerous bacterial infections such as respiratory tract infections, bone and joint infections, skin infections, urinary tract infections and intra-abdominal infections [4, 5]. However, GAT and CIP are easily accumulated in the environment and they are extensively detected in water surface because of their persistency as well as toxicity [6]. Therefore, a potential method is needed for the degradation and detoxification of GAT and CIP in water.

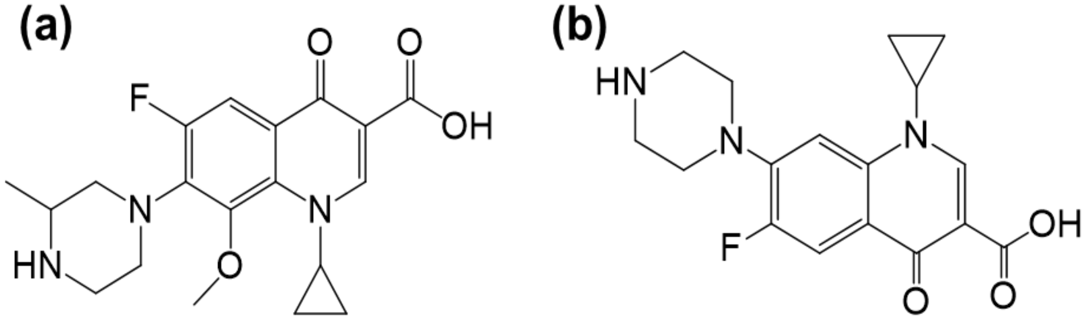

Figure 1.1: Molecular structure of (a) GAT and (b) CIP.

In the early 20th century, numerous techniques such as physical adsorption, electrolysis and biological treatment have been proposed to remove antibiotics in water bodies [7-9]. However, these methods cause some limitations as in adsorption method, saturation and clogging of the reactors may occurred. On the other hand, electrolysis is less cost effective as the equipment requires high initial cost. Biological method is a slow process as a favorable environment is needed for the microorganism to conduct degradation [10]. The detailed advantages and disadvantages of the degradation methods are presented in **Table 1.1**. Recently, the advancements in science and technology have established sulfate ($SO_4^{\bullet -}$) radical-based advanced oxidation technology for environmental remediation. Basically, the formation of $SO_4^{\bullet -}$ can be done by peroxymonosulfate (PMS) activation via ultraviolet irradiation, catalyst, ultrasound and heat [11]. Among all, catalytic PMS activation is preferable due to its cost effectiveness. Catalytic activation proceed without external energy supply also an advantage for the use of catalyst as an activator [12]. The benefits of PMS activation for degradation of organic pollutants such as versatility and easy in operation have presented it as a desirable wastewater treatment technology [13-15].

Table 1.1: The advantages and disadvantages of removal technologies [10, 16].

Removal technologies	**Advantage**	**Disadvantage**
Adsorption	- Simple and flexible - Highly effective - Excellent quality	- Expensive adsorbents - Non-destructive processes - Non-selective method - Rapid saturation and clogging of the reactor
Membrane filtration	- Effective - Low solid waste generated	- Need periodic replacement - Membrane fouling - Specific process - Limited flow rates - Require high energy
Ion exchange	- High efficiency - Low costs - Able to be regenerated - Simple	- Not effective to treat all category of pollutants - Rapid saturation and clogging of the reactor
Biological treatment	- Non-toxic - Cost effective - Environmentally friendly	- Unstable - pH and temperature sensitive - Slow process - Poor decolorization - Complexity of the microbiological mechanisms
Coagulation	- Cost effective - Simple - Bacterial inactivation capability	- Produce concentrated sludge - pH dependent
Electrochemical	- No sludge production - Adaption to different pollutant loads	- Expensive (high electricity cost) - Less effective - Filtration process for floes
Advanced oxidation processes	- Rapid degradation - No sludge generation - Faster reaction kinetics - Little or no consumption of chemicals	- Expensive - Might forms undesired by-product

Various types of catalysts have been used as PMS activator to degrade organic pollutants in water bodies, including metal- and non-metal-based catalysts. Carbon-based catalysts such as graphene and nano diamonds are less active and the synthesis require expensive precursors. Therefore, metal-based catalyst has been widely investigated as a PMS activator. In metal-based catalysts, heterogeneous catalyst is preferred to activate PMS compared to homogeneous catalyst due to the ease of catalyst recovery, minimum release of secondary pollutants and the potential to operate under extreme conditions (high pressure and temperature) and wider pH range [17, 18]. Hence, interest on the activation of PMS using heterogeneous metal-based catalysts such as metal oxides, perovskite-based and mullite-based catalyst is increasing. Among heterogeneous catalysts, mullite-based catalyst exhibits excellent catalytic performance in wastewater treatment as it possesses abundant oxygen vacancies, synergistic mechanism between the metals and high conversion efficiency [19, 20]. However, there are still a lack of researches reported in PMS activation by mullite-based catalyst.

Bismuth ferrite mullite ($Bi_2Fe_4O_9$) is a common crystal structure applied widely in fibre optic and catalysis as it exhibits excellent catalytic and electronic performance [21, 22]. The addition of dopants such as Ca into metal-catalyst can induce the formation of abundant oxygen vacancies whereas the introduction of transition metals including Co, Cu and Mn into metal catalyst will promote synergistic mechanism between the metal species. Both doping will further enhance the catalytic performance. Hence, the mechanism of $Bi_2Fe_4O_9$ and metal-doped $Bi_2Fe_4O_9$ (metal = Ca, Cu, Mn, Co and Zn) as PMS activator for degradation needs further elucidation.

1.2 Problem statements

Nowadays, researchers have put much efforts on wastewater treatment as the accumulation of organic pollutants such as antibiotics will lead to huge impacts on environmental and human health. For example, CIP (8.5%) is considered as top 4 of the most common antibiotics existed in fresh market wastewater [23]. Advanced oxidation process (AOP) has been proposed and PMS activation has frequently used to perform antibiotic degradation. Heterogeneous metal-based catalysis with its notable advantages was widely study to enhance the efficiency of the catalyst for PMS activation in antibiotic degradation. The challenges in terms of performance and stability are the main concern for every metal-based catalyst as PMS activator. Several core limitations of employing mullite-based nanomaterials as PMS activator must be addressed include performance uncertainty, the risk of metal leaching (due to the reaction with PMS and dissolution in acidic medium) during application [24] and their relatively low specific surface area (<10.0 m^2 g^{-1}) [25]. Due to environmentally friendly, cost-effectiveness and the efficiency of Fe-based catalyst, it is commonly employed as catalyst for PMS activation [26]. However, Fe-leaching existed in Fe-based catalyst will lead to the contamination of groundwater and thus causes chronic Fe poisoning to the consumers. A high Fe content in groundwater might results in the blockage of water withdraw facilities due to the formation of red oxyhydroxide precipitate [27]. Recently, the Fe concentration detected in groundwater was increased significantly and exceed the acceptable limit (300 μg L^{-1}) in World Health Organization (WHO) standard [28]. Therefore, a $Bi_2Fe_4O_9$ catalyst with low metal leaching rate (< 0.2 μg L^{-1}) was proposed to activate PMS in pollutant degradation [11]. The degradation performance and the stability of $Bi_2Fe_4O_9$ catalyst can be further enhanced by the modification via dopants such as

Co, Cu, Mn and Zn. To date, there are limited studies on PMS activation mechanism by using metal-doped $Bi_2Fe_4O_9$ as a catalyst. The combination of best cations to prepare high performance of $Bi_2Fe_4O_9$ for PMS activation is still an ongoing subject of investigation. Furthermore, the effects of several parameters such as catalyst loading, initial pH and PMS dosage on PMS activation via $Bi_2Fe_4O_9$ are rarely reported and studied. There are limited investigation on the underlying activation mechanism and the degradation pathways of CIP and GAT.

1.3 Objectives

The main objective of this research is to synthesize, characterize and evaluate the performance of the Ca- and M-doped $Bi_2Fe_4O_9$ (M = Zn, Mn, Cu and Co) for fluoroquinolone antibiotics degradation in water via PMS activation. The specific objectives are listed below:

1. To synthesize Ca- and M-doped $Bi_2Fe_4O_9$ via facile hydrothermal method.
2. To characterize the physical and chemical properties of the Ca- and M-doped $Bi_2Fe_4O_9$.
3. To evaluate the performance of the Ca- and M-doped $Bi_2Fe_4O_9$ on the degradation of fluoroquinolone antibiotics.
4. To investigate the mechanism of PMS activation by Ca- and M-doped $Bi_2Fe_4O_9$ during fluoroquinolone antibiotic degradation.

1.4 Scope of study

This study consists of two parts. In the first part of the study, Ca-doped $Bi_2Fe_4O_9$ was developed via hydrothermal method to activate PMS for GAT degradation in water bodies. In the second part of the study, various M-doped $Bi_2Fe_4O_9$ (M = Cu, Co, Mn and Zn) was fabricated for CIP removal via PMS activation. The characterization of proposed $Bi_2Fe_4O_9$ were investigated by using X-ray diffractometry (XRD), fourier transform infrared spectrometry (FTIR) and porosimetry and X-ray photoelectron spectrometry (XPS) methods. The best Ca- and M-doped catalysts were further characterized by scanning electron microscope (SEM), energy dispersive X-ray analysis (EDX) and transmission electron microscope (TEM). In the performance evaluation part, the comparison of pure $Bi_2Fe_4O_9$ and doping $Bi_2Fe_4O_9$ toward degradation of fluoroquinolone antibiotics was determined. The performance of the best Ca- and M-doped $Bi_2Fe_4O_9$ catalyst were then evaluated by investigating the effects of catalyst loading, PMS dosage and initial pH on degradation of fluoroquinolone antibiotics. The effects of common ions on PMS activation and types of water matrices also conducted to further evaluate the degradation performance of the catalyst. The mechanisms of the fluoroquinolone antibiotics degradation were determined using the radical scavengers' method. The reusability of the best Ca- and Cu-doped $Bi_2Fe_4O_9$ were analyzed to compromise their degradation performance.

1.5 Organization of thesis

There are six chapters comprized in this thesis, including Introduction, Literature Review, Materials and Methodology, two chapters of Results and Discussion and Conclusions.

Chapter 1: Introduction

This chapter covers a summary of background, introduction and the problem faced in recent years for the study. Furthermore, the objectives and the scopes to conduct the research together with the organization of this thesis are discussed in the chapter.

Chapter 2: Literature review

In this chapter, an up-to-date literature review of the fundamental of ROS, the mechanism of PMS activation, heterogeneous metal-based catalysts as PMS activator, the development of Bi-based catalyst and the addition of dopant into mullite $Bi_2Fe_4O_9$ for pollutant degradation are outlined.

Chapter 3: Materials and methodology

This chapter presents the chemicals, apparatus and materials applying in the research. Apart from that, the chapter also covers the details of the synthesis process, methods for the characterization studies and the performance evaluation.

Chapter 4: Calcium-doped $Bi_2Fe_4O_9$ as peroxymonosulfate activator for gatifloxacin removal

This chapter outlines the comparison of $Bi_2Fe_4O_9$ and Ca-doped $Bi_2Fe_4O_9$ on their degradation performance. Characterization studies such as SEM, EDX, XRD, FTIR, TEM and BET are proposed in this chapter. Furthermore, the performance of the catalyst is presented detailly in this chapter with the evaluation of general parameters (initial pH, catalyst loading and PMS dosage), types of real water bodies and the effect of different ion species. Recyclability, metal leaching, mechanism of the degradation, extent of mineralization and the intermediates contained during the reaction are covered in this chapter.

Chapter 5: M-doped $Bi_2Fe_4O_9$ (M = Zn, Cu, Co, Mn) as peroxymonosulfate activator for ciprofloxacin removal

In this chapter, the modification on $Bi_2Fe_4O_9$ through Mn, Zn, Co and Cu doping is proposed. This chapter covers XRD, FTIR, SEM, TEM, EDX and BET characterization results of certain catalysts. Moreover, the comparison of the degradation performance for various $Bi_2Fe_4O_9$ and M-doped $Bi_2Fe_4O_9$ are proposed in this chapter. This chapter outlines the effects of catalyst loading, initial pH of the medium, PMS dosage and different types of water matrixes on the catalytic performance of the catalysts. Metal leaching of the catalyst, PMS activation mechanism, extent of mineralization and the degradation pathways are presented in this chapter.

Chapter 6: Conclusion and future recommendations

This chapter concludes the findings in the research work and gives several perspectives for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 The chemistry of reactive oxygen species (ROS)

Several highly reactive species such as $SO_4^{\bullet-}$, $^{\bullet}OH$ and $^1O_2$ are generated in PMS activation for pollutant degradation. Sulfate radical-advanced oxidation process (SR-AOP) is a desirable degradation method compared to hydroxyl radical-advanced oxidation process ($^{\bullet}OH$-AOP) as $SO_4^{\bullet-}$ possesses numerous outstanding advantages: (i) excellent oxidant, (ii) freely diffusible, (iii) longer lifetime, (iv) selectively reacted with the organic pollutant (v) high reaction stoichiometric efficiency and (vi) form in wider pH range [29]. The summary of standard reduction potentials for various species is shown in **Table 2.1**. Generally, $SO_4^{\bullet-}$ is an excellent oxidant as it has higher standard redox potential (E^0 vs NHE (normal hydrogen electrode) = +2.50 to +3.10 V) than $^{\bullet}OH$ (E^0 vs NHE = +1.80 to +2.70 V), indicating $SO_4^{\bullet-}$ can remove most of the pollutants in wastewater [30]. Apart from that, $SO_4^{\bullet-}$ can diffuse freely to oxidize the organic pollutants in solution. Due to the preference of electron transfer reaction, $^{\bullet}OH$ has shorter lifetime (20 ns) compared to $SO_4^{\bullet-}$ (30–40 µs) which implies $SO_4^{\bullet-}$ has higher chances to contact and react with the pollutants in the system [31, 32]. $SO_4^{\bullet-}$ is a high selectively species as only small amount of $SO_4^{\bullet-}$ is needed to react directly with the pollutant at its specific functional groups through electron transfer reaction. Electrophilic $SO_4^{\bullet-}$ is more likely to attack the electron donating groups, including alkoxyl (–OR), hydroxyl (–OH), amino ($–NH_2$), π electrons located in aromatic rings and saturated bonds presented in the compounds while it is less likely to react with electron withdrawing groups (carbonyl (C=O) and nitro ($–NO_2$)). Meanwhile, huge amount of relatively non-selective $^{\bullet}OH$ is needed to react with the functional groups of pollutants via a series of reactions including transfer of electron, addition of electrophilic or radical and abstraction of hydrogen. Moreover, $SO_4^{\bullet-}$ is preferable in degradation system as its second-order reaction rate constant (10^5 to 10^9 $M^{-1} s^{-1}$) is slightly lower than $^{\bullet}OH$ ranging from 10^6 to 10^{11} $M^{-1} s^{-1}$ which indicates $SO_4^{\bullet-}$ exhibit fast reaction with the organic pollutants [33].

Table 2.1: Standard reduction potential for various species.

Half equation	**Standard reduction potential, E⁰ (V)**	**Reference**
$SO_4^{\bullet-} + e^- \rightarrow SO_4^{2-}$	2.50 – 3.10	[30]
$SO_5^{\bullet-} + e^- \rightarrow SO_5^{2-}$	1.10	[12]
$HO^{\bullet} + e^- \rightarrow OH^-$	1.80 – 2.70	[30]
$HSO_5^- + 2H^+ + 2e^- \leftrightarrow HSO_4^- + 2H_2O$	1.82	[12]
$HSO_5^- + H^+ + 2e^- \leftrightarrow SO_4^{2-} + H_2O$	1.75	[12]
$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O$	1.78	[12]
$O_3 + 2H^+ + 2e^- \leftrightarrow O_2 + H_2O$	2.08	[12]
$O_3 + 2H_2O + 2e^- \leftrightarrow O_2 + 2OH^-$	1.24	[12]

The pH of the medium is one of the main factors that will affect the degradation method, the removal efficiency of SR-AOP is independent to the pH of the medium whereas $^{\bullet}OH$ is dependent to the pH which the increment of pH will lead to the reduction in the reactivity of $^{\bullet}OH$ [33]. The formation of $^{\bullet}OH$ from the reaction of $SO_4^{\bullet-}$ and water could be found in the degradation system (**Eq. 2.1**). Furthermore, in alkaline medium, the $^{\bullet}OH$ will be generated by the reaction between $SO_4^{\bullet-}$ and OH^- (**Eq. 2.2**).

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + OH^{\bullet}, k_{SO_4^{\bullet-} + H_2O} < 1.0 \times 10^3\ M^{-1}s^{-1} \quad (2.1)$$

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + OH^{\bullet}, k_{SO_4^{\bullet-} + OH^-} = (6.5 \pm 1.0) \times 10^7\ M^{-1}s^{-1} \quad (2.2)$$

The presence of dissolved organic matter (DOM) and anionic species will affect the degradation efficiency of the reaction by quenching the reactive radicals

($SO_4^{\bullet-}$ and $^{\bullet}OH$). In the presence of DOM, $SO_4^{\bullet-}$ ($k_{SO_4^{\bullet-}+DOM} = 6.8 \times 10^3\ \mathrm{mg\ C^{-1}\ s^{-1}}$) is more desirable reactive species to attack the organic pollutants than $^{\bullet}OH$ ($k_{HO^{\bullet}+DOM} = 1.4 \times 10^4\ \mathrm{mg\ C^{-1}\ s^{-1}}$) as it is less likely to be affected by DOM. In contrast, the removal efficiency of SR-AOP is more influenced by the presence of anionic species such as Cl^-, Br^-, HCO_3^-, CO_3^{2-}, HPO_4^{2-} and PO_4^{3-} in the solution [12].

Non-radical pathway such as the production of $^1O_2$ species and electron transfer can be used in degradation of organic pollutant. The non-radical oxidation pathway was exploited due to several advantages: (i) prevent self-scavenging effect that happen in radicals ($SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-}$), (ii) resist to organic compounds and inorganic ions in water matrix and (iii) fully utilize the oxidizing capacity of PMS [12, 34]. **Figure 2.1** showed the organic pollutant degradation via radicals and non-radical pathway by metal-based catalyst.

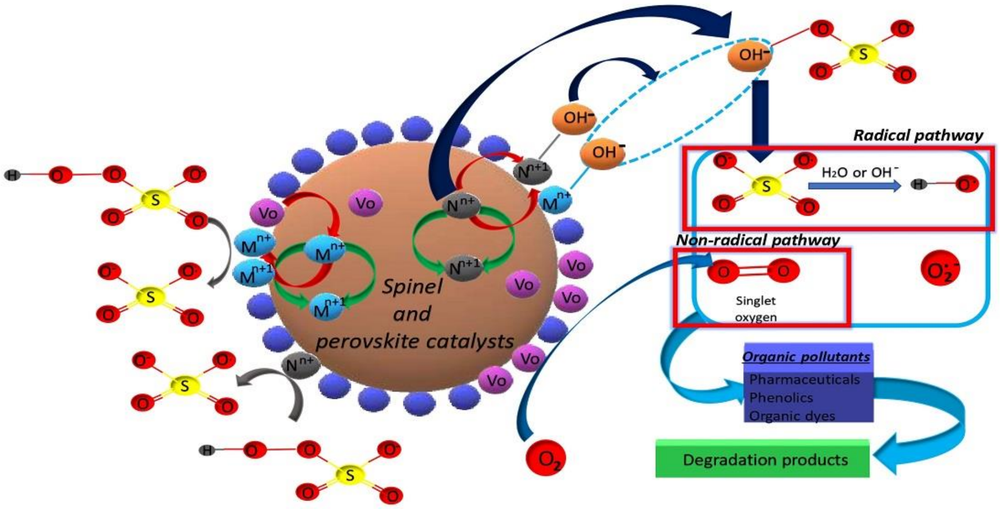

Figure 2.1: Organic pollutant degradation via radicals and non-radical pathway by metal-based catalysts. Reproduced with permission from [35].

2.2 Mechanism of PMS activation

In catalytic PMS activation, the catalyst plays a crucial role in providing a platform to convert PMS into ROS such as $SO_4^{\bullet-}$ (E^0 vs NHE = 2.50–3.10 V), $^{\bullet}OH$ (E^0 vs NHE = 1.80–2.70 V), and $^1O_2$ through electron transfer mechanisms [30, 36]. The decomposition of PMS and pathways of the generation of reactive species can affected by oxygen vacancies, surface hydroxyl groups and metal ions [37]. Aside from extrinsic properties which include specific surface area and porosity, the intrinsic characteristics of the catalytic platform (affinity for PMS adsorption, presence of redox-active moieties, surface energy, oxygen vacancy, etc.) determine the performance of the catalyst. Typically, heterogeneous metal-based catalysts can activate PMS through redox reaction involving transition metal and oxygen vacancies. The transition metal confined within the heterogeneous metal lattice can undergo rapid redox cycling between its various oxidation states (e.g. Co^{2+}/Co^{3+}, Fe^{2+}/Fe^{3+}, Cu^{+}/Cu^{2+} etc.) with PMS, leading to homolytic cleavage of the peroxide bond of PMS, and the generation of $SO_4^{\bullet-}$, $SO_5^{\bullet-}$, and $^{\bullet}OH$ (**Eq. 2.3-2.5**) [12].

$$\mathrm{Me^{n+} + HSO_5^- \rightarrow Me^{(n+1)+} + SO_4^{\bullet-} + HO^-} \tag{2.3}$$

$$\mathrm{Me^{n+} + HSO_5^- \rightarrow Me^{(n+1)+} + SO_4^{2-} + HO^{\bullet}} \tag{2.4}$$

$$\mathrm{Me^{(n+1)+} + HSO_5^- \rightarrow Me^{n+} + SO_5^{\bullet-} + H^+} \tag{2.5}$$

In the presence of two or more compatible transition metals within the perovskite lattice (such as Cu^{2+} and Fe^{3+}), these transition metals can also interact synergistically to enhance PMS activation [38]. Meanwhile, oxygen vacancies can adsorb PMS and promote the $^1O_2$ liberation as active ROS for pollutant degradation. Recent studies have also found that the density of surface oxygen vacancy plays a crucial role in facilitating the evolution of $^1O_2$ [39]. In some cases, the transition metals and oxygen vacancy may interact with each other, improving the ROS generation [40]. A $^1O_2$ species can be generated through certain pathways: (i) self-decaying through the combination of HSO_5^- and SO_5^{2-}, (ii) the reaction between water and SO_5^{2-}, (iii) reaction of catalyst with the dissolved oxygen and (iv) formation of superoxide radical ($O_2^{\bullet-}$) which subsequently form $^1O_2$ species [41, 42]. However, knowledge on the exact $^1O_2$ generation mechanism from PMS at the oxygen vacancies remain limited. Synergistic interaction between the transition metal and oxygen vacancies may also contributed to the enhanced PMS activation. Typically, oxygen vacancies can lead to various effects including (i) binding with water to form hydroxyl group that can facilitate PMS activation, (ii) altering the characteristics of the perovskite, and (iii) reduce the valency of B-site metal ions in perovskite [43]. It has been previously reported that the interaction of transition metal and oxygen vacancies can increase the performance of heterogeneous metal catalysts for various applications including oxygen reduction reaction [44], photocatalysis [45], and PMS activation [46]. However, excessive oxygen vacancies could lead to the increased resistivity, affecting the performance of perovskite as PMS activator [47]. A typical schematic illustration of PMS activation by perovskite is presented in **Figure 2.2**.

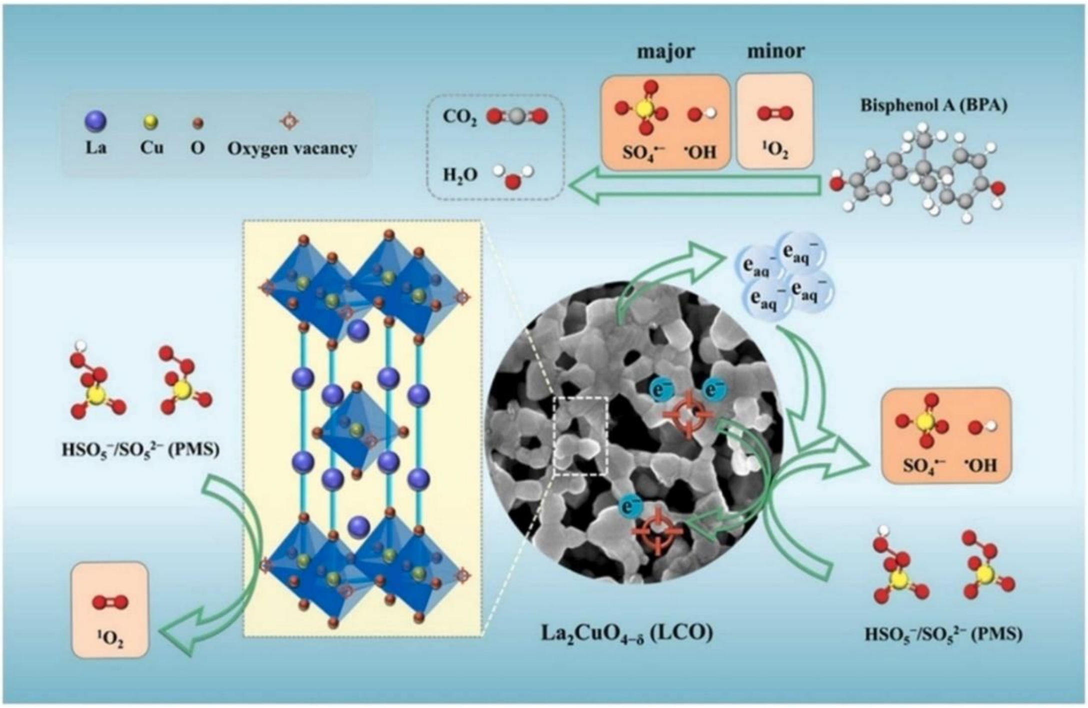

Figure 2.2: Schematic illustration of the PMS activation mechanism by perovskite. Reactive radicals such as $SO_4^{\bullet-}$, ${}^{\bullet}OH$ and ${}^1O_2$ are produced for organic pollutant oxidation. Reproduced with permission from [40].

2.3 Heterogeneous metal-based catalysts

In heterogeneous system, different phase of catalyst and reaction medium were used in the degradation system. Undeniably, heterogeneous catalysis has been regarded as effective wastewater treatment technique as it possesses various advantages which listed as follows: (i) cost effectiveness as the spent catalyst can be easily separated from the reaction medium, (ii) it have higher chances to work under extreme conditions, (iii) the catalyst can be reused and recycled for few cycles, (iv) avoid the release of catalyst into the environment which further minimize secondary pollutants, (iv) no extra energy input is needed [34, 48]. Several studies have proposed to develop various types of metals and metal oxides as heterogeneous catalysts to activate PMS for organic pollutant degradation. Usually, Fe, Co, Mn and Cu are the transition metals that used to synthesize the heterogeneous catalyst [48].

Heterogeneous metal-based catalyst is classified into single-metal and mixed-metal catalysts.

2.3.1 Single metal catalyst

Single metal catalyst has been proposed for PMS activation in organic pollutant degradation. From here, the generation of the reactive species such as $^{\bullet}OH$ and $SO_4^{\bullet -}$ was done by $Metal^{x+}/Metal^{(x+1)+}$ redox cycle [34]. Iron oxide-based such as Fe_2O_3, Fe_3O_4 and zero valent iron (ZVI) and cobalt oxide-based catalysts are the common single metal catalyst for PMS activation [48]. Iron is an abundant transition element that usually use as an activator to activate PMS for pollutant degradation. However, due to the poor activation efficiency Fe_2O_3 (Fe^{3+} species and slow regeneration of Fe^{2+} on Fe_2O_3 surface), modification of Fe_2O_3 has been done to transform it as a promising catalyst in the PMS activation. Sulfurization of Fe_2O_3 was proposed to enhance the activation of PMS in atrazine (ATZ) degradation as it can speed up the electron transfer of Fe^{2+}/Fe^{3+} cycle. Both surface hydroxyl group and Fe^{2+}/Fe^{3+} cycle was contributed in the activation of PMS. Some possible catalytic mechanism for ATZ degradation in the research were proposed: (i) $SO_5^{\bullet -}$ and $SO_4^{\bullet -}$ were generated via PMS activation by Fe^{2+} and Fe^{3+} ions, (ii) electron transfer between the catalyst and PMS was speed up by sulfur as it could enhance Fe^{2+} regeneration which further accelerate activation of PMS, (iii) more surface hydroxyl groups were formed due to the consumption of sulfur on the surface of the catalyst and (iv) $SO_4^{\bullet -}$ can oxidize H_2O or OH^- to produce more $^{\bullet}OH$ for degradation [49]. A α-Fe_2O_3 was synthesized by thermal decomposition of α-FeOOH to remove sulfamethoxazole (SMX). The synthesized α-Fe_2O_3 consists of high oxygen vacancies which enhance the PMS activation and further improve the degradation efficiency. The presence of oxygen vacancies will facilitate the formation of reactive oxygen which further react with PMS to produce $^1O_2$ for SMX degradation [50]. Apart from that, Fe_3O_4 was also proposed as a PMS activator and modification or addition of light were applied to introduce an excellent Fe_3O_4 catalyst in degradation system. Fu et al. reported the preparation of Fe_3O_4 via K_2FeO_4 which possessed high mesoporous ratio and graphitization degree that can further enhance the catalytic efficiency. From here, PMS will act as an electron donor to reduce Fe^{3+} and regenerate Fe^{2+}. There is an alternative way which $O_2^{\bullet-}$ can reduce Fe^{3+} and regenerate Fe^{2+} in the reaction. Similar to previous reported research, $^{\bullet}OH$ could be generated via the reaction of $SO_4^{\bullet-}$ and H_2O to undergo p-hydroxybenzoic acid degradation [51]. Fadaei et al. reported the improvement of PMS activation by Fe_3O_4 via ultraviolet (UV), ultrasound (US) and heat. The proposed Fe_3O_4 exhibited excellent electric and magnetic properties in electron transfer of Fe^{2+}/Fe^{3+} cycle as well as stability in degradation. Similarly, the Fe^{2+}/Fe^{3+} cycle is responsible for the activation of PMS in pollutant degradation. From here, the ROS such as $SO_4^{\bullet-}$ and $^{\bullet}OH$ were contributed in the removal of Reactive Black 5 (RB5) [52]. A simple schematic diagram with contribution of Fe^{2+}/Fe^{3+} cycle in PMS activation was showed in **Figure 2.3**.

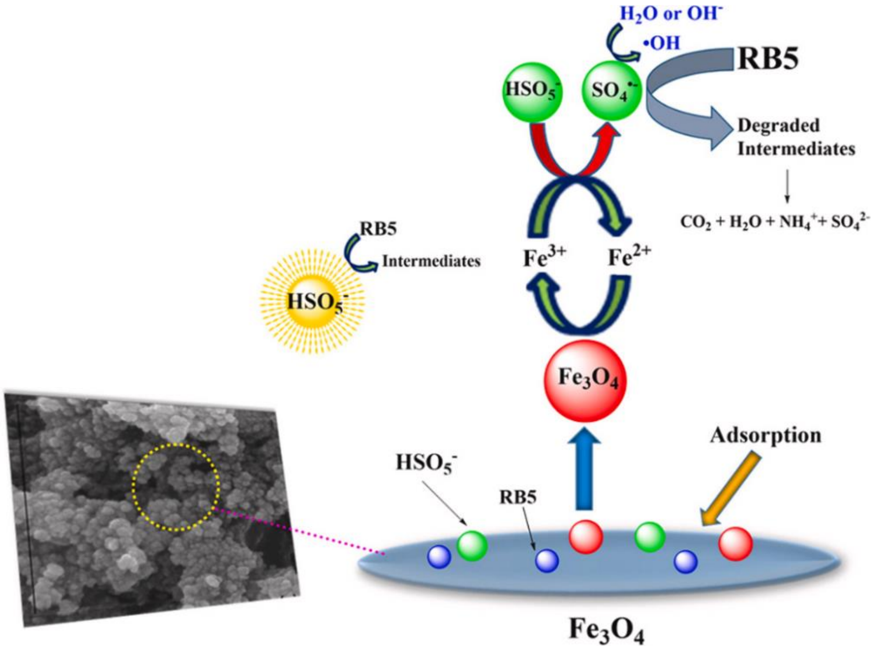

Figure 2.3: Contribution of Fe^{2+}/Fe^{3+} cycle in PMS activation for RB5 degradation. Reproduced with permission from [52].

ZVI also a-type of iron metal which can be acted as PMS activator. Most of the researchers have proposed US-assisted ZVI due to the synergistic mechanism which can further improve the catalytic efficiency and the reusability. The presence of US will speed up the corrosion rate of ZVI and further assist in Fe^{2+} formation (**Eq. 2.6**). The generated Fe^{2+} was oxidized by PMS to produce $SO_4^{\bullet -}$ for pollutant degradation (**Eq. 2.7**). The Fe^{2+} could continuously produce (**Eq. 2.8**) due to the US cavitation effect which would clean Fe^0 surface and speed up Fe^{3+} cycle [53, 54].

$$Fe^0 + HSO_5^- + H^+ \rightarrow Fe^{2+} + SO_4^{\bullet -} + H_2O \qquad (2.6)$$

$$Fe^{2+} + HSO_5^- \rightarrow Fe^{3+} + SO_4^{\bullet -} + OH^- \qquad (2.7)$$

$$Fe^0 + Fe^{3+} \rightarrow Fe^{2+} \qquad (2.8)$$

Apart from Fe-based catalysts, Co-based catalyst is a common activator for PMS activation in organic pollutant degradation. Co-based catalyst such as Co_3O_4 was usually used to activate PMS as it has high stability. However, due to the smaller number of active sites and poor electron transfer efficiency of Co_3O_4, some modification such as addition of supporter or light assistance were done to improve the catalytic activity of Co_3O_4. Xu et al. reported that Co_3O_4 dispersed on biochar (BC) supporter was more efficient in activating PMS for pollutant degradation. Due to the synergistic effects between Co_3O_4 and BC, almost 100% of chloramphenicol (CAP) was degraded in 10 min. BC-Co^{2+} will act as the electron donor and react with PMS to form BC-Co^{3+} and $SO_4^{\bullet-}$. Then, BC-Co^{3+} can reduce back to BC-Co^{2+} by receiving an electron from PMS. The $^{\bullet}OH$ could be generated from the reaction of $SO_4^{\bullet-}$ with H_2O or OH^-. The addition of BC supporter could facilitate the electron transfer between Co^{2+} or Co^{3+} and PMS and further enhance the catalytic activation [55]. The fabrication of two-dimensional ultrathin perforated Co_3O_4 nanosheets was reported to improve PMS activation for selective organic pollutant oxidation. In the research, a wet-chemical synthesis was used to design the nanosheet. Generally, PMS is reacting with Co^{2+} and Co^{3+} to produce $SO_4^{\bullet-}$ and regenerate Co^{2+}, respectively. A non-radical species, $^1O_2$ was produced from the reaction between PMS and SO_5^{2-} and also contributed in biphenol A (BPA) degradation [56]. Moreover, a heat treatment synthesized Co_3O_4 was observed to be a potential PMS activator as the synthesized Co_3O_4 has high number of oxygen vacancies and efficient charge transfer in between catalyst and PMS [57]. In summary, single Co-based metals were widely used in PMS activation system and a general mechanism of PMS activation by Co_3O_4 was shown (**Figure 2.4**). However, Co leaching is still the main issue faced as Co has high carcinogenicity and the leaching will lead to the release of secondary pollution.

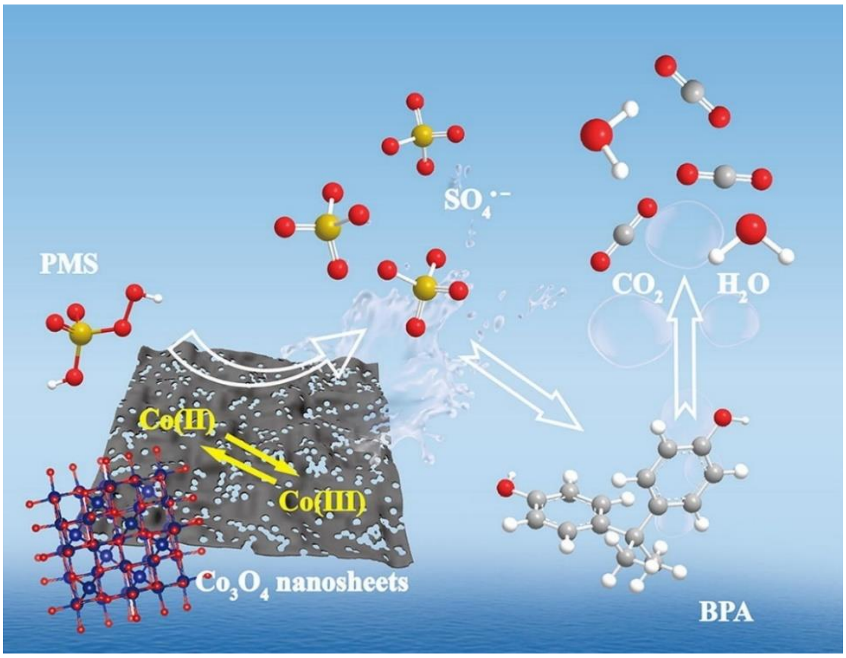

Figure 2.4: General PMS activation mechanism of Co_3O_4 in BPA degradation. Reproduced with permission from [56].

Apart from that, non-radical mechanism was also explored in other single metal catalysts. For instance, Zhang et al. reported NiO has used to activate PMS and $O_2^{\bullet-}$ was produced through the absorption of oxygen on the oxygen vacancies. The generated $O_2^{\bullet-}$ was responsible in the formation of $^1O_2$ to degrade acid orange 7 (AO7) [58]. Li et al. proposed the formation of non-radical species, $^1O_2$ in the activation of PMS via cubic Cu_2O (c-Cu_2O) [59].

2.3.2 Mixed-metal catalyst

Mixed-metal catalysts are desire PMS activator over single metal catalysts due to its advantages: (i) more redox active contributed in the system (synergistic effect between the metal), (ii) high number of surface hydroxyl group (better catalytic activity), (iii) polyfunctional (e.g. magnetically separable, photoactive etc.), and (iv) high stability (less metal leaching). The remarkable synergistic effect between the metal ions in the mixed-metal catalyst will facilitate the electron transfer and thus accelerate the catalytic reaction [34]. Mixed-metal that are active as PMS activator usually contain transition metals such as Co, Fe, Mn, Ni and Cu. Various mixed-metal materials have been demonstrated as effective PMS activator for treating several anthropogenic organic pollutants. For instance, Co mixed-metal catalysts such as $LaCoO_3$ has been successfully employed to remove pharmaceuticals, dyes, and endocrine disruptors. In most cases, the reported active ROS involved were $SO_4^{\bullet-}$ and $^{\bullet}OH$ from the redox reaction involving Co^{2+} species in $LaCoO_3$ with PMS. $LaCoO_3$ can also be designed to have deficient B-site cation with active sites consisting of Co^{2+}, hydroxyl group and oxygen vacancy which generate $SO_4^{\bullet-}$ and $^1O_2$ as the predominant species (**Figure 2.5a**) [60]. It is also reported that $LaCoO_3$ is superior to other mixed-metal with similar structure, namely $LaNiO_3$, $LaCuO_3$ and $LaFeO_3$ and this is expected considering Co is one of the most effective PMS activators compared to Ni, Cu and Fe [12, 61]. There are some other variations of mixed-metal containing Co such as $PrBaCo_2O_{5+\delta}$, $Ca_2Co_2O_5$, $SrCoO_3$ and $SrCo_{0.6}Ti_{0.4}O_{3-\delta}$@CoOOH have also been evaluated as PMS activator [24, 62-64]. However, despite being reusable for several cycles without performance loss, application of Co-based mixed-metal presented a serious risk of Co leaching. For instance, it is reported that Co leaching in $LaCoO_3$ can exceed > 5 mg L^{-1}, creating potential adverse effect to the environment [65]. As mentioned previously. mixed-metal catalyst has numerous advantages over single metal catalyst and hence Co mixed-metal catalyst has superior catalytic activity attributed to its relatively higher number of active sites and synergistic interaction of the cations compared to Co-based catalyst such as Co_3O_4 [66, 67]. For example, Duan et al. showed that $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ catalyst possessed superb catalytic activity and exhibited better performance in wider pH range compared to Co_3O_4 [46]. Meanwhile, the activation of PMS in 2,4-Dichlorophenol (2,4-DCP) degradation by mono-metallic catalysts (Fe_3O_4 and Co_3O_4) were less efficient compared to bi-metallic $FeCo_2O_4$ catalyst. In this work, Zhou et al. reported that the interaction between the hydroxyl groups that formed on the catalyst surface together with the transition metals played a key role in PMS activation [68]. However, comparison between the mixed-metal catalysts and Co-based catalysts under realistic condition is still lacking and more studies should be done to provide a useful guide to the selection of a suitable Co-based catalyst for upscaling and further development.

In search of an alternative to Co-based catalyst, other mixed-metal (without Co) such as La, Mn, Bi, Ni mixed-metal based catalysts were also studied. $LaFeO_3$, $LaNiO_3$ and $LaMnO_3$ were investigated previously and it has been reported that the performance of $LaNiO_3$ was superior to $LaFeO_3$, $LaZnO_3$ and $LaMnO_3$ under same condition due to the lower energy barrier provided by $LaNiO_3$, generating $^1O_2$ as the dominant ROS (**Figure 2.5b**) [39, 69-71]. In other studies, it is also found that $LaMnO_3$ and $LaCu_XFe_{1-X}O_3$ can be used to activate PMS for palm oil mill secondary effluent and resin wastewater purification, respectively, suggesting that the catalyst has potential for practical uses [72, 73]. However, these mixed-metal are regarded as inferior to $LaCoO_3$ and metal leaching (Fe, Ni, Mn or Zn) during treatment is practically still a concern. On the other hand, Huang et al. reported $Mn_{1.8}Fe_{1.2}O_4$ as PMS activator for BPA degradation. From the work, the synergistic mechanism was found between Mn and Fe in $Mn_{1.8}Fe_{1.2}O_4$ catalyst. Both Fe and Mn played different key roles, which Fe is the main adsorption site which synergized with the primary active site Mn in the degradation reaction (**Figure 2.5c**). Unsurprisingly, mixed metallic catalyst ($Mn_{1.8}Fe_{1.2}O_4$) still exhibited higher degradation efficiency compared to mono-metallic catalysts (Mn_3O_4 and Fe_2O_3) due to the presence of high surface hydroxyl groups and synergistic effect between the solid-state of metal ions.

However, Mn leaching in $Mn_{1.8}Fe_{1.2}O_4$ was extremely high, which is 713.19 and 19.25 µg L^{-1} in pH 4.2 and 7.5, respectively [74]. In particular, under realistic condition, acidic pH and the presence of ligands can further increase the metal leaching (>10 times increase in Mn leaching of $LaMnO_3$ in the presence of nitrilotriacetic acid) [75].

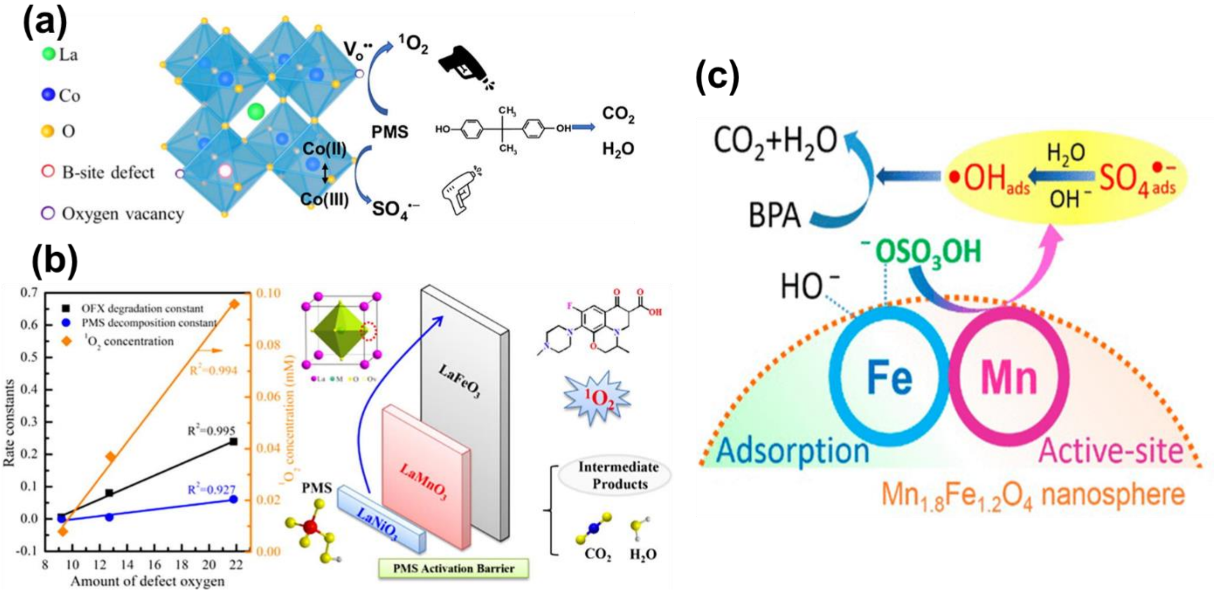

Figure 2.5: (a) B-site cation deficient $LaCoO_3$ with active sites consisting of Co^{2+}, hydroxyl group, and oxygen vacancy, (b) Comparison and mechanism of PMS activation by $LaXO_3$ (X = Ni, Mn and Fe) and (c) Synergistic effects between Fe and Mn which undergo adsorption and act as an active site, respectively. Reproduced with permission from [39, 60, 74].

To eliminate the metal leaching risk, mixed metal can be supported on a suitable material such as Al_2O_3, monolith, and ZrO_2 [76-78]. The supported mixed metal provides enhanced stability and reduce metal leaching through the strong metal to support interactions. Moreover, the supported mixed-metal catalyst may also benefit from the additional functionalities of the support including having (i) ferromagnetism (incorporating magnetic), (ii) adsorption functionality (incorporating adsorbent), (iii) high density of hydroxyl groups (incorporating alkaline earth oxide), and (iv) synergistic interaction with the mixed-metal (incorporating inorganic support with suitable species). While developing supported mixed-metal catalyst is beneficial, it has not been fully explored yet. Titanate nanotubes (TNTs) were used to support $CoFe_2O_4$ nanoparticles for PMS activation in organic pollutants degradation. From here, the proposed $CoFe_2O_4$/TNTs catalyst has successfully reduced the Co leaching from 711 (pure $CoFe_2O_4$) to 390 µg L^{-1} [79]. Further development of supported mixed-metal catalyst should prioritize on reducing the metal leaching by incorporating a support that can be used to adsorb the leached metal. For instance, CuO loaded on hexagonal boron nitride (*h*-BN) was developed and the *h*-BN can act as Cu adsorbent to minimize the Cu leaching risk. The spent catalyst can be fully regenerated through simple calcination. This approach can improve the sustainability of the supported catalyst for long-term application [80].

Aside from simple mixed-metal catalyst, more complex mixed-metal catalyst such as double or layered catalyst are hardly developed for PMS activation. Several Layered Double Hydroxides (LDHs) have been extensively studied due to their outstanding advantages: (i) cost effective, (ii) easy to prepare, (iii) non-toxicity, (iv) unique structure and (v) large surface area [34, 48]. In LDHs catalytic PMS activation mechanism, the production of ROS is similar to simple mixed-metal catalyst, depending on the redox reaction between metal ions and PMS (radicals) and the direct electron transfer between pollutant and PMS (non-radical). For instance, CoMn-LDH as a PMS activator exhibited high catalytic performance in organic dyes degradation. The $SO_4^{\bullet-}$ and $^{\bullet}OH$ could be generated from the electron transfer between PMS and Co^{2+} and Mn^{3+} on catalyst surface. Furthermore, the redox coupling cycle between Co^{3+}/Co^{2+} and Mn^{4+}/Mn^{3+} could responsible for the regeneration of Mn^{3+} to activate PMS for the formation of radicals [81]. Zeng and